ABSTRACT

THERMOCHEMISTRY AND KINETICS IN PYROLYSIS AND OXIDATION OF OXYGENATED CHLOROCARBONS AND CHLORINATED AROMATICS

by
Li Zhu

Thermochemical properties, $\Delta_fH^o_{298}$, S^o_{298}, and $C_p^o(T)$ ($5 \le T/K \le 6000$), are determined using different *ab initio* and density functional theory methods for three chloromethyl radicals, CH_2Cl, $CHCl_2$, CCl_3, all chlorobenzenes from monochlorobenzene to hexachlorobenzene, and all chlorophenols from ortho-, meta-, para-chlorophenol to pentachlorophenol. The B3LYP/6-31G(d,p) method is used in the structure optimization. The B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p), and CBS-Q methods are used in single point calculations of total electronic energies. Harmonic vibration frequencies are scaled for zero point energies and thermal corrections. Isodesmic reaction(s) are utilized at each calculation level to determine $\Delta_fH^o_{298}$ of each species. Contributions to S^o_{298} and $C_p^o(T)$ from translation, vibration, and external rotations are calculated using the rigid-rotor-harmonic-oscillator approximation. Hindered internal rotational contributions to entropies and heat capacities are calculated by summation over the energy levels obtained from direct diagonalizations of the Hamiltonian matrix of the internal rotation. The C-H and C-Cl bond energies in methyl chlorides are also calculated. Group values are derived for use of group additivity estimation for higher chlorinated or oxy-chlorinated molecules.

Trends of kinetic parameters are estimated for: (1) association reactions of chloromethyl radicals, (2) association reactions of Cl atom with chloroalkyl radicals, (3) addition reactions of chlorine atom with chloroethylenes, (4) three types of abstraction

reactions, including Cl + RX → HCl + R•X, Cl + R → HCl + R• (hydrocarbons only), and H + RCl → HCl + R• (or R•X).

Elementary reaction kinetic models for the thermal pyrolysis and oxidation of: chloroform, 1,3-hexachlorobutadiene, and ortho-chlorophenol, are developed. Thermochemical properties, $\Delta_f H^\circ_{298}$, S°_{298}, and $C_p^\circ(T)$, for reactants, intermediate species, and products are determined by *ab initio* or density functional theory when no literature are available, or from a modified group additivity. High-pressure limit rate constants are also calculated by *ab initio* or density functional theory or in some cases, or are estimated based on trends of chlorinated species when no literature data are available. Pressure and temperature dependent (1 atm Ar and 808 – 1073 K for chloroform, 1 atm air and 773 – 1373 K for 1,3-hexachlorobutadiene, 4% O_2 in 1 atm He and 400 – 800 K for ortho-chlorophenol) mechanisms are constructed utilizing QRRK for *k(E)* with master equation for fall-off. The mechanisms are compared with corresponding experimental profiles, respectively.

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This thesis is dedicated to
my parents, Jinliang Zhu and Fengzhen Gao,
my husband, Huale Huang,
and
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CHAPTER 1

THERMOCHEMICAL KINETICS

1.1 Overview

Detail reaction kinetic models using mechanisms, based upon fundamental thermochemical and kinetic principles are presently used and being developed by researchers attempting to optimize or more fully understand a number of systems comprised of many complex chemical reactions. These include combustion, and flame inhibition, ignition, atmospheric smog formation and transport, stratospheric ozone depletion, municipal and hazardous wastes incineration, chemical vapor deposition, semiconductor etching, rocket propulsion and other related fields.

One important requirement for modeling and simulation of these systems is accurate thermochemical property data for molecular, intermediate radical and transition states. These data allow determination of equilibrium, and reverse rate constants from the forward rate constant and the equilibrium constant. *Ab initio* and density functional calculations provide an opportunity to accurately estimate thermochemical properties of reactants, intermediate radicals, and products, plus estimate properties for transition states which is often impossible to obtain through experiment.

1.2 Computational Chemistry

Ab initio molecular orbital theory is concerned with predicting the properties of atomic and molecular systems. It is based upon the fundamental laws of quantum mechanics and uses a variety of mathematical transformation and approximation techniques to solve the fundamental equations, i.e. Schrödinger Equation,

$$H\Psi = E\Psi$$

Here H is the *Hamiltonian*, a differential operator representing the total energy. E is the numerical value of the energy of the state, in term of kinetic energy of symbolized by T and potential energy V. Ψ is the wavefunction.

Model chemistry is characterized by the combination of theoretical procedure and a basis set. A basis set is a mathematical representation of the molecular orbitals within a molecule. The basis set can be interpreted as restricting each electron to a particular region of space. Large basis sets impose fewer constraints on electrons to particular accurately approximate exact molecular orbitals. The computation of atomic or molecular properties with large basis sets requires correspondingly more and more computational resources, however.

Standard basis sets for electronic structure calculation use linear combinations of Gaussian functions to form the orbitals. Basis sets assign a group of basis functions to each atom within a molecule to approximate its orbitals. These basis functions themselves are composed of a linear combination of Gaussian functions. The linear combined basis functions are refereed to as contracted functions, and the component Gaussian functions are referred to as primitives. A basis function consisting of a single

Gaussian function is termed uncontracted. Explanation of the nomenclature of 6-31G basis set is:

6 primitive Gaussians in the core function,

2 sets of function in the valence region (one function consisting of 3 primitive Gaussian, one consisting of 1 primitive Gaussian).

The 6-31G(d) indicates it is the 6-31G basis set with one d polarization function added to the heavy atoms (now hydrogen atoms). The 6-311+G(3df,2p) is three d functions and one f function on heavy atoms (+ means adding diffuse functions to heavy atoms), and 2 p functions added on the hydrogen atoms. If 6-311++G(3df,2p), then the one more + means also adding diffuse functions to hydrogen atoms.

The Hartree-Fock (HF) calculation method does not include a full treatment of the effects of electron correction, i.e. it does not include the energy contributions arising from electrons interacting with one another (electron – electron repulsion). A variety of theoretical methods, such as Møller-Plesset perturbation (MP2), and density functional have been developed which include some effects of electron correction. Traditionally, such methods are referred as post-SCF methods because they add this electron correlation correction to the basic Hartree-Fock model.

Density functional theory (DFT) methods have recently received widespread use in computational chemistry. DFT methods compute electron correlation via general functional of the electron density. These DFT functionals partition the electronic energy into several components, which are computed separately. They include: the kinetic energy, the electron-nuclear interaction, the coulomb repulsion, and an exchange-correlation term, which accounts for the remainder of the electron-electron interactions (the exchange-correlation term is, itself, also divided into separate exchange and correlation components in most actual DFT functions). A variety of functionals have been defined, generally distinguished by the way that they treat exchange and correlation components:

Local exchange and correlation functions involve only the values of the electron spin densities.

Gradient-corrected functionals involve both the values of electron spin density and the gradients.

A popular gradient-corrected exchange functional is proposed by Becke; [1] a widely used gradient-corrected correlation functional is the LYP functional of Lee, Yang and Parr. The combination of the two forms the B-LYP method. B3LYP is Becke-style3-parameter density functional theory (using the Lee-Yang-Parr correlation functional).

1.3 Kinetics

1.3.1 Lindemann-Hinshelwood Mechanism for Unimolecular Reactions

Perrin [2] proposed in 1919 that reactant molecules acquire energy by absorbing radiation from the walls of the reaction vessel. Langmuir [3] showed that the amount of energy radiated to the gas would be insufficient to account for observed unimolecular reaction rate. The argument which is fatal to the Radiation Hypothesis is a thermodynamic one. If the reaction vessel can do work to the gas to induce chemical reaction, then the second law of thermodynamics states that a lower temperature reservoir is needed to absorb excess heat, because the reaction vessel and the gas are at the same temperature.

In 1922, Lindemann [4] proposed a general theory for the thermal unimolecular reaction which forms the basis for the current theory of thermal unimolecular rate. He proposed that molecules become energized by bimolecular collisions, with a time lag between the moment of collision energy transfer and the time the molecule decomposes. Energized molecule can then undergo deactivating collisions before decomposition occurred. A major achievement of Lindemann's theory is its ability to explain the experimental finding that the reaction rate is pressure dependent, which is a failure in the Radiation Hypothesis. The mechanism in Lindemann theory is written as:

$$A + M \xrightarrow{k1} A^* + M$$

$$A^* + M \xrightarrow{k-1} A + M$$

$$A^* \xrightarrow{k2} \text{Products}$$

Rate k_{uni} and k_{kine} are defined as d [product]/dt = $k_{uni} \times [A] = k2 \times [A^*]$.

The asterisk indicates that A contains sufficient internal vibration energy to decompose. This energy is denoted by E and must be greater than the unimolecular decomposition threshold energy E_0.The concept is that:

(a) A certain fraction of the molecules become energized by collision, i.e. gain energy in excess of E_0.

(b) The rate of the energy transfer process depends upon the rate of bimolecular collisions. Energized molecules are de-energized by collision, which is a reverse reaction. This de-energized rate is taken to be energy-independent and is equated with the collision number Z_1 by assuming that every collision of A^* leads to a de-energized state. This is known as "strong collision assumption" for de-energizing collisions.

(c) There is a time-lag between the energy transfer and unimolecular dissociation and isomerization of the energized molecules. This unimolecular dissociation also occurs with a rate constant k_3 independent of the energy content of A^*.

The overall concept can be expressed by the equations below, where M can represent a generic bath gas molecule, an added "inert" gas molecule; it may also represent a second molecule of reactant or product. In the simple Lindemann theory k_1, along with k_2 and k_3 are taken to be energy-independent and are calculated from the simple collision theory equation.

Application of the steady-state hypothesis to the concentration of A^*, allows the unimolecular rate constant and the high pressure and low pressure limit rate and rate constants to be determined as follows:

Rate = k_{uni} [A] = k_2 [A*] = k_1k_2 [A] [M] / (k_{-1} [M]+k_2)

$k_{uni} = k_1k_2 [M] / (k_{-1} [M]+k_2)$

High-pressure limit rate, $[M] \rightarrow \infty$, $k_{uni} = k_\infty = k_1k_2 / k_{-1}$

Low-pressure limit rate, $[M] \rightarrow 0$, $k_{uni} = k_0 = k_1 [M]$

The unimolecular rate constant is then written as $k_{uni} = k_\infty / (1 + k_\infty / k_1 [M])$.

One can expect the Lindemann theory to predict a linear change in the initial rate of a unimolecular reaction with respect to concentration of M at low pressure. The transition from high-pressure rate constant to low pressure is called "fall-off region".

The k_1 in the original Lindemann theory is taken from the collision theory expression ($k_1 = Z_1\exp(-E_0/k_BT)$ with $Z_1 = (\sigma_d^2N_A/R)(8\pi N_Ak/\mu)^{1/2}(1/T)^{1/2}$, where Z_1 will be in $Torr^{-1}$-s^{-1} (consistent with [M] in Torr and k_2 in s^{-1}) when σ_d = collision diameter in cm; μ = reduced molar mass in g-mol^{-1} = $(1/M_A + 1/M_B)^{-1}$; T = temperature in Kelvin; N_A

is Avogadro constant 6.022×10^{23} mol^{-1}; R is gas constant 6.2326×10^{4} cm^{3}-Torr-K^{-1}-mol^{-1} or 0.082 atm-lit/mol-K; k_B (Bolzmann constant) = 1.3805×10^{-16} erg-K^{-1}.

The Lindemann theory, unfortunately, predicts the fall-off in k_{uni} to occur at much higher pressure than what is observed experimentally.

Based on the Lindemann's suggestion that k_1 could be increased by assuming that the required energy (energized molecules) could be drawn in part from the internal degrees of freedom (mainly vibration) of the reactant molecule, Hinshelwood [5] increases k_1 by using a much higher probability of a molecule possessing total energy ≥ E_0 in s classical degrees of freedom, $(E_0/k_BT)^{s-1}\exp(-E_0/k_BT)/(s-1)!$, than the simpler $\exp(-E_0/k_BT)$ Lindemann used. The result is

$$k_1 = [Z_1/(s-1)!](E_0/k_BT)^{s-1}\exp(-E_0/k_BT).$$

Since k_1 increases with s classical degrees of freedom in the Lindemann-Hinshelwood theory, then $k_2 = k_\infty k_{-1}/k_1$ should decrease with s. Thus the lifetime of the energized molecule $t \approx 1/k_2$ increases when the molecule can store energy among a greater number of degrees of freedom. Then k_2 is expected to depend on the energy of A*. Making k_2 energy-dependent, expressed as k(E), the energy interval from E to E+dE is considered:

$$A + M \xrightarrow{dk1} A^* (E, E+dE) + M$$

$$A^*(E, E+dE) + M \xrightarrow{k-1} A + M$$

$$A^*(E, E+dE) \xrightarrow{k(E)} \text{Products}$$

Then $dk_{uni}(E, E+dE) = k(E)(dk_1/k_{-1}) / (1 + k(E)/k_{-1}[M])$

It is assumed that for all pressure dk_1/k_{-1} represents the equilibrium probability and that the A* has energy between E and E+dE. This probability may be denoted P(E)dE. Also k_{-1} [M] is the collision frequency ω between A* and M, then

$$k_{uni} = \int_{E0}^{\infty} k(E)P(E)dE/(k(E)+\omega)$$

In order to make accurate quantitative predictions of the fall-off behavior of a unimolecular reaction it is essential to take into account the energy dependence of the rate constant k(E) (or k_2) for the conversion of energized molecules into activated complexes where products result from decomposition or reaction of the energized complex. Two quite different approaches may be taken to determine k(E). One is to consider the explicit nature of the intramolecular motion of highly energized molecules, such as Slater theory. The other approach is based on statistical assumptions, such as RRK theory and its extension, RRKM theory. Most modern theories of unimolecular reaction rates, including the Slater theory, the RRK theory and the RRKM theory, are based on the fundamental Lindemann mechanism involving collision energy transfer of the reactant molecules, and more specifically on Hinshelwood's development (see above).

1.3.2 Slater Theory

Slater [6] in 1939 pictured a molecule as an assembly of harmonic oscillators. Decomposition is assumed to occur when a critical coordinate (i.e. a bond length or bond angle) attains a critical displacement. The attainment of the reaction coordinate critical extension is not a statistical random process as in RRKM Theory, but depends on the energies and phases of the specific normal mode excited. Since energy does not flow freely within the molecule, the theory predicts intrinsic non-RRKM behavior.

Overall the Slater Theory is unsuccessful in interpreting experiments.

1.3.3 RRK Theory of Unimolecular Reactions

The RRK theory was developed independently by Rice and Ramsperger [7] and Kassel [8-10].

Both Rice and Ramsperger theory and Kassel theory consider that for reaction to occur a critical energy E_0 must become concentrated in one part (specific vibration) of the molecule. They used the basic Lindemann-Hinshelwood mechanism of collision energy transfer and de-energization, but assumed more realistically that the rate constant for conversion of an energized molecule into products is proportional to a specific probability. This is a finite statistical probability that energy, E_0, is found in the relevant part of the energized molecule which contains total energy, E, is greater than E_0 since E of the molecule under consideration is assumed to be rapidly redistributed around the molecule. This probability will increase with E and make k_2 a function of its energy content; k_2 is not "energy" dependent.

The difference between the two models (Rice and Ramsperger versus Kassel) is two-fold. First, Rice and Ramsperger used classical statistical mechanics throughout, while Kassel used classical methods and also developed a quantum treatment. The quantum method turns out to be much more realistic and accurate. Second, different assumptions were made about the part of the molecule into which the critical energy E_0 has to be concentrated. The Kassel's model seems slightly more realistic by assuming the energy had to be concentrated into one oscillator. **The quantum version of the Kassel theory serves as a theoretical basis for calculations performed in this thesis.**

The classical RRK theory is based on the notion that the probability that a molecule of s classical oscillators with total energy E has energy greater than E_0 in one chosen oscillator, which is the critical mode leading to reaction. The assumptions used to derive the quantum RRK rate constant are similar to those for classical theory. In the quantum theory it is assumed there are s identical oscillators in the molecule, all having frequency ν. The energized molecule has n quanta, so E = nhν. The critical oscillator must have m quanta for dissociation occurrence, $m = E_0/h\nu$.

The probability that one oscillator contains at least m quanta; probability (energy ≥ m quanta in one chosen oscillator) is then equal to [11]:

$$\text{Probability} = \frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!}$$

Hence,

$$k_a\,(nh\upsilon) = A\frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!}$$

Where A is a proportion constant and the same as the classical one.

The corresponding $k_1(E)$ of the Hinshelwood expression is now derived. It refers to energy transfer into a specific quantum state rather than into an energy range E to E+dE, as

$$k_1\,(nh\upsilon) = k_2\alpha^{\nu}(1-\alpha)^{s-1}\frac{(n+s-1)!}{n!(s-1)!}$$

Where $\alpha = \exp(-h\nu/k_BT)$.

Both classical and quantum versions RRK theory were developed, and in the limit of a large excitation energy E the two versions become identical.

In RRK theory the assumption is made that the rate of conversion of energized molecules into products is related to the probability that the critical energy E_0 is concentrated in one part of the molecule, e.g. in one oscillator (Kassel theory) or in one squared term (Rice-Ramsperger theory). This probability is a function of the total energy E of the energized molecule, and the total vibrations among which the vibration energy quanta can be distributed.

1.3.4 RRKM Theory of Unimolecular Reactions

The RRKM theory was developed using the RRK model and extending it to consider explicitly vibration and rotation energies and to include zero point energies. Several minor modifications of the theory have been made, primarily as a result of improved treatments of external degrees of freedom.

RRKM theory is a microcanonical transition state theory.

$$A^* \xrightarrow{k(E)} A^{\neq} \rightarrow \text{Products}$$

Where $A^{\neq}$ is the transition state.

Different experimental techniques, including static pyrolysis, carrier (flow) techniques, shock tube methods, and very-low-pressure-pyrolysis, have been used to measure k_{uni} as a function of temperature and pressure. One of the most significant achievements of RRKM theory is its ability to match measurements of k_{uni} with pressure.

1.3.5 Chemical Activation Reactions

The energization methods other than by molecular collision, such as photoactivation and chemical activation, may produce a non-equilibrium situation in which molecules acquire energies far in excess of the average thermal energy. This presence of excess energy in the energized adduct makes chemical activation reactions much more important in these systems. A treatment for the rate of conversion, which includes decomposition of energized adduct to product(s) (including back to reactant) and the competing rate of its collision stabilization, is needed.

An example of a chemically activated reaction system is OH radical + C_2H_3Cl system. As is discussed by Zhu et al. [12], OH radical reacts with C_2H_3Cl to form a chemically activated, energized adduct [$CHClOHC.H_2^*$], this process of forming adduct is much more efficient than that by thermal molecular collision, and adduct contains excess energy from the new bond formed in this chemical (addition) reaction. The energized adduct [$CHClOHC.H_2$*] could go back to reactant OH + C_2H_3Cl, or could go to products C_2H_3OH + Cl via an intramolecular H shift. The QRRK analysis (A + BC → ABC*) shows that the chemical activation process is more important than thermal dissociation process.

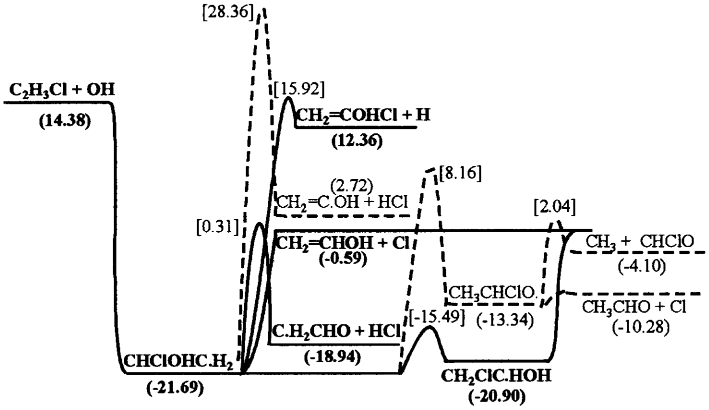


Figure 1.1 Potential Energy Diagram of α-Addition of OH + C_2H_3Cl.

The basic idea of the treatment of a chemical activation system is that a vibration excited molecule ABC^* formed by an association of reactants can reform reactants A + BC with a rate constant k'(E), form decomposition products, AB + C, with a rate constant $k_a(E)$ or be de-energized to stable molecules ABC.

In the strong collision assumption the first order rate constant for de-energization is equal to the collision frequency, $\omega = Zp$ where p is the total pressure and Z is collision number (see "1.3.1 Lindemann-Hinshelwood Mechanism for Unimolecular Reactions" on page 4). This assumes that stabilization occurs at energy collision.

Suppose that the fraction of molecules which are energized per unit time into the energy range between E and E+dE is f(E)dE. To simplify, one can consider decomposition path (back to reactant, A + BC, as the decomposition path), then the fraction of ABC^* decomposing (path A + BC) compared with those stabilized (path ABC) is $k(E)/ [k(E)+\omega]$. The fraction of molecules in the energy range between E and E+dE decomposing to products is therefore $\{k(E)/ [k(E)+\omega]\}f(E)dE$, and the total number of molecules decomposing per unit time (D), at all energies above the critical energy E_0, is:

$$D = \int_{E_0}^{\infty} \frac{k(E)}{k(E)+\omega} f(E) dE$$

Corresponding, the total rate of stabilization (S) is:

$$S = \int_{E_0}^{\infty} \frac{\omega}{k(E)+\omega} f(E) dE$$

Considering an average rate constant <k> for all energies above E_0, one would have:

$$\frac{<k>}{\omega} = \frac{D}{S} = \frac{\text{No. molecules decomposing per unit time}}{\text{No. of molecules being stabilized per unit time}}$$

So,

$$<k> = \omega \frac{\int_{E_0}^{\infty} \{k(E)/[k(E)+\omega]\} f(E) dE}{\int_{E_0}^{\infty} \{\omega/[k(E)+\omega]\} f(E) dE}$$

The f(E) is the distribution function of energized molecules in the energy range between E and E+dE. In the thermal energy transfer systems, this distribution function is simply the thermal quantum Boltzmann distribution $K(E)$ and the rate of energy transfer into the energy range between E and E+dE is $K(E)dE = dk_1/k_2$. For the chemically activated system described here, the distribution function can be derived by applying the principle of detailed balancing to the reverse process to reactants. Consider a situation in which other processes can be ignored and equilibrium is established between A^* and reactants. Then the fraction of molecules with energy between E and E+dE is Boltzmann distribution $K(E)dE$, so the rate of dissociation to reactants is then $K'(E)K(E)dE$, and by the principle of detailed balancing this also gives the rate of combination of reactants to give A^* in this energy range. The total rate of energy transfer to all levels above the minimum energy E_{min} (the minimum energy of A^*) is:

$$\text{Total rate of energization} = \int_{E_0}^{\infty} k'(E) K(E) dE$$

Therefore, the distribution function is given by:

$$f(E)\delta E = \frac{k'(E)K(E)dE}{\int_{E_0}^{\infty} k'(E)K(E)dE}$$

The $f(E)dE$ can be incorporated into QRRK theory for $k(E)$ and $k_1(E)$ serves as a basis for the calculations for chemical activation reaction systems.

1.3.6 QRRK Analysis for Unimolecular and Chemical Activation Reactions

QRRK analysis, as initially presented by Dean [13-15] combined with the modified strong collision approach of Gilbert et al. [16-18], to compute rate constants for both chemical activation and unimolecular reactions, over a range of temperature and pressure. The computer program CHEMDIS, based on the QRRK theory outlined as above, and unimolecular dissociation and chemical activation formalism carries out all unimolecular and chemical activation reactions involved in this thesis. The input parameters for CHEMDIS are: (1) High-pressure limit rate constants (Arrhenius A factor and activation energy E_a) for each reaction included for analysis; (2) A reduced set of three vibration frequencies and their associated degeneracy; (3) Lennard-Jones transport parameters, (s (Angstroms) and e/k (Kelvin)), and (4) molecular weight of well species. .

1.3.6.1 Input Information Requirements for QRRK Calculation. k_∞'s are fitted by three parameters A_∞, n, and Ea over temperature range from 298 to 2000K, $k_\infty = A_\infty(T)^n \exp(-Ea / RT)$. Entropy differences between reactant and transition state are used to determine the pre-exponential factor, A, via canonical Transition State Theory (TST):

$$A = (k_BT/h)\exp(\Delta S^{\neq}/R), \qquad Ea = \Delta H^{\neq}$$

Where h is the Planck constant and k_B is the Boltzmann constant. $\Delta S^{\neq}$ = S(TST) – S(reactants) and $\Delta H^{\neq}$ = H(TST) – H(reactants). Treatment of the internal rotors for S and Cp(T) of reactants and the TST's is important here because these internal rotors are often lost in the cyclic transition state structures. Pre-exponential factors (A_∞), are calculated from structures determined by (Density Functional Theory) DFT or estimated from the literature and from trends in homologous series of reactions. Activation energies come from DFT plus evaluated endothermicity of reaction ΔU_{rxn}, from analysis of Evans-

Polanyi relationships for abstractions plus evaluation of ring strain energy, and from analogy to similar reactions with known energies. Thermochemical properties are provided for each system.

Reduced sets of three vibration frequencies and their associated degeneracies are computed from fits to heat capacity data, as described by Ritter and Bozzelli et al. [19,20] These have been shown by Ritter to accurately reproduce molecular heat capacities, Cp(T), and by Bozzelli et al. [20] to yield accurate ratios of density of states to partition coefficient, $\rho(E)/Q$.

Lennard-Jones parameters, sigma (angstroms) and ε/k (Kelvin's), are obtained from tabulations [21] and from a calculation method based on molar volumes and compressibility [22].

When necessary, estimation is done in a consistent and uniform manner via use of generic reaction rate constants with reference to literature, experiment or theoretical calculation in each case. The QRRK calculation input parameters and their references are listed in the table associated with the respective reaction system.

1.3.6.2 Quantum RRK /Master Equation Calculation. The quantum RRK (QRRK) / master equation analysis is described by Chang et al. [13,23]. The QRRK code utilizes a reduced set of three vibration frequencies which accurately reproduce the molecule's (adduct) heat capacity; the code includes contribution from one external rotation in calculation of the ratio of the density of states to the partition coefficient $\rho(E)/Q$.

Comparisons of ratios of these $\rho(E)/Q$ with direct count $\rho(E)/Q$'s are shown to be in good agreement [20]. Rate constant results from the quantum RRK - Master equation analysis are shown to accurately reproduce (model) experimental data on several complex systems. They also provide a reasonable method to estimate rate constants for numerical integration codes by which the effects of temperature and pressure can be evaluated in complex reaction systems.

Multifrequency quantum Rice-Ramsperger-Kassel (QRRK) analysis is used to calculate k(E) with a master equation analysis [23] for fall-off. A 500 cal. energy grain interval is used for the energy intervals. Rate constants are obtained as a function of temperature and pressure for the chemical activation and dissociation reactions. The master equation analysis [23] uses an exponential-down model for the energy transfer function with $(\Delta E)^{\circ}_{\text{down}} = 1000$ cal/mol (for N_2 as bath gas). Troe et al. [24,25] conclude that $(\Delta E)^{\circ}_{\text{down}}$ is independent of temperature (293 – 866 K) for the rare and diatomic bath gases and Hann et al. [26] recently determined a value of $(\Delta E)^{\circ}_{\text{down}} = 500$ cm^{-1} for matching the two-dimensional master equation solutions to the experimental fall-off behavior in the $C_3H_3 + O_2$ system with N_2 bath gas. Knyazev and Slagle [27] reported that $(\Delta E)^{\circ}_{\text{down}}$ changes with temperature; they compared three models, two of which are $(\Delta E)^{\circ}_{\text{down}} = \alpha T$ and $(\Delta E)^{\circ}_{\text{down}}$ = constant, in reaction of n-$C_4H_9 \Leftrightarrow C_2H_5 + C_2H_4$ with He as bath gas. The difference between the values of the energy barrier height (E) needed to fit the experimental data with these two models (temperature dependent versus non-temperature dependent) for $(\Delta E)^{\circ}_{\text{down}}$ is only 0.4 kJ/mol; but this is over a relatively narrow temperature range (560 – 620 K). A larger temperature range of 298 – 2000 K and a constant $(\Delta E)^{\circ}_{\text{down}}$ (where N_2 is the third body) are used in this study.

CHAPTER 2

GAS-PHASE THERMOCHEMICAL PROPERTIES, $\Delta_F H^O_{298}$, S^O_{298}, AND $C_P^O(T)$ ($300 \leq T/K \leq 1500$), OF CHLOROMETHYL RADICALS

2.1 Overview

Chloromethyl radicals and chloroethyl radicals are important species in reaction systems containing chlorinated compounds. However, there are still up to 2 kcal/mol discrepancies in the literature values of chloromethyl radicals, which will be shown in the discussion of this chapter. This chapter presents our current calculation results. Higher level calculations and added literature analysis are needed. The calculation results of the chloromethyl radicals at four DFT and composite levels, with a comparison to the literature values are presented.

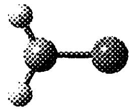
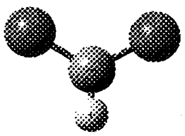
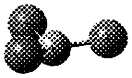
2.2 Methodology

All calculations are performed using the Gaussian94 [28] program suite. The structures of three chloromethyl radicals, CH_2Cl, $CHCl_2$, and CCl_3, are fully optimized at B3LYP/6-31G(d,p) level of theory. Harmonic vibration frequencies and zero point vibrational energies (ZPVE) are computed at the same level. The B3LYP/6-31G(d,p) optimized geometrical parameters are used to obtain single total electronic energies in B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q calculations. The B3LYP/6-31G(d,p) is chosen because it is reported to give accurate structural parameters and it includes electron correlation. The B3LYP/6-311+G(3df,2p) is a larger basis set with diffuse functions allowing more overlap of the Cl electrons. QCISD(T)/6-31G(d,p) is considered high-level *ab initio* method and CBS-Q//B3LYP/6-31G(d,p) is a composite calculation method with corrections for electron type and spin contamination.

The above methods coupled with isodesmic reactions are proven to give precise results for enthalpies of formation for various chloro and oxychloro hydrocarbons. [29-36]

2.3 Results and Discussion

Table 2.1 Geometries at B3LYP/6-31G(d,p) Level for Chloromethyl Radicals

Species (ID#)	Structure	Bond length	(angstrom)	Bond angle	(degree)	Dihedral angle	(degree)
CH_2Cl		r21	1.080				
(1)		r31	1.080	<312	124.47		
		r41	1.715	<412	117.75	<4123	179.97
$CHCl_2$		r21	1.079				
(2)		r31	1.710	<312	119.47		
		r41	1.710	<412	119.47	<4123	179.95
CCl_3		r21	1.731				
(3)		r31	1.731	<312	116.93		
		r41	1.731	<412	116.93	<4123	-145.87

2.3.1 Geometries

The fully optimized geometries at the B3LYP/6-31G(d,p) level for CH_2Cl, $CHCl_2$, and CCl_3, are shown in Table 2.1. Harmonic vibration frequencies and moments of inertia are calculated for each chloromethyl radical on the basis of optimized geometries at this same level of theory (Table 2.2). It is seen from the optimized structures that CH_2Cl and $CHCl_2$ are planar but CCl_3 looks like a tripod with dihedral angle of 146 degree. There is a negative frequency in CH_2Cl and $CHCl_2$. All frequencies in CCl_3 are positive. The negative frequencies (inversion frequencies, –42 cm^{-1} in chloromethyl radical and –358 cm^{-1} in dichloromethyl radical) correspond to the umbrella conversion modes in CH_2Cl and $CHCl_2$. The activation energy for the same umbrella conversion in CCl_3 may be too high to overcome at room temperature.

Table 2.2 The B3LYP/6-31G(d,p) Harmonic Vibrational Frequencies (cm^{-1}) and Moments of Inertia (amu-Bohr^2) for Chloromethyl Radicals

Species	Freq	Ia	Ib	Ic
CH_2Cl (**1**) Sym = 2	-42.2304^a 833.8118 1003.7384 1428.6759 3192.4576 3346.8430	6.57216	115.68419	122.25635
$CHCl_2$ (**2**) Sym = 2	-357.5697^a 311.9876 746.0265 911.2675 1252.3811 3278.2398	37.37094	553.70697	591.07791
CCl_3 (**3**) Sym = 3	275.0138 275.3181 333.8380 482.7123 877.5146 878.2292	547.03643	547.11970	1086.91978

a: Negative frequency is for internal conversion, not to be used for S and Cp calculations.

Table 2.3 Calculated Total Energies at 298 K for Chloromethyl Radicals ^{a,b}

Species	B3LYP/ 6-31G(d,p)	B3LYP/6-311+G(3df,2p)	QCISD(t)/ 6-31G(d,p)	CBS-Q	ZPVE^{c,d}	H_{298}-H_0^{d}
	//B3LYP/6-31G(d,p)					
1	-499.41558	-499.46420	-498.72393	-498.90110	13.75	2.44
2	-959.01597	-959.09948	-957.76116	-958.05963	9.11	2.73
3	-1418.61110	-1418.72951	-1416.79521	-1417.21615	4.38	3.40

a: All calculations are based on B3LYP/6-31G(d,p) optimized structures;

b: Total energies (ZPVE and thermal corrections are included) in hartree, 1 hartree = 627.51 kcal/mol;

c: Scaled by 0.9806; [37]

d: In units of kcal/mol.

2.3.2 $\Delta_f H^o_{298}$

$\Delta_f H^o_{298}$ for three chloromethyl radicals are obtained using the isodesmic reaction method with total energies at four different DFT levels of theory, i.e. B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q (Table 2.3).

The following isodesmic reactions are selected to determine $\Delta_fH^\circ_{298}$ of three chloromethyl radicals.

$CH_2Cl + CH_4 \rightarrow CH_3Cl + CH_3$ (R1a)

$CH_2Cl + C_2H_6 \rightarrow CH_3Cl + C_2H_5$ (R1b)

$CH_2Cl + C_2H_5Cl \rightarrow CH_3Cl + CH_3C{\bullet}HCl$ (R1c)

$CH_2Cl + CH_3OH \rightarrow CH_3Cl + CH_2OH$ (R1d)

$CHCl_2 + CH_4 \rightarrow CH_2Cl_2 + CH_3$ (R2a)

$CHCl_2 + C_2H_6 \rightarrow CH_2Cl_2 + C_2H_5$ (R2b)

$CHCl_2 + C_2H_5Cl \rightarrow CH_2Cl_2 + CH_3C{\bullet}HCl$ (R2c)

$CHCl_2 + CH_3OH \rightarrow CH_2Cl_2 + CH_2OH$ (R2d)

$CHCl_2 + CH_3Cl \rightarrow CH_2Cl_2 + CH_2Cl$ (R2e)

$CCl_3 + CH_4 \rightarrow CHCl_3 + CH_3$ (R3a)

$CCl_3 + C_2H_6 \rightarrow CHCl_3 + C_2H_5$ (R3b)

$CCl_3 + C_2H_5Cl \rightarrow CHCl_3 + CH_3C{\bullet}HCl$ (R3c)

$CCl_3 + CH_3OH \rightarrow CHCl_3 + CH_2OH$ (R3d)

$CCl_3 + CH_3Cl \rightarrow CHCl_3 + CH_2Cl$ (R3e)

$CCl_3 + CH_3Cl \rightarrow CH_2Cl_3 + CHCl_2$ (R3f)

The reference species used in the isodesmic reactions are collected in Table 2.4.

Table 2.4 $\Delta_fH^\circ_{298}$ (kcal/mol) for Reference Species Used in Working Reactions

CH_3	35.10±0.20 [38]	$C{\bullet}H_2OH$	-3.97±0.22 [30]
CH_4	-17.83±0.07 [39]	C_2H_5	28.80±0.50 [40]
CH_3Cl	-19.57±0.36 [39]	C_2H_6	-20.08±0.10 [39]
CH_2Cl_2	-22.72±0.60 [39]	C_2H_5Cl	-26.79±0.17 [39]
$CHCl_3$	-24.52±0.60 [39]	$CH_3C{\bullet}HCl$	18.51 [41]±0.50 (uncertainty is estimated here)
CH_3OH	-48.08±0.05 [42]		

Table 2.5 $\Delta_f H^\circ_{298}$ (kcal/mol) for Chloromethyl Radicals by Isodesmic Reactions and Theoretical Calculation Methods

		B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	QCISD(T)/6-31G(d,p)	CBS-Q	Avg.^{a}	Uncert.	
							SD^a	ref^b
		B3LYP/6-31G(d,p)						
1	(R1a)	26.73	26.64	27.71	27.36			0.63
	(R1b)	27.43	27.29	26.64	26.96			0.96
	(R1c)	28.11	27.91	26.95	26.89			1.03
	(R1d)	28.48	27.48	27.17	27.06	27.07	0.21	0.63
2	(R2a)	19.62	19.60	21.32	21.11			0.87
	(R2b)	20.32	20.25	20.25	20.71			1.20
	(R2c)	21.00	20.87	20.56	20.64			1.27
	(R2d)	21.37	20.44	20.78	20.82	20.82	0.21	0.87
	(R2e) ^{c}	*19.95*	*20.03*	*20.68*	*20.82*			
3	(R3a)	14.59	15.09	16.67	17.48			0.87
	(R3b)	15.29	15.74	15.60	17.09			1.20
	(R3c)	15.97	16.36	15.90	17.02			1.27
	(R3d)	16.34	15.93	16.13	17.19	17.20	0.21	0.87
	(R3e) ^{c}	*14.93*	*15.52*	*16.02*	*17.20*			
	(R3f) ^{c}	*15.79*	*16.31*	*16.16*	*17.20*			

a: Average and standard deviations for CBS-Q levels of theory;

b: Cumulative uncertainties from reference species in isodesmic reactions;

c: This reaction is not used in calculations of recommended $\Delta_f H^\circ_{298}$.

The calculated $\Delta_f H^\circ_{298}$ for three chloromethyl radicals are shown in Table 2.5. The average values calculated at CBS-Q//B3LYP/6-31G(d,p) by the first four isodesmic reactions is taken as the recommended $\Delta_f H^\circ_{298}$ for each species. Other sources of error listed in Table 2.5 comprise the standard deviation of calculated $\Delta_f H^\circ_{298}$ values (one level and first four isodesmic reactions), plus the cumulative uncertainties in $\Delta_f H^\circ_{298}$ for the reference species, as well as the uncertainty from ZPVE calculations, 0.44 kcal/mol. [35,37] The results are listed in Table 2.6 as well as some of the literature values.

Comparison of the results obtained in this chapter with literature values show the discrepancies are as large as 2.8 kcal/mol. The unpublished website data at the BAC-MP4 calculation level by Melius [43] are within 1 kcal/mol of the values obtained in this work.

Table 2.6 Ideal Gas-phase Thermochemical Properties for Chloromethyl Radicals[a,b]

	$\Delta_f H°_{298}$	$S°_{298}$	$C_p°(T)$						
			300K	400K	500K	600K	800K	1000K	1500K
CH_2Cl **(1)**	**27.07±1.68**	**57.08**	**9.04**	**10.00**	**10.84**	**11.55**	**12.70**	**13.62**	**15.24**
Melius [43]	27.07±1.50								
Seetula [44]	29.09±1.08								
Lee and Bozzelli [45]	27.99	58.61	10.08	11.45	12.53	13.38	14.66	15.64	17.30
$CHCl_2$ **(2)**	**20.82±1.92**	**64.98**	**11.13**	**12.20**	**13.10**	**13.77**	**14.71**	**15.37**	**16.38**
Melius [43]	20.35±2.45								
Seetula [44]	22.04±0.93								
Lee and Bozzelli [45]	23.50	68.10	12.90	14.16	15.09	15.79	16.76	17.44	18.46
CCl_3 **(3)**	**17.20±1.92**	72.06	15.38	16.78	17.66	18.23	18.88	19.22	19.57
JANAF [46]	19.00	**70.92**	**17.56**	**15.24**	**16.66**	**17.56**	**18.16**	**18.83**	**19.56**
Gurvich [47]	19.12±1.20								
Melius [43]	16.58±2.60								
Seetula [44]	16.87±0.88								
Lee and Bozzelli [45]	19.00	70.92	15.25	16.66	17.56	18.16	18.83	19.18	19.56

a: $\Delta_f H°_{298}$ in kcal/mol, S and Cp in cal/mol.K;

b: Data in bold are calculated and recommended in this work.

2.3.3 $S°_{298}$ and $C_p°(T)$ ($300 \leq T/K \leq 1500$)

$S°_{298}$ and $C_p°(T)$ obtained from the frequencies along with moments of inertia based on the optimized B3LYP/6-31G(d,p) structure, using "SMCPS" computer program, [48] are listed in Table 2.6. An example in detail of this calculation procesure is given by Zhu and Bozzelli. [36]

2.3.4 The C–H and C–Cl Bond Energies

The C–H and C–Cl bond energies at 298 K in CH_3Cl, CH_2Cl_2, CH_3Cl, and CCl_4 are shown in Table 2.7, which are determined using the corresponding enthalpy change of the bond dissociation reactions and the thermochemical data of each species as listed in Table 2.6.

It is seen from Table 2.7 that the C-Cl bond and C-H bond energies become weaker when the number of Cl substitution increases on the carbon.

Table 2.7 The C—H and C—Cl Bond Energies (kcal/mol) at 298 K

Bond	Bond Energy (This work)	Bond	Bond Energy (This work)
CH_3—Cl	83.66	CH_3—H	105.03
CH_2Cl—Cl	78.79	CH_2Cl—H	98.74
$CHCl_2$—Cl	74.33	$CHCl_2$—H	95.65
CCl_3—Cl	69.04	CCl_3—H	93.82

2.4 Summary

Thermochemical parameters, $\Delta_fH^o_{298}$, S^o_{298}, and $C_p^o(T)$ ($300 \leq T/K \leq 1500$), for CH_2Cl, $CHCl_2$, and CCl_3 are studied in this work. Recommended $\Delta_fH^o_{298}$ of each species is the average value of data using isodesmic reactions computed at CBS-Q//B3LYP/6-31G(d,p). S^o_{298} and $Cp^o(T)$ of CH_2Cl, $CHCl_2$, and CCl_3 are determined from harmonic frequencies and moments of inertia at the same levels for the geometries, i.e. B3LYP/6-31G(d,p). C-Cl and C-H bond energies in methyl chlorides are computed.

CHAPTER 3

GAS-PHASE THERMOCHEMICAL PROPERTIES, $\Delta_F H^O_{298}$, S^O_{298}, AND $C_P{}^O(T)$ ($300 \leq T/K \leq 1500$), OF CHLOROBENZENES BY DENSITY FUNCTIONAL CALCULATIONS

3.1 Overview

Multi-substituted aromatics or polyaromatic molecules such as chlorinated dibenzo-*p*-dioxins and dibenzofurans are often observed in the effluent streams from combustion or incinerators. These compounds are thought to be hazardous and toxic and as a consequence are highly undesirable products of incomplete combustion.

Slow combustion of chlorobenzene at ~ 500°C gives phenol produces three chlorophenols, dibenzofuran, four isomers of monochloro dibenzofurans (MCDFs), ten dichlorodibenzofurans (DCDFs), but dibenzo-*p*-dioxins (dioxin) were not detected. [49] The thermal oxidation processes of chlorobenzene are investigated at 575 – 825 °C by Fadli et al. [50] It is found that the PCDD/Fs formation from 2,4-dichlorophenol is ~ 100 times faster than that from 1,2-dichlorobenzene. [51] The dioxin formation from phenoxy radical reactions with chloro- and bromo- benzenes are studied by Louw et al. [52,53] The rates and mechanisms of gas-phase substitution of X in hexadeuteriobenzene and benzene derivatives (C_6H_5X, X = CH_3, CF_3, OH, Cl, F) by H atoms are studied by Manion and Louw. [54] When X = D, CH_3, CF_3, OH, substitution of X by H occurs by addition of H then loss of X. When X = Cl, direct addition also takes place. When X = F, abstraction is the only operative mechanism. No evidence for H migration around ring in cyclohexadienyl intermediates is found.

It would be of significant value to have knowledge of the fundamental thermochemical properties of chlorobenzenes which would help to have an accurate and fundamental understanding of their reaction pathways of the formations of PCDD/Fs.

There are a number of literarure evaluation studies for the thermochemical properties on chlorobenzenes, such as Pedley et al., [42] Cox, [55] TRC, [41] etc… These are reviews of limited experimental data. Platnov and Simulin [56] published the $\Delta_f H^o_{298}$ for 1,2,3-tri, 1,2,4,5-tetra-, and per- chlorobenzenes in 1983. Next year, Platnov and Simulin [57] published the $\Delta_f H^o_{298}$ for the three dichlorobenznes. A year later, Platnov and Simulin [58] studied the $\Delta_f H^o_{298}$ of five species, i.e. chlorobenzene, 1,2,4-tri, 1,3,5-tri-, 1,2,3,4-tetra-, and 1,2,3,5-tetra- chlorobenzenes. Later in 1985, Platnov, Simulin, and Rozenberg [59] finished the last species, pentachlorobenzene. In 1987, Yan et al. [60] presented the standard enthalpies of formation of three trichlorobenzenes, which had 0.8 to 2.7 kcal/mol differences from Platnov's. All experiments by Platnov et al. and Yan et al. used the method of rotating bomb calorimetry.

It is difficult to determine the $\Delta_f H$ of chlorinated species accurately because in these oxygen bomb calorimeters it is not known accurately – as to identification and quantities.

Shaub [61] developed a procedure in 1982 to estimate gas-phase enthalpies of formation of aromatic compounds: chlorinated benzenes, phenols and dioxins. His approach is to start from benzene, which has the well-known gas-phase enthalpy of formation from Pedley et al. [42], Cox [55], and SWS [62]. Then two effects are considered for a substituted benzene: (1) the primary effects of replacing hydrogen atom with substituent x = Benzene – 1-Chloro benzene, and (2) the secondary effect of *ortho*-, *meta*-, and *para*-*x* groups as in *ortho*-, *meta*-, and *para*-dichlorobenzene, for example.

O = 1,2-Dichloro benzene – Benzene + 2 x

These effects are summarized in Table 3.1.

Table 3.1 Summary of (x, o, m, p) effects (kcal/mol) in Chlorobenzenes by Shaub [61]

Effect	-Cl	-OH	-F	$-CH_3$
x	7.6	42.85	47.57	7.82
o	2.09		5.07	0.39
m	0.99	0.19	1.37	-0.03
p	0.39	2.51	2.00	0.14

For an example, hexachlorobenzene = benzene – 6 x + 6 o + 6 m + 3 p = -6.14 kcal/mol, close to the literature value of –8.6±2.3 by Cox. [55]

Shaub [61] described the estimation scheme of Prosen et al. [63] for alkyl substituent and a weighted least square method of Good [64] who found a "buttress" effect.

Another estimation method for the enthalpies of formation of benzene derivatives in the gas-phase is developed by Cox in 1978. [65] This method assumes that each group when substituted into the benzene ring produces a characteristic increment in $\Delta_f H°_{298}$. The $\Delta_f H°_{298}$ of some dichlorophenols estimated using this scheme are in good agreement with the experimental values of Ribeiro Da Silva et al. [66].

A series of interaction groups was developed by Wu et al. in 1993 to improve the accuracy of thermochemical properties of multi-substituted aromatic compounds. [67] Comparison of this group additivity estimation shows better agreement with the literature values by TRC [41], than just using the Benson's groups [68].

Cioslowski et al. [69] calculated C-H and C-Cl bond energies in polychloro benzenes from total energies at BLYP/6-311G(d,p) level, and found that

$$\text{BD (C-H)} = 107.24 + 1.20N_o - 0.24N_m + 0.79N_p;$$

$$\text{BD (C-Cl)} = 88.49 - 2.30N_o - 1.07N_m + 0.14N_p;$$

Where N_o, N_m, and N_p are numbers of chlorine substitutuents at *ortho-*, *meta-*, and *para-* positions with respect to the abstraction site.

This chapter estimates fundamental thermochemical properties, $\Delta_f H^\circ_{298}$, S°_{298}, and $C_p^\circ(T)$, for all chlorinated benzenes using two density functional calculation methods. Enthalpy of formation of each chlorobenzene is determined at each calculation level using two isodesmic reactions. The results will be compared with above literature values.

3.2 Methodology

All calculations are performed using the Gaussian94 or Gaussian98 program suite. [28,70] The structures of 12 chlorobenzenes are fully optimized at B3LYP/6-31G(d,p) level of theory. Harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. Then B3LYP/6-31G(d,p) optimized geometries are used to obtain single point total electronic energies in B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) calculations. [71,72] Total energies are corrected by ZPVE's which are scaled by 0.9806 as recommended by Scott and Radom. [37] Thermal corrections (0 K to 298 K) are calculated to estimate H_{298} from H_0. [73]

3.2.1 $\Delta_f H^\circ_{298}$

Standard enthalpies of formation are obtained using total energies obtained by the B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) calculation methods and two generic isodesmic reactions.

The following isodesmic reactions are selected to determine $\Delta_f H^\circ_{298}$ of chlorobenzenes.

Chlorobenzene + C_2H_4 → benzene + CH_2=CHCl (R1a)

Chlorobenzene + CH_2=CHCl → benzene + CH_2=CCl_2 (R1b)

1,2-dichlorobenzene + benzene → 2 × chlorobenzene (R2a)

1,2-dichlorobenzene + C_2H_4 → benzene + CH_2=CCl_2 (R2b)

1,3-dichlorobenzene + benzene → 2 × chlorobenzene (R3a)

1,3-dichlorobenzene + C_2H_4 → benzene + CH_2=CCl_2 (R3b)

1,4-dichlorobenzene + benzene → 2 × chlorobenzene (R4a)

1,4-dichlorobenzene + C_2H_4 → benzene + CH_2=CCl_2 (R4b)

1,2,3-trichlorobenzene + 2 × benzene → 3 × chlorobenzene (R5a)

1,2,3-trichlorobenzene + benzene → chlorobenzene + 1,2-dichlorobenzene (R5b)

1,2,4-trichlorobenzene + 2 × benzene → 3 × chlorobenzene (R6a)

1,2,4-trichlorobenzene + benzene → chlorobenzene + 1,2-dichlorobenzene (R6b)

1,3,5-trichlorobenzene + 2 × benzene → 3 × chlorobenzene (R7a)

1,3,5-trichlorobenzene + benzene → chlorobenzene + 1,3-dichlorobenzene (R7b)

1,2,3,4-tetrachlorobenzene + benzene → 2 × 1,2-dichlorobenzene (R8a)

1,2,3,4-tetrachlorobenzene + benzene → chlorobenzene + 1,2,3-trichlorobenzene (R8b)

1,2,3,5-tetrachlorobenzene + benzene → 1,2-dichlorobenzene + 1,3-dichlorobenzene (R9a)

1,2,3,5-tetrachlorobenzene + benzene → chlorobenzene + 1,2,3-trichlorobenzene (R9b)

1,2,4,5-tetrachlorobenzene + benzene → 2 × 1,2-dichlorobenzene (R10a)

1,2,4,5-tetrachlorobenzene + benzene → chlorobenzene + 1,2,4-trichlorobenzene (R10b)

pentachlorobenzene + benzene → 1,2,3,4-tetrachlorobenzene (R11a)

pentachlorobenzene + benzene → 1,2-dichlorobenzene + 1,2,3-trichlorobenzene (R11b)

hexachlorobenzene + benzene → chlorobenzene + hexachlorobenzene (R12a)

hexachlorobenzene + benzene → 2 × 1,2,3-trichlorobenzene (R12b)

3.2.2 S^o_{298} and $C_p^o(T)$ ($300 \leq T/K \leq 1500$)

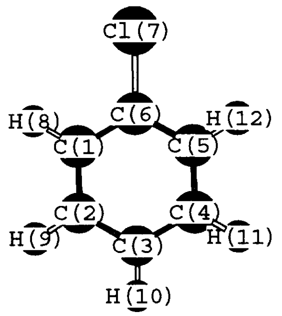
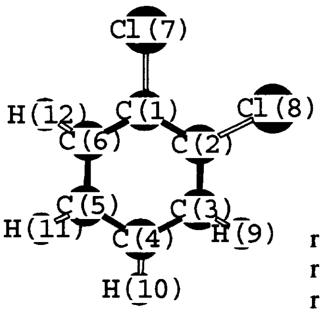
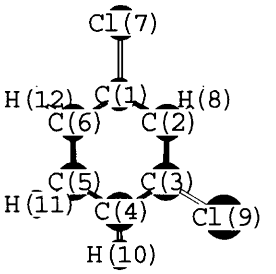
Contributions to S^o_{298} and $C_p^o(T)$ from translation, vibrations, and external rotation (TVR) of each chlorinated benzene are obtained using the rigid-rotor-harmonic-oscillator approximation from the frequencies along with moments of inertia based on the optimized B3LYP/6-31G(d,p) structure, though the aid of "SMCPS" computer program. [48]

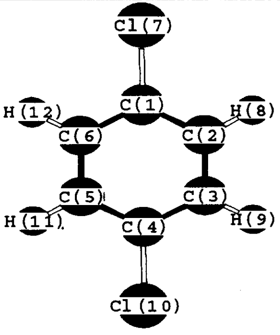
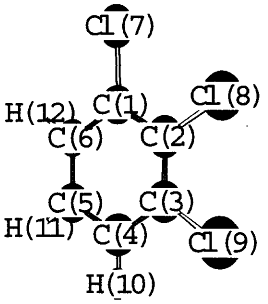
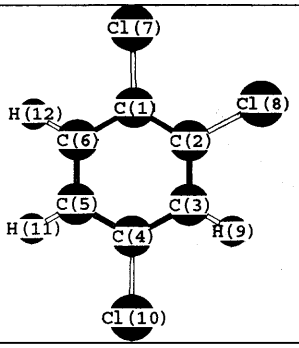
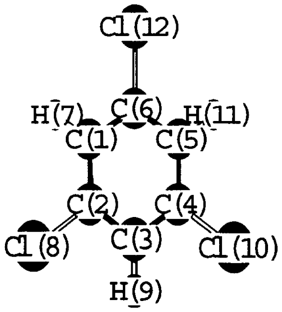
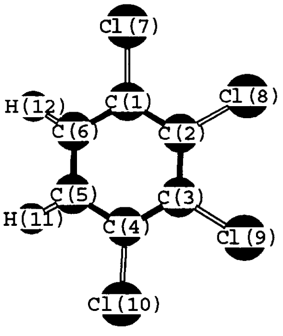
3.3 Results and Discussion

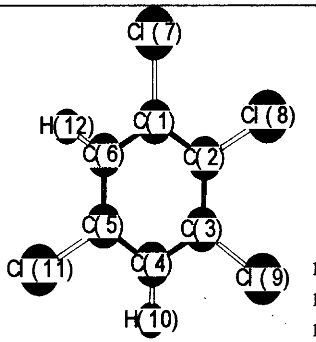
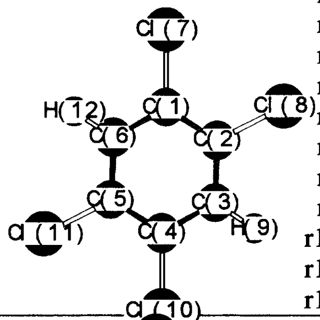
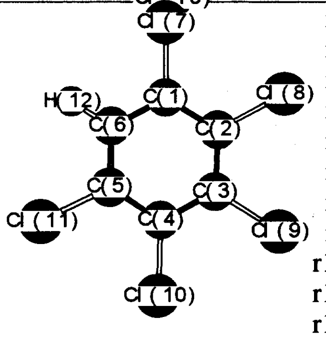
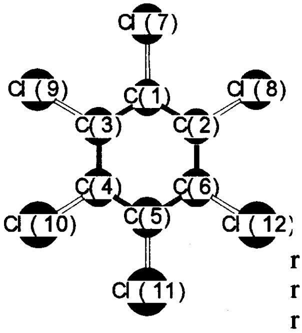
3.3.1 Geometries

The fully optimized geometries at B3LYP/6-31G(d,p) level for the twelve chlorinated benzenes are shown in Table 3.2. For each species the optimized geometry shows a planar structure. The C-C bond is in the range of 1.40 to 1.41 Å when they are both chlorinated, whereas the C-C bond is in the range of 1.39 to 1.40 Å when one or both are bonded to hydrogen atom. All C-H and C-Cl bonds are in the ranges of 1.08 to 1.09 and 1.74 to 1.75 Å, respectively.

Table 3.2 Optimized Geometries of Chlorobenzenes at B3LYP/6-31G(d,p) Level

Species (ID#)	Structure	Bond length (angs-trom)		Bond angle (degree)		Dihedral angle (degree)	
Chlorobenzene (1)		r21	1.396				
		r32	1.396	<321	120.50		
		r43	1.396	<432	119.73	<4321	0.02
		r54	1.396	<543	120.49	<5432	0.00
		r65	1.394	<654	118.96	<6543	0.00
		r76	1.761	<765	119.31	<7654	179.96
		r81	1.084	<812	121.02	<8123	179.96
		r92	1.086	<921	119.29	<9213	-179.93
		r103	1.085	<1032	120.13	<10321	179.97
		r114	1.086	<1143	120.22	<11432	-179.97
		r125	1.084	<1254	121.01	<12543	-179.95
1,2-dichloro benzene (2)		r21	1.402				
		r32	1.397	<321	119.76		
		r43	1.393	<432	120.24	<4321	0.00
		r54	1.395	<543	120.01	<5432	0.03
		r65	1.393	<654	119.99	<6543	-0.03
		r71	1.749	<712	121.48	<7123	-179.98
		r82	1.748	<821	121.48	<8213	-180.00
		r93	1.084	<932	118.85	<9321	-179.98
		r104	1.085	<1043	119.50	<10432	180.00
		r115	1.085	<1154	120.50	<11543	179.99
		r126	1.084	<1265	120.91	<12654	-179.98
1,3-dichloro benzene (3)		r21	1.394				
		r32	1.394	<321	118.17		
		r43	1.394	<432	121.66	<4321	0.00
		r54	1.395	<543	118.73	<5432	0.00
		r61	1.394	<612	121.65	<6123	0.00
		r71	1.757	<712	118.85	<7123	-180.00
		r82	1.083	<821	120.93	<8213	-180.00
		r93	1.757	<932	118.84	<9321	-180.00
		r104	1.084	<1043	120.15	<10432	-180.00
		r115	1.086	<1154	119.49	<11543	-180.00

		r126	1.084	<1265	120.15	<12654	-180.00
1,4-dichloro benzene (4)		r21	1.394				
		r32	1.394	<321	119.51		
		r43	1.394	<432	119.50	<4321	0.00
		r54	1.394	<543	120.99	<5432	0.00
		r61	1.394	<612	120.99	<6123	0.00
		r71	1.757	<712	119.50	<7123	180.00
		r82	1.084	<821	120.20	<8213	-180.00
		r93	1.084	<932	120.30	<9321	180.00
		r104	1.757	<1043	119.51	<10432	180.00
		r115	1.084	<1154	120.20	<11543	-180.00
		r126	1.084	<1261	120.20	<12612	-180.00
1,2,3-trichloro benzene (5)		r21	1.405				
		r32	1.405	<321	118.39		
		r43	1.395	<432	120.82	<4321	0.00
		r54	1.392	<543	119.82	<5432	0.00
		r65	1.392	<654	120.33	<6543	0.00
		r71	1.747	<712	120.83	<7123	-180.00
		r82	1.738	<821	120.79	<8213	180.00
		r93	1.747	<932	120.84	<9321	180.00
		r104	1.084	<1043	119.09	<10432	-180.00
		r115	1.085	<1154	119.84	<11543	-180.00
		r126	1.084	<1265	121.09	<12654	180.00
1,2,4-trichloro benzene (6)		r21	1.402				
		r32	1.396	<321	120.12		
		r43	1.392	<432	119.46	<4321	0.00
		r54	1.394	<543	121.09	<5432	0.00
		r65	1.391	<654	119.06	<6543	0.00
		r71	1.746	<712	121.60	<7123	179.99
		r82	1.746	<821	121.54	<8213	-179.99
		r93	1.083	<932	119.76	<9321	180.00
		r104	1.753	<1043	119.15	<10432	-180.00
		r115	1.084	<1154	120.46	<11543	-180.00
		r126	1.084	<1265	120.18	<12654	-180.00
1,3,5-trichloro benzene (7)		r21	1.394				
		r32	1.394	<321	121.99		
		r43	1.394	<432	118.01	<4321	0.00
		r54	1.394	<543	121.99	<5432	0.00
		r61	1.394	<612	118.01	<6123	0.00
		r71	1.082	<712	121.00	<7123	-180.00
		r82	1.753	<821	119.00	<8213	180.00
		r93	1.082	<932	120.99	<9321	180.00
		r104	1.753	<1043	119.00	<10432	180.00
		r115	1.082	<1154	121.00	<11543	180.00
		r126	1.753	<1261	119.00	<12612	-180.00
1,2,3,4- tetrachloro benzene (8)		r21	1.403				
		r32	1.409	<321	119.46		
		r43	1.403	<432	119.46	<4321	0.00
		r54	1.394	<543	120.37	<5432	0.00
		r65	1.388	<654	120.17	<6543	0.00
		r71	1.745	<712	121.16	<7123	180.00
		r82	1.737	<821	120.31	<8213	180.00
		r93	1.737	<932	120.23	<9321	180.00
		r104	1.745	<1043	121.17	<10432	180.00
		r115	1.084	<1154	119.36	<11543	-180.00

		r126	1.083	<1265	120.47	<12654	-180.00
1,2,3,5-tetrachloro benzene (9)		r21	1.405				
		r32	1.405	<321	118.17		
		r43	1.394	<432	121.21	<4321	0.00
		r54	1.391	<543	119.04	<5432	0.00
		r65	1.391	<654	121.31	<6543	0.00
		r71	1.744	<712	120.87	<7123	180.00
		r82	1.736	<821	120.91	<8213	-180.00
		r93	1.744	<932	120.88	<9321	-180.00
		r104	1.082	<1043	119.98	<10432	180.00
		r115	1.750	<1154	119.34	<11543	-180.00
		r126	1.082	<1265	120.97	<12654	-180.00
1,2,4,5-tetrachloro benzene **(10)**		r21	1.402				
		r32	1.394	<321	119.63		
		r43	1.394	<432	120.73	<4321	0.00
		r54	1.402	<543	119.63	<5432	0.00
		r61	1.394	<612	119.63	<6123	0.00
		r71	1.743	<712	121.70	<7123	179.98
		r82	1.743	<821	121.71	<8213	-179.99
		r93	1.083	<932	119.64	<9321	-180.00
		r104	1.743	<1043	118.66	<10432	180.00
		r115	1.743	<1154	121.71	<11543	-179.99
		r126	1.083	<1261	119.63	<12612	180.00
Pentachloro benzene (11)		r21	1.403				
		r32	1.407	<321	119.07		
		r43	1.407	<432	120.54	<4321	0.00
		r54	1.403	<543	119.07	<5432	0.00
		r61	1.391	<612	120.58	<6123	0.00
		r71	1.742	<712	121.29	<7123	-180.00
		r82	1.735	<821	120.39	<8213	180.00
		r93	1.736	<932	119.73	<9321	180.00
		r104	1.735	<1043	120.55	<10432	180.00
		r115	1.742	<1154	121.29	<11543	180.00
		r126	1.082	<1261	119.91	<12612	-180.00
Hexachloro benzene **(12)**		r21	1.404				
		r31	1.404	<312	120.00		
		r43	1.404	<431	120.01	<4312	0.00
		r54	1.404	<543	120.00	<5431	0.00
		r62	1.404	<621	120.00	<6213	0.00
		r71	1.735	<712	120.01	<7123	179.99
		r82	1.735	<821	120.01	<8213	-180.00
		r93	1.734	<931	120.00	<9312	179.99
		r104	1.735	<1043	120.00	<10431	180.00
		r115	1.735	<1154	120.00	<11543	-180.00
		r126	1.734	<1262	119.99	<12621	180.00

Harmonic vibration frequencies and moments of inertia are calculated for each chlorinated benzene at B3LYP/6-31G(d,p) level on the basis of optimized geometries at this same level of theory (Table 3.3).

Table 3.3 The B3LYP/6-31G(d,p) Harmonic Vibrational Frequencies (cm^{-1}) and Moments of Inertia ($amu\text{-}Bohr^2$) of Chlorobenzenes

Species	Freq	Ia	Ib	Ic
Chlorobenzene (1) Sym = 2	480 627 699 711 756 844 916 970 997 1014 1048 1103 1106 1187 1202 1330 1353 1487 1520 1640 1641 3186 3195 3208 3219 3221	318.08489	1159.65776	1477.74256
1,2-Dichloro benzene (2) Sym = 2	137 202 236 339 429 449 480 522 672 704 749 766 869 952 989 1040 1064 1150 1156 1190 1282 1330 1472 1500 1624 1634 3196 3208 3220 3224	956.27021	1272.30846	2228.57866
1,3-Dichloro benzene (3) Sym = 2	169 198 205 370 399 432 445 541 675 684 787 788 882 905 981 1010 1101 1106 1138 1194 1298 1345 1452 1503 1628 1630 3199 3226 3230 3237	642.94579	2122.29648	2765.24227
1,4-Dichloro benzene (4) Sym = 4	103 221 298 329 356 422 494 544 640 698 757 828 831 955 964 1023 1108 1111 1130 1201 1319 1329 1432 1517 1626 1633 3214 3215 3227 3229	318.90465	2733.30303	3052.20768
1,2,3-Trichloro benzene (5) Sym = 2	85 216 406 517 744 906 1110 1226 1472 3205 205 251 490 532 786 978 1176 1313 1614 3226 209 348 510 703 792 1051 1182 1446 1619 3231	1214.27878	2164.15712	3378.43590
1,2,4-Trichloro benzene (6) Sym = 1	97 173 195 210 307 330 401 450 461 559 574 688 691 819 824 883 958 1041 1120 1157 1169 1275 1319 1411 1495 1607 1625 3217 3231 3238	994.32664	3045.41425	4039.74089
1,3,5-Trichloro benzene (7) Sym = 6	135 189 189 206 206 376 431 431 447 538 538 670 809 809 861 881 881 1009 1126 1126 1162 1269 1339 1451 1451 1617 1617 3242 3243 3245	2121.25827	2121.42543	4242.68370
1,2,3,4-Tetrachloro benzene (8) Sym = 2	81 96 210 213 226 245 307 334 353 489 510 520 566 608 707 777 821 836 954 1070 1160 1190 1202 1300 1388 1460 1595 1608 3222 3235	1578.86611	3344.62363	4923.48974
1,2,3,5-Tetrachloro benzene (9) Sym = 1	75 139 191 205 206 219 317 328 378 439 528 529 566 597 692 811 837 869 882 1051 1145 1188 1219 1306 1410 1447 1593 1611 3242 3245	2162.64391	3120.65270	5283.29660
1,2,4,5-Tetrachloro benzene (10) Sym = 4	69 132 190 207 210 220 316 351 353 451 506 516 609 646 679 698 873 874 895 1063 1143 1184 1267 1310 1358 1484 1582 1617 3236 3237	1599.74141	3876.96069	5476.70207
Pentachloro benzene (11) Sym = 2	69 82 146 200 214 220 231 273 321 346 348 380 537 560 564 606 677 699 822 875 876 1079 1196 1203 1289 1357 1427 1568 1594 3245	2615.48144	3910.91539	6526.39683
Hexachloro benzene (12) Sym = 12	66 66 92 168 221 221 227 227 244 324 324 344 344 371 393 603 603 630 693 693 703 883 883 1096 1223 1272 1362 1363 1551 1551	3944.23559	3944.64047	7888.87604

3.3.2 $\Delta_f H^o_{298}$

$\Delta_f H^o_{298}$ for all twelve chlorobenzenes are obtained using the isodesmic reaction method with total energies at two different DFT levels of theory (Table 3.4).

Table 3.4 Calculated Total Energies of Chlorobenzene at 298 K[a,b]

Species	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	ZPVE[c,d]	H_{298}-H_0[d]
C_2H_4	-78.5396914	-78.5669819	31.46	2.50
C_2H_3Cl	-538.1437498	-538.2042235	26.31	2.81
CH_2=CCl_2	-997.7403027	-997.8353681	20.72	3.28
Benzene	-232.1542480	-232.2236166	61.89	3.35
Chlorobenzene (**1**)	-691.7571765	-691.8599727	56.05	4.04
1,2-Dichlorobenzene (**2**)	-1151.3545624	-1151.4914479	50.17	4.76
1,3-Dichlorobenzene (**3**)	-1151.3584207	-1151.4950480	50.13	4.78
1,4-Dichlorobenzene (**4**)	-1151.3585325	-1151.4950426	50.12	4.79
1,2,3-Trichlorobenzene (**5**)	-1610.9505665	-1611.1217504	44.22	5.52
1,2,4-Trichlorobenzene (**6**)	-1610.9547169	-1611.1256052	44.19	5.54
1,3,5-Trichlorobenzene (**7**)	-1610.9581253	-1611.1289303	44.15	5.56
1,2,3,4-Tetrachlorobenzene (**8**)	-2070.5457293	-2070.7513729	38.25	6.29
1,2,3,5-Tetrachlorobenzene (**9**)	-2070.5495463	-2070.7550129	38.22	6.32
1,2,4,5-Tetrachlorobenzene (**10**)	-2070.5501548	-2070.7554958	38.23	6.32
Pentachlorobenzene (**11**)	-2530.1399439	-2530.3802113	32.25	7.08
Hexachlorobenzene (**12**)	-2989.7289657	-2990.0042438	26.27	7.84

a: All calculations are based on B3LYP/6-31G(d,p) optimized structures;

b: Total energies (ZPVE and thermal corrections are included) in hartree, 1 hartree = 627.51 kcal/mol;

c: Scaled by 0.9806; [37]

d: In units of kcal/mol.

The enthalpy changes of the isodesmic reactions are calculated from the total energies (Table 3.5). The reference species used in the isodesmic reactions are collected in Table 3.6. The calculated $\Delta_f H^o_{298}$ for monochlorobenzene (**1**) is in good agreement with the literature (0.5 kcal/mol higher than the value by Pedley [42]), and the Pedley's value for monochlorobenzene (**1**) is used in this work.

Table 3.5 Calculated $\Delta H_{rxn,298}$ of Isodesmic Reactions for Chlorobenzenes[a]

Isodesmic Reactions	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)
	// B3LYP/6-31G(d,p)	
(R1a) Clbz + C_2H_4 → benzene + CH_2=CHCl	-0.71	-0.56
(R1b) Clbz + CH_2=CHCl → benzene + CH_2=CCl_2	4.00	3.27
(R2a) 1,2-di Clbz + benzene → 2 × Clbz	-3.48	-3.06
(R2b) 1,2- Clbz + C_2H_4 → benzene + CH_2=CCl_2	-0.19	-0.35
(R3a) 1,3-di Clbz + benzene → 2 × Clbz	-1.06	-0.80
(R3b) 1,3-di Clbz + C_2H_4 → benzene + CH_2=CCl_2	2.23	1.91
(R4a) 1,4-di Clbz + benzene → 2 × Clbz	-0.99	-0.81
(R4b) 1,4-di Clbz + C_2H_4 → benzene + CH_2=CCl_2	2.31	1.91
(R5a) 1,2,3-tri Clbz + 2 benzene → 3 × Clbz	-7.82	-6.86
(R5b) 1,2,3-tri Clbz + benzene → Clbz + 1,2-di Clbz	-4.35	-3.80
(R6a) 1,2,4-tri Clbz + 2 benzene → 3 × Clbz	-5.22	-4.44
(R6b) 1,2,4-tri Clbz + benzene → chlorobenzene + 1,2-di Clbz	-1.74	-1.38
(R7a) 1,3,5-tri Clbz + 2 benzene → 3 × Clbz	-3.08	-2.36
(R7b) 1,3,5-tri Clbz + benzene → chlorobenzene + 1,3-di Clbz	-2.02	-1.55
(R8a) 1,2,3,4-tetra Clbz + benzene → 2 × 1,2-di Clbz	-5.74	-4.96
(R8b) 1,2,3,4-tetra Clbz + benzene → Clbz + 1,2,3-tri Clbz	-4.87	-4.23
(R9a) 1,2,3,5-tetra Clbz + benzene → 1,2-di Clbz + 1,3-di Clbz	-5.77	-4.94
(R9b) 1,2,3,5-tetra Clbz + benzene → Clbz + 1,2,3-tri Clbz	-2.48	-1.94
(R10a) 1,2,4,5-tetra Clbz + benzene → 2 × 1,2-di Clbz	-2.96	-2.37
(R10b) 1,2,4,5-tetra Clbz + benzene → Clbz + 1,2,4-tri Clbz	-4.70	-4.06
(R11a) penta Clbz + benzene → 1,2,3,4-tetra Clbz + Clbz	-5.47	-4.72
(R11b) penta Clbz + benzene → 1,2-di Clbz + 1,2,3-tri Clbz	-6.86	-5.88
(R12a) hexa Clbz + benzene → Clbz + penta Clbz	-8.73	-7.73
(R12b) hexa Clbz + benzene → 2 × 1,2,3-tri Clbz	-11.24	-9.81

a: In kcal/mol.

Table 3.6 Enthalpies of Formation for Reference Species (and Literature Citations)[a]

Species	$\Delta_f H^\circ_{298}$ (in kcal/mol)
C_2H_4	12.55±0.10 [42]
C_2H_3Cl	5.21±0.50 [74]
CH_2CCl_2	0.62±0.31 [42]
Benzene	19.74±0.17(Pedley et al. [42]), 19.82(TRC [41]), 19.81±0.13(Cox [55]), 19.80(Benson [68]), 19.82±0.12(Prosen [75]), 17.00±1.53(Melius [43])
Chlorobenzene	12.43±0.31(Pedley et al. [42]), 12.39(SWS [62]), 12.22(TRC [41]), 12.21±0.16(Cox [55]), 13.01(Platnov [58]), 8.27±1.83(Melius [43])

a: Underlined values are used in this work;

The calculated $\Delta_f H^o_{298}$ for twelve chlorobenzenes are shown in Table 3.7. The literature review for $\Delta_f H^o_{298}$ of C_2H_4, C_2H_3Cl, and CH_2CCl_2, which are used as reference compounds, have been discussed [35]. Pedley et al.'s values [42] for $\Delta_f H^o_{298}$ of benzene and chlorobenzene are chosen since in fact all literature values for these species are in good agreement. The out exception is the BAC-MP4 data by Melius [43] which are 3 to 4 kcal/mol lower. We take the average of two values calculated at B3LYP/6-311+G(3df,2p) by two isodesmic reactions as the recommended $\Delta_f H^o_{298}$ for each species of **2** to **12** (Table 3.7).

Table 3.7 Calculated $\Delta_f H^o_{298}$ of Chlorobenzenes Using Isodesmic Reactions

Species	From Rxns	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	$X_{avg}{}^{a}\pm\sigma$
		// B3LYP/6-31G(d,p)		
Monochlorobenzene	(R1a)	13.11	12.96	
	(R1b)	11.15	11.88	12.42±0.76^{b}
1,2-Dichlorobenzene (**2**)	(R2a)	8.60	8.18	
	(R2b)	8.00	8.16	8.17±0.02
1,3-Dichlorobenzene (**3**)	(R3a)	6.18	5.92	
	(R2b)	5.58	5.90	5.91±0.02
1,4-Dichlorobenzene (**4**)	(R4a)	6.11	5.93	
	(R4b)	5.50	5.90	5.91±0.02
1,2,3-Trichlorobenzene (**5**)	(R5a)	5.63	4.67	
	(R5b)	5.21	5.38	4.67±0.01
1,2,4-Trichlorobenzene (**6**)	(R6a)	3.03	2.25	
	(R6b)	2.60	2.24	2.25±0.01
1,3,5-Trichlorobenzene (**7**)	(R7a)	0.89	0.17	
	(R7b)	0.62	0.15	0.16±0.01
1,2,3,4-Tetrachlorobenzene (**8**)	(R8a)	2.34	1.56	
	(R8b)	2.23	1.58	1.57±0.01
1,2,3,5-Tetrachlorobenzene (**9**)	(R9a)	0.11	-0.72	
	(R9b)	-0.17	-0.70	-0.71±0.01
1,2,4,5-Tetrachlorobenzene (**10**)	(R10a)	-0.44	-1.02	
	(R10b)	-0.36	-1.01	-1.02±0.01
Pentachlorobenzene (**11**)	(R11a)	-0.27	-1.02	
	(R11b)	-0.04	-1.02	-1.02±0.00
Hexachlorobenzene (**12**)	(R12a)	0.39	-0.60	
	(R12b)	0.84	-0.59	-0.60±0.00

a: average of B3LYP/6-311+G(3df,2p) only; b: this value is not used in the isodesmic reactions for other chlorobenzenes, the value in Table 3.6 is used instead.

Other sources of error listed in Table 3.8 comprise the standard deviation of two calculated $\Delta_fH^o_{298}$ values (one level and two isodesmic reactions), plus the cumulative uncertainties in $\Delta_fH^o_{298}$ for the reference species, as well as the uncertainty from ZPVE calculations, 0.44 kcal/mol. [35,37] A recent calculation by León et al. [76] at similar DFT level will also be compared.

Table 3.8 Ideal Gas-phase Thermochemical Properties for Chlorobenzenes[a]

	$\Delta_fH^o_{298}$	S^o_{298}	$C_p^o(T)$						
			300K	400K	500K	600K	800K	1000K	1500K
Benzene	**19.74±0.17 [42]**	**64.06**	**19.29**	**26.41**	**32.51**	**37.46**	**44.74**	**49.80**	**57.32**
TRC [41]	19.82	64.36	19.76	26.81	33.30	38.64	45.42	50.25	58.08
Chlorobenzene (1)	12.42 (R1)	**74.84**	**23.15**	**30.09**	**35.90**	**40.54**	**47.27**	**51.87**	**58.58**
Pedley et al. [42]	**12.43±0.31**								
Platonov and Simulin [59]	13.01								
TRC [41]	12.22	75.07	23.63	30.48	36.37	41.19	47.87	52.33	59.09
1,2-Dichlorobenzene (2)	**8.17±1.25**	**81.71**	**26.90**	**33.66**	**39.19**	**43.56**	**49.78**	**53.93**	**59.85**
León et al. [76]	8.13±0.48								
Platonov and Simulin [57]	7.89								
TRC [41]	7.11	81.74	27.30	34.04	39.62	44.11	50.31	54.37	60.28
Pedley [42]	7.22±0.50								
Cox [55]	7.10±0.40								
1,3-Dichlorobenzene (3)	**5.91±1.25**	**82.01**	**27.01**	**33.76**	**39.28**	**43.62**	**49.82**	**53.95**	**59.85**
León et al. [76]	5.88±0.48								
Platonov and Simulin [57]	6.72								
TRC [41]	6.10	82.14	27.42	34.15	39.73	44.20	50.36	54.40	60.30
Pedley [42]	6.14±0.50								
Cox [55]	6.10±0.50								
1,4-Dichlorobenzene (4)	**5.91±1.25**	**80.66**	**27.01**	**33.75**	**39.26**	**43.61**	**49.81**	**53.95**	**59.85**
León et al. [76]	5.93±0.48								
Platonov and Simulin [57]	5.88								
TRC [41]	5.30	80.52	27.38	34.12	39.71	44.19	50.37	54.40	60.31
Pedley [42]	5.38±0.36								
Cox [55]	5.30±0.30								
1,2,3-Trichlorobenzene (5)	**4.67±2.18**	**88.48**	**30.68**	**37.26**	**42.51**	**46.59**	**52.30**	**56.01**	**61.14**
León et al. [76]	4.59±0.60								
Platonov and Simulin [56]	0.903								
TRC [41]	2.16	88.36	30.94	37.53	42.83	47.00	52.70	56.35	61.45
Yan et al. [60]	1.97±0.44								
Platnov [58]	0.90								
1,2,4-Trichlorobenzene (6)	**2.25±2.18**	**90.27**	**30.77**	**37.33**	**42.56**	**46.62**	**52.31**	**56.01**	**61.13**
León et al. [76]	2.17±0.60								
Platonov and Simulin [58]	-1.92								
TRC [41]	-0.05	90.01	31.04	37.61	42.90	47.05	52.73	56.37	61.46
Yan [60]	1.16±0.38								
1,3,5-Trichlorobenzene (7)	**0.16±2.18**	**86.97**	**30.88**	**37.42**	**42.64**	**46.69**	**52.35**	**56.03**	**61.13**

León et al. [76]	0.14±0.60								
Platonov and Simulin [58]	-3.193								
TRC [41]	-1.65	86.72	31.05	37.63	42.92	47.07	52.74	56.37	61.47
Yan [60]	-0.61±0.34								
1,2,3,4-Tetrachlorobenzene (8)	**1.57±3.12**	**95.27**	**34.45**	**40.84**	**45.81**	**49.61**	**54.81**	**58.08**	**62.42**
León et al. [76]	1.48±0.69								
Platonov and Simulin [58]	-6.07								
TRC [41]	-2.30	94.96	34.61	41.05	46.07	49.92	55.12	58.36	62.60
1,2,3,5-Tetrachlorobenzene (9)	**-0.71±3.12**	**97.01**	**34.55**	**40.91**	**45.86**	**49.65**	**54.83**	**58.09**	**62.42**
León et al. [76]	-0.81±0.69								
Platonov and Simulin [58]	-8.34								
TRC [41]	-4.80	95.52	34.74	41.15	46.15	49.99	55.16	58.39	62.65
1,2,4,5-Tetrachlorobenzene (10)	**-1.02±3.12**	**97.22**	**34.54**	**40.89**	**45.83**	**49.62**	**54.80**	**58.07**	**62.41**
León et al. [76]	-1.15±0.69								
Platonov and Simulin [56]	-7.796								
TRC [41]	-5.59	94.06	34.76	41.17	46.16	49.99	55.15	58.36	62.63
Pentachlorobenzene (11)	**-1.02±4.04**	**102.03**	**38.23**	**44.42**	**49.11**	**52.63**	**57.32**	**60.16**	**63.71**
León et al. [76]	-1.41±0.76								
Platnov et al. [59]	-9.6								
TRC [41]	-6.93	101.75	38.38	44.62	49.33	52.87	57.55	60.38	63.85
Hexachlorobenzene (12)	**-0.60±4.97**	**104.81**	**41.89**	**47.91**	**52.34**	**55.61**	**59.82**	**62.23**	**65.00**
León et al. [76]	-1.08±0.76								
Platonov and Simulin [56]	-10.68								
TRC [41]	-8.10	104.38	42.00	48.09	52.53	55.77	59.94	62.35	65.08
Pedley [42]	-8.48±2.25								
Cox [55]	-8.60±2.30								

a: $\Delta_f H^o_{298}$ in kcal/mol, S^o_{298} and $C_p{}^o(T)$ in cal/mol.K.

3.3.3 S^o_{298} and $C_p{}^o(T)$ ($300 \leq T/K \leq 1500$)

S^o_{298} and $C_p{}^o(T)$ obtained from the frequencies along with moments of inertia based on the optimized B3LYP/6-31G(d,p) structure, using "SMCPS" computer program, [48] are listed in Table 3.8.

The calculated $\Delta_f H^o_{298}$ for chlorobenzene is in good agreement with the literature data of Pedley et al. [42] and the value of Pedley et al., 19.74 kcal/mol is recommended. The calculated $\Delta_f H^o_{298}$ for three dichlorobenzenes are within 1 kcal/mol with the values of Platnov and Simulin [57]. The calculated $\Delta_f H^o_{298}$ for three trichlorobenzenes are within 2 kcal/mol with the values of Platnov and Simulin [56,58] and Yan et al. [60]. For tetra-, penta-, and hexa-chlorobenzenes, the results in this study are 4 to 10 kcal/mol higher than the data of Platnov et al. [56,58,59]. The two sets of DFT results, from this work and by

León et al. [76], are similar: the biggest difference is less than 2 kcal/mol for hexachlorobenzene.

The calculated S^{o}_{298} and $C_p^{o}(T)$ are in good agreement with the TRC values. [41]

3.3.4 Group Values

Group additivity is straightforward and a reasonably accurate method for estimation of thermochemical properties of hydrocarbons and oxygenated hydrocarbons. [68] It is particularly useful for larger molecules where high level *ab initio* or density functional calculations are not practical.

Wu and Bozzelli [67] developed the additivity groups used in multi-substituted aromatics. Their estimations from group additivity show improved agreement with the literature values. The TRC data are adopted when they derived and optimized the non-next-nearest neighbor interaction groups. Here is the summary of Wu and Bozzelli [67]'s counting rules:

If a species has:	Then:
(I) One type of interaction	$X = X_{GA} + \#$ of interaction(s)
(II) Two or more types of interaction from same substituent	$X = X_{GA} +$ all ortho interaction(s) + integer [0.5(# of meta + para interaction(s)]

So:

$X_{1,2\text{-dichlorobenzene}} = X_{GA} + X_{ORT/Cl/Cl}$

$X_{1,3\text{-dichlorobenzene}} = X_{GA} + X_{MET/Cl/Cl}$

$X_{1,4\text{-dichlorobenzene}} = X_{GA} + X_{PAR/Cl/Cl}$

$X_{1,2,3\text{-trichlorobenzene}} = X_{GA} + 2\ X_{ORT/Cl/Cl}$

$X_{1,2,4\text{-trichlorobenzene}} = X_{GA} + X_{ORT/Cl/Cl}$

$X_{1,3,5\text{-trichlorobenzene}} = X_{GA} + 3\ X_{MET/Cl/Cl}$

$X_{1,2,3,4\text{-tetrachlorobenzene}} = X_{GA} + 3\ X_{ORT/Cl/Cl} + X_{MET/Cl/Cl}$

$X_{1,2,3,5\text{-tetrachlorobenzene}} = X_{GA} + 2\ X_{ORT/Cl/Cl} + X_{MET/Cl/Cl}$

$X_{1,2,4,5\text{-tetrachlorobenzene}} = X_{GA} + X_{ORT/Cl/Cl} + X_{MET/Cl/Cl}$

$X_{\text{pentachlorobenzene}} = X_{GA} + 4\ X_{ORT/Cl/Cl} + 2\ X_{MET/Cl/Cl} + 1\ X_{PAR/Cl/Cl}$

$X_{\text{perchlorobenzene}} = X_{GA} + 6\ X_{ORT/Cl/Cl} + 3\ X_{MET/Cl/Cl} + 1\ X_{PAR/Cl/Cl}$

All groups in chlorobenzene species are listed in Table 3.9. The group values obtained from the recommended thermochemical properties in Table 3.8 are all consistent with Benson's values. [68]

Table 3.9 Group Values for Chlorobenzenes

Groups		$\Delta_f H°_{298}$	$S°_{298}$	$C_p°(T)$						
				300K	400K	500K	600K	800K	1000K	1500K
			Central groups							
C_B/H	This work	3.29	11.50	3.22	4.40	5.42	6.24	7.46	8.30	9.55
	Benson [68]	3.30	11.53	3.24	4.44	5.46	6.30	7.54	8.41	9.73
	Cohen [77]	3.30								
	Dorofeeva [78]	3.29	11.55	5.03						13.41
C_B/Cl	This work	-4.02	18.72	7.08	8.08	8.81	9.32	9.99	10.37	10.81
	Benson [68]	-3.80	18.90	7.40	8.40	9.20	9.70	10.20	10.40	
	Dorofeeva [78]	-4.02	18.56	8.71						14.63
			Interaction groups							
Ortho/Cl/Cl	This work	3.05	-0.35	-0.11	-0.11	-0.10	-0.06	-0.02	-0.01	0.01
	Benson [68]	2.20								
	Wu and Bozzelli [67]	8.87	-1.30	-0.84	-1.63	-1.97	-2.01	-1.84	-1.59	-2.38
	Cioslowski et al. [69]	3.7								
Meta/Cl/Cl	This work	0.79	-0.05	0.00	-0.01	-0.01	0.00	0.02	0.01	0.01
	Wu and Bozzelli [67]	4.69	0.71	-0.50	-1.38	-1.55	-1.88	-1.80	-1.59	-2.38
	Cioslowski et al. [69]	1.1								
Para/Cl/Cl	This work	0.79	1.35	0.00	-0.02	-0.03	-0.01	0.01	0.01	0.01
	Wu and Bozzelli [67]	1.34	-0.33	-0.42	1.21	1.59	1.13	-0.25	-0.96	1.30
	Cioslowski et al. [69]	1.1								

C_B/H is calculated from one sixth of benzene. C_B/Cl is from chlorobenzene minus five times of C_B/H group.

Three Cl/Cl interaction groups, ortho/Cl/Cl, meta/Cl/Cl, and para/Cl/Cl, for chlorinated aromatics are calculated from 1,2-, 1,3-, and 1,4-dichlorobenzenes, respectively.

Table 3.10 Comparison of Thermochemical Properties from Group Additivity with Recommended Values

		$\Delta_fH°_{298}$	$S°_{298}$	$C_p°(T)$						
				300K	400K	500K	600K	800K	1000K	1500K
1,2,3- Trichloro benzene	Calc'd	4.65	88.48	30.68	37.26	42.51	46.59	52.30	56.01	61.14
	GA (Wu and Bozzelli)	3.89	88.58	30.65	37.23	42.48	46.58	52.29	55.99	61.12
	GA (this work)	4.67	88.53	30.65	37.22	42.47	46.58	52.31	56.00	61.13
1,2,4- Trichloro benzene	Calc'd	2.23	90.27	30.77	37.33	42.56	46.62	52.31	56.01	61.13
	GA (Wu and Bozzelli)	0.85	90.31	30.76	37.34	42.58	46.64	52.31	56.00	61.11
	GA (this work)	2.41	90.23	30.76	37.31	42.54	46.63	52.34	56.02	61.13
1,3,5- Trichloro benzene	Calc'd	0.15	86.97	30.88	37.42	42.64	46.69	52.35	56.03	61.13
	GA (Wu and Bozzelli)	0.15	86.95	30.87	37.42	42.65	46.70	52.39	56.04	61.13
	GA (this work)	0.15	86.95	30.87	37.42	42.65	46.70	52.39	56.04	61.13
1,2,3,4- Tetrachloro benzene	Calc'd	1.55	95.27	34.45	40.84	45.81	49.61	54.81	58.08	62.42
	GA (Wu and Bozzelli)	0.40	95.40	34.40	40.79	45.76	49.60	54.82	58.06	62.40
	GA (this work)	1.96	95.33	34.40	40.76	45.72	49.59	54.85	58.08	62.42
1,2,3,5- Tetrachloro benzene	Calc'd	-0.73	95.63	34.55	40.91	45.86	49.65	54.83	58.09	62.42
	GA (Wu and Bozzelli)	-2.64	97.13	34.51	40.90	45.86	49.66	54.84	58.07	62.39
	GA (this work)	-0.30	95.63	34.51	40.86	45.81	49.65	54.89	58.10	62.42
1,2,4,5- Tetrachloro benzene	Calc'd	-1.04	94.38	34.54	40.89	45.83	49.62	54.80	58.07	62.41
	GA (Wu and Bozzelli)	-1.86	94.35	34.51	40.88	45.83	49.65	54.85	58.08	62.40
	GA (this work)	-0.30	94.28	34.51	40.85	45.79	49.64	54.88	58.10	62.42
Pentachloro benzene	Calc'd	-1.05	102.03	38.23	44.42	49.11	52.63	57.32	60.16	63.71
	GA (Wu and Bozzelli)	-2.31	102.20	38.15	44.33	49.01	52.61	57.36	60.14	63.69
	GA (this work)	-0.75	102.13	38.15	44.30	48.97	52.60	57.39	60.16	63.71
Hexachloro benzene	Calc'd	-0.62	104.81	41.89	47.91	52.34	55.61	59.82	62.23	65.00
	GA (Wu and Bozzelli)	-2.76	105.11	41.79	47.78	52.19	55.57	59.87	62.20	64.98
	GA (this work)	3.48	104.85	41.79	47.65	52.01	55.52	59.98	62.28	65.06

Wu and Bozzelli's rules above are adopted for group values to obtained the thermochemical parameters of chlorobenzenes, as listed in Table 3.10. Generally the GA results are in good agreement with the recommended values. The two worst cases are for 1,2,3,5-tetrachlorobenzene and hexachlorobenzene, where the standard enthalpies of formation by GA are 1.9 and 2.1 kcal/mol lower than the recommended values.

If the Wu and Bozzelli's rules are further simplified, i.e. the number of interactions of meta/Cl/Cl and para/Cl/Cl are also count as whole as ortho/Cl/Cl, instead of half, this GA results are also compared in Table 3.10 as GA (this work). This new simplified GA strategy gives generally good agreements with the DFT-calculated values for most of the twelve species. It gives improved results for six chlorobenzenes, 1,2,3-, 1,2,4-, 1,2,3,4-, 1,2,3,5-, 1,2,4,5-, and penta-chlorobenzenes than GA of Wu and Bozzelli. For the rest six chlorobenznens, it gives similar or worse results than the GA of Wu and Bozzelli.

3.4 Summary

The geometry of twelve chlorobenzenes are studied by B3LYP/6-31G(d,p) DFT calculation. Recommended $\Delta_f H^o_{298}$ of each species (except chlorobenzene) is the average value of two data using two isodesmic reactions calculated B3LYP/6-311+G(3df,2p) level of calculation based on B3LYP/6-31G(d,p) optimized geometry. S^o_{298} and $C_p^o(T)$ ($300 \leq T/K \leq 1500$) are determined by B3LYP/6-31G(d,p) optimized geometries and frequencies. Thermodynamic properties are determined for five groups, C_B/H, C_B/Cl, ortho/Cl/Cl, meta/Cl/Cl, and para/Cl/Cl, which are useful for group additivity estimation of higher chlorinated aromatic molecules.

CHAPTER 4

GAS-PHASE THERMOCHEMICAL PROPERTIES, $\Delta_F H^O{}_{298}$, $S^O{}_{298}$, AND $C_P{}^O(T)$ ($300 \le T/K \le 1500$), OF CHLOROPHENOLS BY DENSITY FUNCTIONAL CALCULATIONS

4.1 Overview

The motivation for this study is from a kinetic modeling study performed in this research group. The pyrolysis and oxidation of 2-chlorophenol and chloroanisole gives two dichlorophenols, 2,4- and 2,6-dichlorophenol, as major products. It would be of significant value to have knowledge of their fundamental thermochemical properties and for use in developing accurate and fundamental understanding of the reaction pathways of their formations.

It would be of significant value to have knowledge of the fundamental thermochemical properties of chlorophenols which would help to have an accurate and fundamental understanding of their reaction pathways of the formations of PCDD/Fs.

There is a number of studies for the thermochemical properties of chlorophenols, such as those of Pedley, [42] Cox, [55] TRC, [41] etc... They are reviews of the previous experimental data. Ribeiro Da Silva et al. [66] studied gas-phase $\Delta_f H^o{}_{298}$ of six dichlorophenols by rotating bomb calorimetry in 1994.

The procedure developed by Shaub [61] in 1982 for estimation of the gas-phase enthalpies of formation of aromatic compounds, chlorinated benzenes, phenols and dioxins. His approach is to start from benzene, which has the well-known gas-phase enthalpy of formation from SWS [62], Cox [55], and Pedley [42]. Then two effects are considered for a substituted benzene: (1) the primary effects of replacing hydrogen atom with Cl substituent x = Benzene – 1-Chloro benzene, or replacing hydrogen atom with OH substituent β = Benzene – Phenol; (2) the secondary effect of *ortho-*, *meta-*, and *para-x* groups as in *ortho-*, *meta-*, and *para*-dichlorobenzene, for example.

These effects are illustrated in Table 4.1.

Table 4.1 Summary of (x, o, m, p) effects (kcal/mol)^{a,b}

Effect	-Cl (1)	-OH (2)	-F	$-CH_3$
x	7.6	42.85	47.57	7.82
o	2.09		5.07	0.39
m	0.99	0.19	1.37	-0.03
p	0.39	2.51	2.00	0.14
o_{12}(I) = ORT/Cl/OH	-0.47			
o_{12}(II) = Cl/OH/Cl	5.96			
m_{12} = MET/Cl/OH	-6.06			
p_{12} = PAR/Cl/OH	-4.26			

a: all interaction effects except the o_{12}(I) effect have been determined from benzene as a reference compound. o_{12}(I) effect was determined from hydroquinone as a reference compound;
b: Subscript 1 denotes Cl, Subscript 2 denotes OH.

As an example, 2,3-dichlorophenol = benzene – 2 x – β + o + o_{12} + m_{12}, This formula gives $\Delta_f H°_{298}$ of 2,3-dichlorophenol to be –42.68 kcal/mol.

Shaub [61] recommended the estimation scheme of Prosen et al. [63] for alkyl substituent and a weighted least square method of Good [64] who evaluated data and determined need for a "buttress" effect.

Another estimation method for the enthalpies of formation of benzene derivatives in the gas-phase is developed by Cox in 1978. [65] This method assumes that each group when substituted into the benzene ring produces a characteristic increment in $\Delta_f H°_{298}$. The $\Delta_f H°_{298}$ of some dichlorophenols estimated by this scheme is in good agreement with the experimental values [66].

A series of interaction groups was developed in the Bozzelli group in 1993 to improve the accuracy of thermochemical properties of multi-substituted aromatic compounds. [67] Comparison of this group additivity estimation with literature values also shows good agreement.

This chapter estimates fundamental thermochemical properties, $\Delta_fH^\circ_{298}$, S°_{298}, and $C_p^\circ(T)$, for all types of chlorinated phenols using two density functional calculation methods. Enthalpy of formation of each chlorophenol is determined at each calculation level using two isodesmic reactions. Results from this work will be compared with the above literature values.

4.2 Methodology

The methods have been discussed in Chapter 2 and summarized here.

All calculations are performed using the Gaussian94 or Gaussian98 program suite. [28,70] The structures of nineteen chlorophenols are fully optimized at B3LYP/6-31G(d,p) level of theory. Harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. Then B3LYP/6-31G(d,p) optimized geometrical parameters are used to obtain total electronic energies in B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) calculations. [71,72] Total energies are corrected by ZPVE's which are scaled by 0.9806 as recommended by Scott and Radom. [37] Thermal corrections (0 K to 298 K) are calculated to estimate H_{298} from H_0. [73]

4.2.1 $\Delta_fH^\circ_{298}$

Standard enthalpies of formation are obtained using total energies obtained by the B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) calculation methods and two generic isodesmic reactions.

The following isodesmic reactions are selected to determine $\Delta_f H^\circ_{298}$ of chlorophenols.

2-chlorophenol + benzene → phenol + chlorobenzene (R1a)

2-chlorophenol + chlorobenzene → benzene + 1,2-dichlorobenzene (R1b)

3-chlorophenol + benzene → phenol + chlorobenzene (R2a)

3-chlorophenol + chlorobenzene → benzene + 1,3-dichlorobenzene (R2b)

4-chlorophenol + benzene → phenol + chlorobenzene (R3a)

4-chlorophenol + chlorobenzene → benzene + 1,4-dichlorobenzene (R3b)

2,3-dichlorophenol + benzene → 2-chlorophenol + chlorobenzene (R4a)

2,3-dichlorophenol + chlorobenzene → phenol + 1,2,3-trichlorobenzene (R4b)

2,4-dichlorophenol + benzene → 2-chlorophenol + chlorobenzene (R5a)

2,4-dichlorophenol + chlorobenzene → phenol + 1,2,4-trichlorobenzene (R5b)

2,5-dichlorophenol + benzene → 2-chlorophenol + chlorobenzene (R6a)

2,5-dichlorophenol + chlorobenzene → phenol + 1,2,4-trichlorobenzene (R6b)

2,6-dichlorophenol + benzene → 2-chlorophenol + chlorobenzene (R7a)

2,6-dichlorophenol + chlorobenzene → phenol + 1,2,3-trichlorobenzene (R7b)

3,4-dichlorophenol + benzene → 3-chlorophenol + chlorobenzene (R8a)

3,4-dichlorophenol + chlorobenzene → phenol + 1,2,4-trichlorobenzene (R8b)

3,5-dichlorophenol + benzene → 3-chlorophenol + chlorobenzene (R9a)

3,5-dichlorophenol + chlorobenzene → phenol + 1,3,5-trichlorobenzene (R9b)

2,3,4-trichlorophenol + benzene → 2-chlorophenol + 1,2-dichlorobenzene (R10a)

2,3,4-trichlorophenol + chlorobenzene → phenol + 1,2,3,4-tetrachlorobenzene

(R10b)

2,3,5-trichlorophenol + benzene → 2-chlorophenol + 1,3-dichlorobenzene (R11a)

2,3,5-trichlorophenol + chlorobenzene → phenol + 1,2,3,5-tetrachlorobenzene

(R11b)

2,3,6-trichlorophenol + benzene → 2-chlorophenol + 1,2-dichlorobenzene (R12a)

2,3,6-trichlorophenol + chlorobenzene → phenol + 1,2,3,4-tetrachlorobenzene

(R12b)

2,4,5-trichlorophenol + benzene → 2-chlorophenol + 1,2-dichlorobenzene (R13a)

2,4,5-trichlorophenol + chlorobenzene → phenol + 1,2,4,5-tetrachlorobenzene

(R13b)

2,4,6-trichlorophenol + benzene → 2-chlorophenol + 1,3-dichlorobenzene (R14a)

2,4,6-trichlorophenol + chlorobenzene → phenol + 1,2,3,5-tetrachlorobenzene

(R14b)

3,4,5-trichlorophenol + benzene → 3-chlorophenol + 1,2-dichlorobenzene (R15a)

3,4,5-trichlorophenol + chlorobenzene → phenol + 1,2,3,4-tetrachlorobenzene

(R15b)

2,3,4,5-tetrachlorophenol + benzene → 2-chlorophenol + 1,2,3-trichlorobenzene

(R16a)

2,3,4,5-tetrachlorophenol + chlorobenzene → phenol + pentachlorobenzene

(R16b)

2,3,4,6-tetrachlorophenol + benzene → 2-chlorophenol + 1,2,3-trichlorobenzene

(R17a)

2,3,4,6-tetrachlorophenol + chlorobenzene → phenol + pentachlorobenzene

(R17b)

2,3,5,6-tetrachlorophenol + benzene → 2-chlorophenol + 1,2,4-trichlorobenzene

(R18a)

2,3,5,6-tetrachlorophenol + chlorobenzene → phenol + pentachlorobenzene

(R18b)

Perchlorophenol + benzene → 2-chlorophenol + 1,2,3,4-tetrachlorobenzene

(R19a)

Perchlorophenol + chlorobenzene → phenol + perchlorobenzene (R19b)

4.2.2 S^o_{298} and $C_p^o(T)$ ($300 \le T/K \le 1500$)

Contributions to S^o_{298} and $C_p^o(T)$ from translation, vibrations, and external rotation (TVR) of each chlorinated benzene are obtained using the rigid-rotor-harmonic-oscillator approximation from the frequencies along with moments of inertia based on the optimized B3LYP/6-31G(d,p) structure, though the aids of "SMCPS" computer program. [48] Harmonic vibrational frequencies and moments of inertia are calculated for at B3LYP/6-31G(d,p) level on the basis of optimized geometries at this same level of theory

Contributions to entropy and heat capacities from intramolecular rotation (C–OH) are determined using direct integration over energy levels of the internal rotation potential energy where barriers are determined at the B3LYP/6-31G(d,p) level. A program “ROTATOR” [48,79] is used for this integration. This technique employs expansion of the hindrance potential in the Fourier series (equation 4.I), calculation of the Hamiltonian matrix in the basis of wave functions of the free internal rotor, and subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix. [80-82] The torsional potential calculated at discrete torsion angles is represented by a truncated Fourier series:

$$V(\Phi) = a_0 + \Sigma\, a_i \cos(i\Phi) + \Sigma\, b_i \sin(i\Phi) \qquad i = 1, 2, 3, \ldots\ldots \qquad \text{(Eq. 4.1)}$$

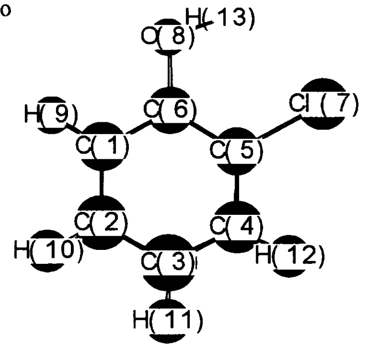
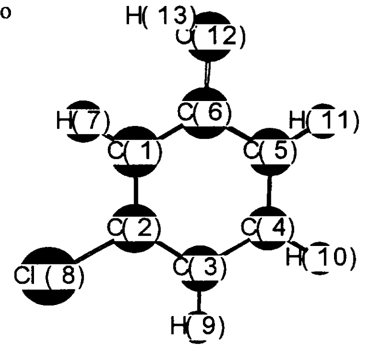
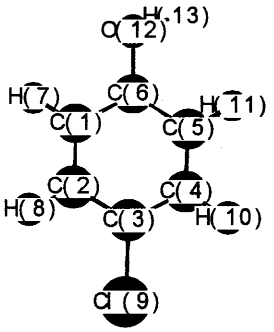
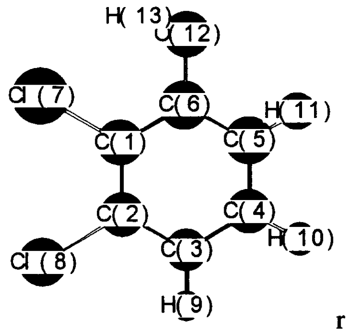
Values of the coefficients (a_0, a_i, and b_i) are calculated to provide the minimum and maximum of the torsional potentials with allowance of a shift of the theoretical extreme angular positions. Contributions to entropy and heat capacities from intramolecular rotation (C–OH) for phenol, 2-chlorophenol, 2,6-dichlorophenol are calculate in this work to represent three types of internal rotors, i.e., two H atoms, one H and one Cl atom, and two Cl atoms, attached to the two adjacent carbons.

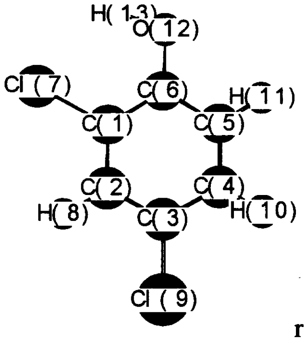
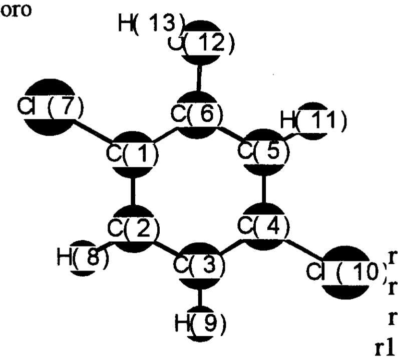
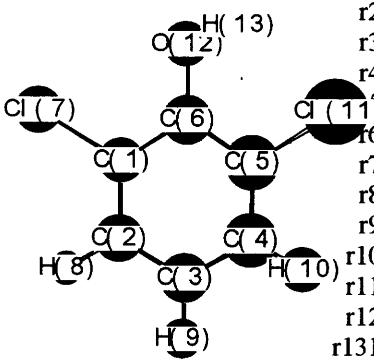
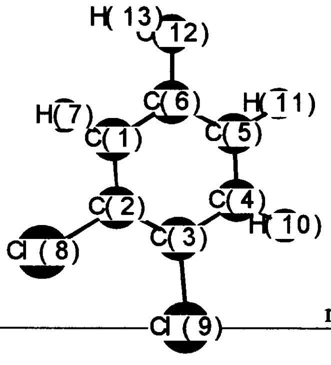
4.3 Results and Discussion

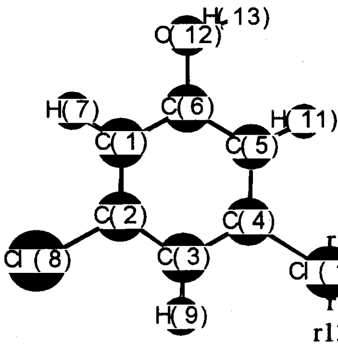
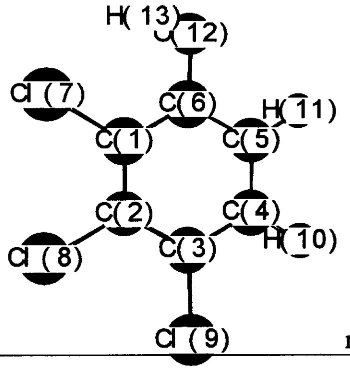
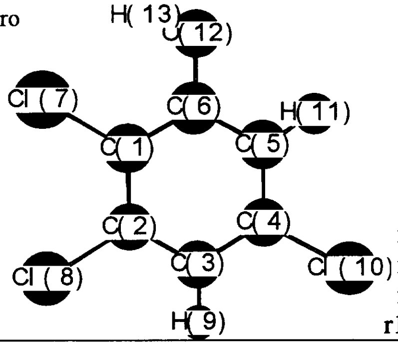
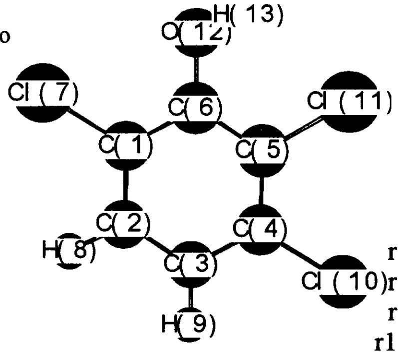
4.3.1 Geometries

The fully optimized geometries at the DFT B3LYP/6-31G(d,p) level for the nineteen chlorinated phenols are shown in Table 4.2. For each species the optimized geometry of the aromatic moiety shows a planar structure. Every non-symmetric chlorophenol has two isomers, identified by the orientation of the hydroxyl H atom. The hydroxyl H atom tends to bend to the Cl side in 2-chlorophenol. The geometries shown in Table 4.2 are the most stable isomers for every chlorophenol studied.

Table 4.2 Optimized Geometries of Chlorophenols at the B3LYP/6-31G(d,p) Level

Species (ID#)	Structure	Bond length	(angstrom)	Bond angle	(degree)	Dihedral angle	(degree)
2-Chloro phenol (1)		r21	1.391				
		r32	1.397	d321	120.65		
		r43	1.394	d432	119.62	d4321	0.00
		r54	1.392	d543	119.48	d5432	0.00
		r61	1.400	d612	120.40	d6123	0.00
		r75	1.767	d754	120.15	d7543	-180.00
		r86	1.356	d861	118.31	d8612	-180.00
		r91	1.085	d912	121.60	d9123	180.00
		r102	1.086	d1021	119.33	d10213	180.00
		r113	1.085	d1132	120.62	d11321	-180.00
		r124	1.084	d1243	121.13	d12432	-180.00
		r138	0.970	d1386	108.81	d13861	179.99
3-Chloro phenol (2)		r21	1.393				
		r32	1.393	d321	121.94		
		r43	1.397	d432	118.15	d4321	0.00
		r54	1.392	d543	121.32	d5432	0.00
		r61	1.399	d612	118.83	d6123	0.00
		r71	1.086	d712	120.23	d7123	180.00
		r82	1.761	d821	118.62	d8213	-180.00
		r93	1.083	d932	120.41	d9321	-180.00
		r104	1.086	d1043	119.30	d10432	180.00
		r115	1.084	d1154	121.58	d11543	180.00
		r126	1.364	d1261	122.28	d12612	-180.00
		r1312	0.966	d13126	109.47	d131261	0.00
4-Chloro phenol (3)		r21	1.391				
		r32	1.396	d321	119.71		
		r43	1.392	d432	120.68	d4321	0.00
		r54	1.395	d543	119.52	d5432	0.00
		r65	1.398	d654	120.22	d6543	0.00
		r71	1.085	d712	120.92	d7123	180.00
		r82	1.084	d821	120.31	d8213	-180.00
		r93	1.761	d932	119.65	d9321	-180.00
		r104	1.084	d1043	120.18	d10432	-180.00
		r115	1.088	d1154	119.63	d11543	-180.00
		r126	1.365	d1265	122.87	d12654	180.00
		r1312	0.966	d13126	109.29	d131265	0.00
2,3-Dihloro phenol (4)		r21	1.400				
		r32	1.394	d321	120.32		
		r43	1.395	d432	119.24	d4321	0.00
		r54	1.390	d543	121.03	d5432	0.00
		r65	1.399	d654	120.03	d6543	0.00
		r71	1.755	d712	121.99	d7123	-180.00
		r82	1.749	d821	120.70	d8213	-180.00
		r93	1.083	d932	119.42	d9321	-180.00
		r104	1.085	d1043	119.39	d10432	-180.00
		r115	1.084	d1154	121.82	d11543	-180.00
		r126	1.354	d1265	118.07	d12654	180.00
		r1312	0.970	d13126	109.04	d131265	-179.99

2,4-Dihloro phenol (**5**)		r21	1.392				
		r32	1.392	d321	118.62		
		r43	1.396	d432	120.90	d4321	0.00
		r54	1.390	d543	119.62	d5432	0.00
		r65	1.400	d654	120.89	d6543	0.00
		r71	1.763	d712	119.73	d7123	-180.00
		r82	1.083	d821	120.33	d8213	-180.00
		r93	1.757	d932	119.27	d9321	180.00
		r104	1.084	d1043	120.03	d10432	-180.00
		r115	1.085	d1154	120.96	d11543	180.00
		r126	1.354	d1265	118.38	d12654	180.00
		r1312	0.970	d13126	109.00	d131265	-180.00
2,5-Dihloro phenol (**6**)		r21	1.391				
		r32	1.393	d321	120.10		
		r43	1.396	d432	118.61	d4321	0.00
		r54	1.390	d543	121.87	d5432	0.00
		r65	1.400	d654	119.52	d6543	0.00
		r71	1.763	d712	120.40	d7123	180.00
		r82	1.084	d821	119.50	d8213	-180.00
		r93	1.083	d932	120.74	d9321	-180.00
		r104	1.757	d1043	119.25	d10432	-180.00
		r115	1.083	d1154	121.59	d11543	180.00
		r126	1.353	d1265	117.84	d12654	-180.00
		r1312	0.970	d13126	108.95	d131265	-180.00
2,6-Dihloro phenol (**7**)		r21	1.392				
		r32	1.395	d321	120.11		
		r43	1.393	d432	120.04	d4321	0.00
		r54	1.391	d543	119.18	d5432	0.00
		r65	1.405	d654	122.24	d6543	0.00
		r71	1.749	d712	119.97	d7123	-180.00
		r82	1.084	d821	118.98	d8213	180.00
		r93	1.085	d932	120.00	d9321	180.00
		r104	1.084	d1043	121.28	d10432	180.00
		r115	1.765	d1154	120.09	d11543	180.00
		r126	1.349	d1265	123.53	d12654	-180.00
		r1312	0.970	d13126	108.64	d131265	0.00
3,4-Dihloro phenol (**8**)		r21	1.396				
		r32	1.399	d321	120.29		
		r43	1.398	d432	119.06	d4321	0.00
		r54	1.389	d543	121.04	d5432	0.00
		r65	1.397	d654	120.06	d6543	0.00
		r71	1.086	d712	119.13	d7123	-180.00
		r82	1.748	d821	118.18	d8213	-180.00
		r93	1.749	d932	121.84	d9321	-180.00
		r104	1.084	d1043	118.83	d10432	-180.00
		r115	1.084	d1154	121.08	d11543	-180.00
		r126	1.363	d1261	122.59	d12612	180.00
		r1312	0.966	d13126	109.64	d131261	0.00

3,5-Dihloro phenol (9)		r21	1.389				
		r32	1.396	d321	122.45		
		r43	1.392	d432	117.34	d4321	0.00
		r54	1.393	d543	122.27	d5432	0.00
		r65	1.399	d654	118.69	d6543	0.00
		r71	1.083	d712	121.64	d7123	-180.00
		r82	1.756	d821	118.92	d8213	-180.00
		r93	1.082	d932	121.31	d9321	180.00
		r104	1.756	d1043	118.96	d10432	180.00
		r115	1.085	d1154	120.25	d11543	-180.00
		r126	1.361	d1265	122.46	d12654	-180.00
		r1312	0.967	d13126	109.61	d131265	-0.04
2,3,4- Trichloro phenol (**10**)		r21	1.404				
		r32	1.402	d321	118.98		
		r43	1.396	d432	119.94	d4321	0.00
		r54	1.387	d543	120.76	d5432	0.00
		r65	1.398	d654	120.33	d6543	0.00
		r71	1.753	d712	121.42	d7123	180.00
		r82	1.739	d821	120.12	d8213	-180.00
		r93	1.748	d932	121.25	d9321	180.00
		r104	1.084	d1043	118.97	d10432	-180.00
		r115	1.084	d1154	121.25	d11543	-180.00
		r126	1.353	d1265	118.06	d12654	-180.00
		r1312	0.970	d13126	109.17	d131265	-180.00
2,3,5- Trichloro phenol (**11**)		r21	1.399				
		r32	1.394	d321	120.77		
		r43	1.394	d432	118.45	d4321	0.00
		r54	1.389	d543	122.06	d5432	0.00
		r65	1.398	d654	119.20	d6543	0.00
		r71	1.751	d712	122.20	d7123	-179.99
		r82	1.746	d821	120.73	d8213	179.99
		r93	1.082	d932	120.28	d9321	179.99
		r104	1.753	d1043	118.85	d10432	-180.00
		r115	1.083	d1154	121.82	d11543	-180.00
		r126	1.351	d1265	117.53	d12654	180.00
		r1312	0.970	d13126	109.15	d131265	180.00
2,3,6- Trichloro phenol (**12**)		r21	1.390				
		r32	1.393	d321	120.53		
		r43	1.393	d432	119.70	d4321	0.00
		r54	1.399	d543	119.95	d5432	0.00
		r61	1.404	d612	120.75	d6123	0.00
		r71	1.746	d712	120.18	d7123	-180.00
		r82	1.084	d821	119.21	d8213	180.00
		r93	1.083	d932	120.70	d9321	180.00
		r104	1.746	d1043	119.16	d10432	180.00
		r115	1.753	d1154	121.85	d11543	-180.00
		r126	1.347	d1261	118.89	d12612	180.00
		r1312	0.970	d13126	108.90	d131261	179.99

Harmonic vibrational frequencies and moments of inertia are calculated for each chlorinated phenol at B3LYP/6-31G(d,p) level on the basis of optimized geometries at this same level of theory (Table 4.3).

Table 4.3 The B3LYP/6-31G(d,p) Harmonic Vibrational Frequencies and Moments of Inertia of Chlorophenols

Species	Freq (cm^{-1})	Ia	Ib	Ic
			(amu-Bohr^2)	
2-Chlorophenol (1) Sym = 1	161 253 266 376 418 448 496 551 564 686 708 763 847 859 940 978 1047 1066 1147 1184 1220 1290 1343 1383 1503 1527 1640 1655 3192 3205 3215 3221 3762	608.59326	1179.22766	1787.82092
3-Chlorophenol (2) Sym = 1	184 351 451 686 834 974 1117 1295 1487 1660 3221 234 408 536 699 886 1010 1186 1346 1532 3194 3230 248 448 583 785 903 1095 1201 1364 1642 3195 3821	524.75419	1524.74890	2049.50309
4-Chlorophenol (3) Sym = 1	127 262 328 351 380 424 426 514 646 649 699 807 837 842 931 956 1024 1108 1127 1195 1199 1310 1326 1370 1470 1540 1644 1663 3172 3209 3219 3223 3821	320.42366	1870.13746	2190.56112
2,3-Dichlorophenol (4) Sym = 1	107 206 218 269 283 382 422 446 506 529 573 580 702 744 783 885 919 972 1053 1115 1177 1203 1252 1343 1366 1485 1505 1630 1645 3200 3222 3231 3758	1177.84848	1539.35018	2717.19866
2,4-Dichlorophenol (5) Sym = 1	127 175 199 280 341 380 399 411 448 516 561 658 696 729 831 865 876 953 1063 1112 1161 1218 1279 1331 1375 1450 1523 1630 1651 3213 3227 3235 3765	833.01226	2485.85888	3318.87114
2,5-Dichlorophenol (6) Sym = 1	100 216 218 271 309 327 421 454 458 560 580 598 694 716 803 867 916 940 1056 1102 1160 1218 1291 1310 1361 1477 1517 1628 1647 3217 3235 3236 3760	609.34287	2846.34095	3455.68382
2,6-Dichlorophenol (7) Sym = 1	109 204 213 280 282 377 406 423 511 546 556 608 716 773 780 847 904 961 1098 1105 1175 1196 1283 1315 1376 1491 1516 1628 1641 3206 3222 3228 3755	866.29813	2125.95147	2992.24961
3,4-Dichlorophenol (8) Sym = 1	113 187 199 272 328 350 378 445 452 489 591 653 684 704 825 839 916 954 1037 1148 1156 1200 1271 1326 1349 1455 1521 1632 1655 3198 3214 3228 3823	989.28733	2046.68849	3035.97582
3,5-Dichlorophenol (9) Sym = 1	152 194 207 235 263 358 396 428 497 540 542 587 672 811 824 844 864 951 1010 1118 1129 1199 1294 1309 1360 1478 1503 1631 1652 3203 3239 3249 3820	1279.60622	2123.59102	3403.19723

2,3,4-Trichlorophenol (**10**) Sym = 1	87 128 209 217 240 298 335 346 412 423 500 507 546 591 686 700 778 827 933 950 1081 1158 1194 1234 1335 1351 1436 1493 1619 1640 3219 3232 3756	1460.02373	2587.76717	4047.79090
2,3,5-Trichlorophenol (**11**) Sym = 1	87 153 195 214 231 294 313 332 409 427 508 548 576 590 604 692 829 841 863 962 1063 1128 1200 1255 1317 1350 1469 1483 1616 1636 3241 3250 3755	1490.66014	3062.88483	4553.54496
2,3,6-Trichlorophenol (**12**) Sym = 1	98 111 204 209 268 299 310 338 401 430 505 520 587 604 630 715 800 807 926 942 1111 1158 1188 1250 1308 1363 1454 1508 1621 1625 3221 3236 3749	1239.09427	3147.48552	4386.57979
2,4,5-Trichlorophenol (**13**) Sym = 1	83 147 195 211 239 290 325 365 395 413 453 528 570 628 679 683 739 858 886 943 1076 1143 1219 1269 1302 1348 1436 1509 1611 1646 3235 3236 3762	1294.41559	3358.65271	4653.06830
2,4,6-Trichlorophenol (**14**) Sym = 1	106 141 188 197 214 298 351 374 383 416 433 508 572 580 710 733 798 866 873 884 1098 1150 1187 1268 1318 1369 1435 1509 1616 1636 3241 3241 3760	2125.10967	2547.09418	4672.20386
3,4,5-Trichlorophenol (**15**) Sym = 1	79 171 206 207 213 278 332 345 349 447 448 534 557 608 657 680 813 827 864 966 1045 1162 1200 1223 1316 1332 1452 1483 1617 1649 3206 3241 3825	2044.58398	2164.17688	4208.76085
2,3,4,5-Tetrachlorophenol (**16**) Sym = 1	78 87 172 209 219 224 269 304 332 357 418 451 43 572 598 631 688 725 841 862 987 1091 1179 1235 1310 1330 1431 1462 1599 1633 3242 3754	2110.16525	3492.84112	5603.00634
2,3,4,6-Tetrachlorophenol (**17**) Sym = 1	75 109 148 194 210 218 284 311 331 360 376 412 422 518 567 624 634 705 756 813 882 951 1125 1189 1232 1314 1349 1411 1487 1607 1619 3240 3753	2422.17352	3376.98810	5799.16162
2,3,5,6-Tetrachlorophenol (**18**) Sym = 1	72 107 155 196 211 216 290 304 339 339 350 436 457 577 581 589 608 696 710 843 871 969 1120 1188 1252 1278 1344 1452 1481 1600 1613 3248 3746	2005.61027	3882.74309	5888.35336
Pentachlorophenol (**19**) Sym = 1	71 78 113 179 212 217 220 231 312 335 341 342 357 378 429 466 587 632 655 698 704 764 878 991 1137 1232 1291 1322 1406 1455 1584 1599 3749	3171.18760	3914.60035	7085.78795

4.3.2 $\Delta_f H^o_{298}$

$\Delta_f H^o_{298}$ for all twelve chlorophenols are obtained using the isodesmic reaction method with total energies at two different DFT levels of theory (Table 4.4).

Table 4.4 Calculated Total Energies of Chlorophenols at 298 K[a,b]

Species	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	ZPEV[c,d]	H_{298}-H_0[d]
Phenol	-307.3692654	-307.4710086	64.47	4.05
2-Chlorophenol (**1**)	-766.9735878	-767.1092016	58.76	4.72
3-Chlorophenol (**2**)	-766.9718586	-767.1076004	58.59	4.78
4-Chlorophenol (**3**)	-766.9713189	-767.1068234	58.59	4.79
2,3-Dichlorophenol (**4**)	-1226.5709415	-1226.7406642	52.86	5.47
2,4-Dichlorophenol (**5**)	-1226.5740778	-1226.7432928	52.82	5.50
2,5-Dichlorophenol (**6**)	-1226.5748451	-1226.7441926	52.80	5.49
2,6-Dichlorophenol (**7**)	-1226.5716607	-1226.7409687	52.89	5.47
3,4-Dichlorophenol (**8**)	-1226.5686395	-1226.7381730	52.70	5.54
3,5-Dichlorophenol (**9**)	-1226.5728233	-1226.7423813	52.65	5.54
2,3,4-Trichlorophenol (**10**)	-1686.1664487	-1686.3703505	46.91	6.24
2,3,5-Trichlorophenol (**11**)	-1686.1709004	-1686.3746932	46.86	6.26
2,3,6-Trichlorophenol (**12**)	-1686.1681094	-1686.3717320	46.96	6.25
2,4,5-Trichlorophenol (**13**)	-1686.1702990	-1686.3738169	46.85	6.27
2,4,6-Trichlorophenol (**14**)	-1686.1707657	-1686.3739738	46.89	6.28
3,4,5-Trichlorophenol (**15**)	-1686.1643251	-1686.3682902	46.72	6.31
2,3,4,5-Tetrachlorophenol (**16**)	-2145.7564750	-2145.9997827	40.85	7.07
2,3,4,6-Tetrachlorophenol (**17**)	-2145.7625134	-2146.0005268	40.97	7.04
2,3,5,6-Tetrachlorophenol (**18**)	-2145.7633489	-2146.0014336	40.98	7.04
Pentachlorophenol (**19**)	-2605.3525674	-2605.6254076	35.00	7.81

a: All calculations are based on B3LYP/6-31G(d,p) optimized structures;

b: Total energies (ZPVE and thermal corrections are included) in hartree, 1 hartree = 627.51 kcal/mol;

c: Scaled by 0.9806; [37]

d: In units of kcal/mol.

Table 4.5 Calculated $\Delta H_{rxn,298}$ (kcal/mol) of Isodesmic Reactions for Chlorophenols[a]

Isodesmic Reactions	B3LYP /6-31G (d,p)	B3LYP/ 6-311+G (3df,2p)
	// B3LYP/6-31G(d,p)	
(R1a) *2-chlorophenol* + benzene → phenol + Clbz	0.87	1.15
(R1b) *2-chlorophenol* + Clbz → benzene + 1,2-di Clbz	4.35	4.22
(R2a) *3-chlorophenol* + benzene → phenol + Clbz	-0.16	0.17
(R2b) *3-chlorophenol* + Clbz → benzene + 1,3-di Clbz	0.90	0.98
(R3a) *4-chlorophenol* + benzene → phenol + Clbz	-0.55	-0.34
(R3b) *4-chlorophenol* + Clbz → benzene + 1,4-di Clbz	0.44	0.47
(R4a) *2,3-dichlorophenol* + benzene → 2-chlorophenol + Clbz	-3.50	-3.07
(R4b) *2,3-dichlorophenol* + Clbz → phenol + 1,2,3-tri Clbz	5.20	4.94
(R5a) *2,4-dichlorophenol* + benzene → 2-chlorophenol + Clbz	-1.53	-1.42
(R5b) *2,4-dichlorophenol* + Clbz → phenol + 1,2,4-tri Clbz	4.56	4.17
(R6a) *2,5-dichlorophenol* + benzene → 2-chlorophenol + Clbz	-1.05	-0.86
(R6b) *2,5-dichlorophenol* + chlorobenzene → phenol + 1,2,4-tri Clbz	5.04	4.74
(R7a) *2,6-dichlorophenol* + benzene → 2-chlorophenol + Clbz	-3.05	-2.88
(R7b) *2,6-dichlorophenol* + Clbz → phenol + 1,2,3-tri Clbz	5.65	5.13
(R8a) *3,4-dichlorophenol* + benzene → 3-chlorophenol + Clbz	-3.91	-3.65

(R8b) *3,4-dichlorophenol* + Clbz → phenol + 1,2,4-tri Clbz	1.15	0.96
(R9a) *3,5-dichlorophenol* + benzene → 3-chlorophenol + Clbz	-1.28	-1.01
(R9b) *3,5-dichlorophenol* + Clbz → phenol + 1,3,5-tri Clbz	1.64	1.52
(R10a) *2,3,4-trichlorophenol* + benzene → 2-chlorophenol + 1,2-di Clbz	-4.68	-4.19
(R10b) *2,3,4-trichlorophenol* + Clbz → phenol + 1,2,3,4-tetra Clbz	5.42	4.98
(R11a) *2,3,5-trichlorophenol* + benzene → 2-chlorophenol + 1,3-di Clbz	-4.30	-3.73
(R11b) *2,3,5-trichlorophenol* + Clbz → phenol + 1,2,3,5-tetra Clbz	5.81	5.42
(R12a) *2,3,6-trichlorophenol* + benzene → 2-chlorophenol + 1,2-di Clbz	-3.64	-3.33
(R12b) *2,3,6-trichlorophenol* + Clbz → phenol + 1,2,3,4-tetra Clbz	6.46	5.85
(R13a) *2,4,5-trichlorophenol* + benzene → 2-chlorophenol + 1,2-di Clbz	-2.26	-2.02
(R13b) *2,4,5-trichlorophenol* + Clbz → phenol + 1,2,4,5-tetra Clbz	5.05	4.57
(R14a) *2,4,6-trichlorophenol* + benzene → 2-chlorophenol + 1,3-di Clbz	-4.39	-4.18
(R14b) *2,4,6-trichlorophenol* + Clbz → phenol + 1,2,3,5-tetra Clbz	5.73	4.97
(R15a) *3,4,5-trichlorophenol* + benzene → 3-chlorophenol + 1,2-di Clbz	-4.98	-4.51
(R15b) *3,4,5-trichlorophenol* + Clbz → phenol + 1,2,3,4-tetra Clbz	4.08	3.69
(R16a) *2,3,4,5-tetrachlorophenol* + benzene → 2-chlorophenol + 1,2,3-tri Clbz	-5.36	-4.74
(R16b) *2,3,4,5-tetrachlorophenol* + Clbz → phenol + penta Clbz	5.86	5.36
(R17a) *2,3,4,6-tetrachlorophenol* + benzene → 2-chlorophenol + 1,2,3-tri Clbz	-4.64	-4.27
(R17b) *2,3,4,6-tetrachlorophenol* + Clbz → phenol + penta Clbz	6.58	5.82
(R18a) *2,3,5,6-tetrachlorophenol* + benzene → 2-chlorophenol + 1,2,4-tri Clbz	-6.72	-6.12
(R18b) *2,3,5,6-tetrachlorophenol* + Clbz → phenol + penta Clbz	7.10	6.39
(R19a) *Perchlorophenol* + benzene → 2-chlorophenol + 1,2,3,4-tetra Clbz	-7.84	-7.25
(R19b) *Perchlorophenol* + Clbz → phenol + per Clbz	7.22	6.36

a: Total energies of benzene and all chlorobenzenes are taken from Chapter of chlorobenzenes.

The enthalpy changes of the isodesmic reactions are calculated from the total energies (Table 4.5). The reference species used in the isodesmic reactions are collected in Table 4.6. The calculated $\Delta_f H^o_{298}$ for nineteen chlorophenols are shown in Table 4.7. The average of two values calculated at B3LYP/6-311+G(3df,2p) by two isodesmic reactions is taken as the recommended $\Delta_f H^o_{298}$ for each species (Table 4.7).

Other sources of error listed in Table 4.8 comprise the standard deviation of the two calculated $\Delta_f H^o_{298}$ values (two isodesmic reactions at the B3LYP/6-311+G(3df,2p) level), plus the cumulative uncertainties in $\Delta_f H^o_{298}$ for the reference species, as well as the uncertainty from ZPVE calculations, 0.44 kcal/mol. [35,37]

Table 4.6 $\Delta_f H^\circ_{298}$ (in kcal/mol) for Reference Species (and Literature Citations)[a]

Species	$\Delta_f H^\circ_{298}$	Species	$\Delta_f H^\circ_{298}$
Benzene	19.74±0.17 [42]	1,2,4-Trichlorobenzene	2.25±2.18
Chlorobenzene	12.43±0.31 [42]	1,3,5-Trichlorobenzene	0.16±2.18
Phenol	-23.04±0.22 [42]	1,2,3,4-Tetrachlorobenzene	1.57±3.12
1,2-Dichlorobenzene	8.17±1.25	1,2,3,5-Tetrachlorobenzene	-0.71±3.12
1,3-Dichlorobenzene	5.91±1.25	1,2,4,5-Tetrachlorobenzene	1.02±3.12
1,4-Dichlorobenzene	5.91±1.25	Pentachlorobenzene	-1.02±4.04
1,2,3-Trichlorobenzene	4.67±2.18		

a: Data for chlorobenzenes are taken from calculation results in Chapter of chlorobenzenes.

Table 4.7 Calculated $\Delta_f H^\circ_{298}$ (in kcal/mol) of Chlorophenols Using Isodesmic Working Reactions

Species	From Rxns	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	$X_{avg}{}^{a}\pm\sigma$
		// B3LYP/6-31G(d,p)		
2-Chlorophenol (**1**)	(R1a)	-31.22	-31.50	
	(R1b)	-31.65	-31.52	-31.51±0.01
3-Chlorophenol (**2**)	(R2a)	-30.19	-30.52	
	(R2b)	-30.46	-30.53	-30.53±0.01
4-Chlorophenol (**3**)	(R3a)	-29.80	-30.01	
	(R2b)	-30.00	-30.03	-30.02±0.01
2,3-Dichlorophenol (**4**)	(R4a)	-35.32	-35.75	
	(R4b)	-36.00	-35.75	-35.75±0.00
2,4-Dichlorophenol (**5**)	(R5a)	-37.29	-37.40	
	(R5b)	-37.79	-37.40	-37.40±0.00
2,5-Dichlorophenol (**6**)	(R6a)	-37.77	-37.96	
	(R6b)	-38.27	-37.96	-37.96±0.00
2,6-Dichlorophenol (**7**)	(R7a)	-35.77	-35.94	
	(R7b)	-36.46	-35.94	-35.94±0.00
3,4-Dichlorophenol (**8**)	(R8a)	-33.93	-34.18	
	(R8b)	-34.37	-34.18	-34.18±0.00
3,5-Dichlorophenol (**9**)	(R9a)	-36.55	-36.83	
	(R9b)	-36.95	-36.83	-36.83±0.00
2,3,4-Trichlorophenol (**10**)	(R10a)	-38.40	-38.89	
	(R10b)	-39.31	-38.88	-38.88±0.00
2,3,5-Trichlorophenol (**11**)	(R11a)	-41.03	-41.61	
	(R11b)	-42.00	-41.61	-41.61±0.00
2,3,6-Trichlorophenol (**12**)	(R12a)	-39.44	-39.75	
	(R12b)	-40.36	-39.75	-39.75±0.00
2,4,5-Trichlorophenol (**13**)	(R13a)	-40.82	-41.06	
	(R13b)	-41.54	-41.06	-41.06±0.00
2,4,6-Trichlorophenol (**14**)	(R14a)	-40.95	-41.16	
	(R14b)	-41.91	-41.16	-41.16±0.00

3,4,5-Trichlorophenol (**15**)	(R15a)	-37.12	-37.59	
	(R15b)	-37.98	-37.59	-37.59±0.00
2,3,4,5-Tetrachlorophenol (**16**)	(R16a)	-41.23	-41.84	
	(R16b)	-42.35	-41.85	-41.85±0.00
2,3,4,6-Tetrachlorophenol (**17**)	(R17a)	-41.94	-42.31	
	(R17b)	-43.07	-42.32	-42.31±0.00
2,3,5,6-Tetrachlorophenol (**18**)	(R18a)	-42.28	-42.88	
	(R18b)	-43.59	-42.88	-42.88±0.00
Pentachlorophenol (**19**)	(R19a)	-41.83	-42.43	
	(R19b)	-43.29	-42.42	-42.43±0.00

a: Average of B3LYP/6-311+G(3df,2p) only.

Table 4.8 Ideal Gas-phase Thermochemical Properties for Chlorophenols[a]

		$\Delta_f H^\circ_{298}$	S°_{298}	$C_p^\circ(T)$						
				300K	400K	500K	600K	800K	1000K	1500K
2-Chlorophenol (**1**)	TVR		78.68	25.71	33.04	39.05	43.83	50.70	55.36	62.18
	IR		1.18	2.05	2.72	3.13	3.27	3.06	2.65	1.89
This work	Total	-31.51±2.23	79.86	27.76	35.76	42.18	47.10	53.76	58.01	64.07
Shaub [83]		-31.11								
3-Chlorophenol (**2**)	TVR		79.47	26.01	33.28	39.25	43.99	50.80	55.43	62.20
	IR		2.84	1.91	2.10	2.13	2.06	1.85	1.65	1.35
	Total	-30.53±2.23	82.31	27.92	35.38	41.38	46.05	52.65	57.08	63.55
Pedley [42]		-36.64±2.08								
Cox [55]		-36.70±2.10								
4-Chlorophenol (**3**)	TVR		78.82	25.94	33.23	39.21	43.96	50.78	55.41	62.20
	IR		2.84	1.91	2.10	2.13	2.06	1.85	1.65	1.35
This work	Total	-30.02±2.23	81.66	27.85	35.33	41.34	46.02	52.63	57.06	63.55
Pedley [42]		-34.85±2.08								
Cox [55]		-34.90±2.10								
2,3-Dichlorophenol (**4**)	TVR		84.72	29.42	36.57	42.32	46.82	53.19	57.41	63.45
	IR		1.18	2.05	2.72	3.13	3.27	3.06	2.65	1.89
	Total	-35.75±3.15	85.90	31.47	39.29	45.45	50.09	56.25	60.06	65.34
TRC [41]		-40.17	88.05	32.21	39.99	45.51	49.67	55.96	60.04	
Shaub [83]		-42.68								
Ribeiro Da Silva [66]		-36.23±0.60								
2,4-Dichlorophenol (**5**)	TVR		85.46	29.57	36.68	42.40	46.87	53.22	57.43	63.45
	IR		1.18	2.05	2.72	3.13	3.27	3.06	2.65	1.89
This work	Total	-37.40±3.15	86.64	31.62	39.40	45.53	50.14	56.28	60.08	65.34
TRC [41]		-39.46	88.43	32.20	39.50	45.19	49.64	55.89	60.04	65.78
Shaub [83]		-41.98								
Ribeiro Da Silva [66]		-37.36±0.45								
2,5-Dichlorophenol (**6**)	TVR		84.95	29.54	36.69	42.41	46.89	53.23	57.44	63.45
	IR		1.18	2.05	2.72	3.13	3.27	3.06	2.65	1.89
	Total	-37.96±3.15	86.13	31.59	39.41	45.54	50.16	56.29	60.09	65.34
TRC [41]		-41.70	88.45	32.22	39.56	45.27	49.71	55.95	60.08	65.58
Shaub [83]		-44.23								
Ribeiro Da Silva [66]		-37.86±0.57								
2,6-Dichlorophenol (**7**)	TVR		83.52	29.42	36.56	42.30	46.80	53.17	57.40	63.44
	IR		2.55	1.73	2.01	2.15	2.19	2.10	1.92	1.56
This work	Total	-35.94±3.15	86.07	31.15	38.57	44.45	48.99	55.27	59.32	65.00

Shaub [83]		-25.33								
Ribeiro Da Silva [66]		-34.97±0.36								
3,4-Dichlorophenol	TVR		85.48	29.71	36.80	42.50	46.96	53.28	57.47	63.46
(**8**)	IR		2.84	1.91	2.10	2.13	2.06	1.85	1.65	1.35
This work	Total	-34.18±3.15	88.32	31.62	38.90	44.63	49.02	55.13	59.12	64.81
TRC [41]		-46.45	88.27	32.21	39.99	45.51	49.67	55.96	60.04	
Shaub [83]		-46.47								
Ribeiro Da Silva [66]		-35.92±0.60								
3,5-Dichlorophenol	TVR		86.23	29.85	36.93	42.62	47.06	53.34	57.50	63.47
(**9**)	IR		2.84	1.91	2.10	2.13	2.06	1.85	1.65	1.35
This work	Total	-36.83±3.15	89.07	31.76	39.03	44.75	49.12	55.19	59.15	64.82
Ribeiro Da Silva [66]		-35.42±0.36								
2,3,4-Trichlorophenol	TVR		91.14	33.19	40.14	45.60	49.82	55.69	59.48	64.73
(**10**)	IR		1.18	2.05	2.72	3.13	3.27	3.06	2.65	1.89
This work	Total	-38.88±4.09	92.32	35.24	42.86	48.73	53.09	58.75	62.13	66.62
2,3,5-Trichlorophenol	TVR		91.47	33.30	40.24	45.69	49.89	55.72	59.50	64.73
(**11**)	IR		1.18	2.05	2.72	3.13	3.27	3.06	2.65	1.89
This work	Total	-41.61±4.09	92.65	35.35	42.96	48.82	53.16	58.78	62.15	66.62
2,3,6-Trichlorophenol	TVR		91.54	33.17	40.10	45.56	49.79	55.66	59.45	64.72
(**12**)	IR		2.55	1.73	2.01	2.15	2.19	2.10	1.92	1.56
This work	Total	-39.75±4.09	94.09	34.90	42.11	47.71	51.98	57.76	61.37	66.28
2,4,5-Trichlorophenol	TVR		91.48	33.32	40.25	45.68	49.88	55.72	59.49	64.73
(**13**)	IR		1.18	2.05	2.72	3.13	3.27	3.06	2.65	1.89
This work	Total	-41.06±4.09	92.66	35.37	42.97	48.81	53.15	58.78	62.14	66.62
Shaub [83]		-53.16								
2,4,6-Trichlorophenol	TVR		92.08	33.32	40.22	45.65	49.85	55.69	59.47	64.72
(**14**)	IR		2.55	1.73	2.01	2.15	2.19	2.10	1.92	1.56
This work	Total	-41.16±4.09	94.63	35.05	42.23	47.80	52.04	57.79	61.39	66.28
TRC [41]		-34.28	94.00	35.98	42.96	48.37	52.55	58.32	62.04	67.61
3,4,5-Trichlorophenol	TVR		91.53	33.49	40.40	45.82	50.00	55.80	59.54	64.75
(**15**)	IR		2.84	1.91	2.10	2.13	2.06	1.85	1.65	1.35
This work	Total	-37.59±4.09	94.37	35.40	42.50	47.95	52.06	57.65	61.19	66.10
2,3,4,5-Tetrachloro phenol (**16**)	TVR		97.75	36.99	43.73	48.90	52.84	58.20	61.55	66.02
	IR		1.18	2.05	2.72	3.13	3.27	3.06	2.65	1.89
This work	Total	-41.85±5.02	98.93	39.04	46.45	52.03	56.11	61.26	64.20	67.91
2,3,4,6-Tetrachloro phenol (**17**)	TVR		97.86	36.96	43.67	48.84	52.79	58.15	61.52	66.00
	IR		2.55	1.73	2.01	2.15	2.19	2.10	1.92	1.56
This work	Total	-42.31±5.02	100.41	38.69	45.68	50.99	54.98	60.25	63.44	67.56
2,3,5,6-Tetrachloro phenol (**18**)	TVR		97.73	36.92	43.66	48.84	52.78	58.15	61.52	66.00
	IR		2.55	1.73	2.01	2.15	2.19	2.10	1.92	1.56
This work	Total	-42.88±5.02	100.28	38.65	45.67	50.99	54.97	60.25	63.44	67.56
Pentachlorophenol	TVR		104.05	40.63	47.16	52.08	55.76	60.65	63.59	67.29
(**19**)	IR		2.55	1.73	2.01	2.15	2.19	2.10	1.92	1.56
This work	Total	-42.43±5.96	106.60	42.36	49.17	54.23	57.95	62.75	65.51	68.85
Pedley [42]		-53.80±0.86								
Cox [55]		-53.90±0.90								

a: Enthalpies in kcal/mol, entropies and heat capacities in cal/mol.K.

4.3.3 Internal Rotational Barriers

The potential barrier for internal rotation of hydroxyl group for phenol, 2-chlorophenol, and 2,6-dichlorophenol, are calculated at the B3LYP/6-31G(d,p) level. Potential energy as a function of dihedral angle is determined by scanning the torsion angle of HO-CC from 0° to 360° at 15° intervals and allowing the remaining molecular structural parameters to be optimized. Then geometries at all maximum and minimum values are fully optimized. Diagrams for potential energy (ZPVE and thermal corrections included) versus torsion angle shown in Figure 4.1 are results of the Fourier expansion (Eq. 4.1). The values of the coefficients of the Fourier expansion, a_i and b_i in equation I are listed in Table 4.9.

It is seen from Figure 4.1 that there are two stable isomers in 2-chlorophenol, one is HO-CCCl = 0° and the other is HO-CCCl = 180°. The later is 3.1 kcal/mol lower in energy. The distance between hydroxyl H and Cl atom is 2.417 Å in 2-chlorophenol, so there maybe a hydrogen bonding between these two atoms.

Table 4.9 Coefficients (kcal/mol) of Truncated Fourier Series Representation Expansions for Internal Rotation Potentials [a,b]

Coeff.	phenol	2-chloro phenol	2,6-dichloro phenol	Coeff.	phenol	2-chloro phenol	2,6-dichlorophenol
a_0	1.9706	3.8661	2.6238				
a_1	-0.0578	1.4942	-0.0870	b_1	-5.6197e-9	1.6789e-9	1.9420e-9
a_2	-1.9882	-2.3168	-2.6134	b_2	-2.9553e-9	1.7357e-9	2.1771e-9
a_3	0.0566	0.0491	0.0865	b_3	1.0198e-8	2.7459e-9	2.0956e-9
a_4	0.0162	1.9910e-3	-7.3134e-3	b_4	1.1993e-8	1.8548e-9	1.8080e-9
a_5	2.8428e-3	7.4491e-3	-6.0667e-4	b_5	-7.1758e-9	2.2911e-9	1.9138e-9

a: Values of rotational barriers computed at B3LYP/6-31G(d,p) level of theory are used to calculate the coefficients;

b: See text for Eq. 4.1: $V(\Phi) = a_0 + \Sigma\, a_i \cos(i\Phi) + \Sigma\, b_i \sin(i\Phi)$ $\quad i = 1, 2, 3, \ldots\ldots$

The C-OH barriers in chlorophenols changing with the dihedral angels are shown in Figure 4.1.

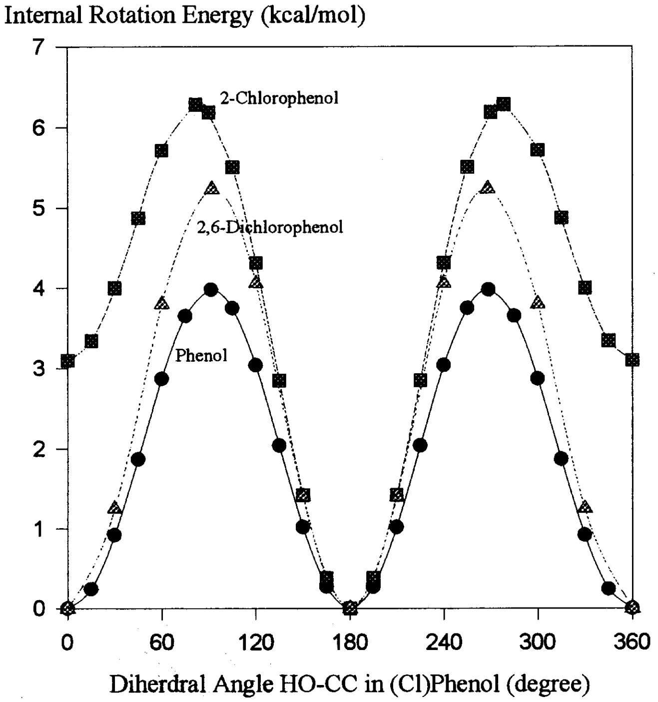
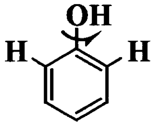


Figure 4.1 Potential Barriers for Internal Rotations About C-OH Bonds in Three Chlorophenols. Curves Are Results of Fourier Expansions (Eq. 4.1).

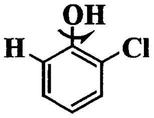
4.3.4 S^o_{298} and $C_p^o(T)$ $(300 \leq T/K \leq 1500)$

S^o_{298} and $C_p^o(T)$ obtained from the frequencies along with moments of inertia based on the optimized B3LYP/6-31G(d,p) structure, using "SMCPS" computer program. [48] are listed in Table 4.8. TVR represent the summation of the contributions from translations, external rotations and vibrations for S^o_{298} and $C_p^o(T)$, and IR's represent the contributions from hindered internal rotations.

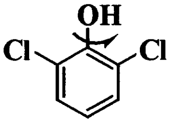
The contributions from hindered internal rotations to S^{o}_{298} and $C_p^{o}(T)$ in phenol is used for 3-chlorophenol, 4-chlorophenol, 3,4-dichlorophenol, 3,5-dichlorophenol, and 3,4,5-trichlorophenol, since they all have similar environment where internal rotor happens, i.e.,



The contributions from hindered internal rotations to S^{o}_{298} and $C_p^{o}(T)$ in 2-chlorophenol is used for 2,3-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,3,4-trichlorophenol, 2,3,5-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4,5-tetrachlorophenol.



The contributions from hindered internal rotations to S^{o}_{298} and $C_p^{o}(T)$ in 2,6-dichlorophenol is used for 2,3,6-trichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, 2,3,5,6-tetrachlorophenol, and pentachlorophenol.



4.3.5 Comparison of Calculation Results with Literature Data

The available literature thermochemical parameters of chlorophenols are listed in Table 9. These literature are either from experiments or review of experiments, such as Pedley, [42] Cox, [55] TRC, [41], Ribeiro Da Silva [66], or from semi-empirical GA, such as Shaub. [83] Most of the GA results are not in good agreement with the calculated values, because the original species where the groups are from, mainly Pedley [42] and Cox, [55] are not in consistent with the calculated values. Ribeiro Da Silva et al. measured the standard enthalpies of combustion of the six dichlorophenols by rotating-bomb calorimetry. [66] The calculated $\Delta_f H^o_{298}$ for 2,3-, 2,4-, and 2,5-dichlorophenols are within ±0.5 kcal/mol of the experimental values by Ribeiro Da Silva et al. For 2,6-, 3,4-, and 3,5-dichlorophenols, the differences are within 1.5 kcal/mol. All data by Ribeiro Da Silva et al. are within the error range of the results in this work.

The differences for S^o_{298} and $C_p^o(T)$ are all within ±2 cal/mol.K between TRC [41] and the results in this work.

4.4 Summary

The geometries of nineteen chlorophenols are studied by B3LYP/6-31G(d,p) DFT calculation. Recommended $\Delta_f H^o_{298}$ of each species is the average value of two data using two isodesmic reactions calculated B3LYP/6-311+G(3df,2p), level of calculation based on B3LYP/6-31G(d,p) optimized geometry. S^o_{298} and $C_p^o(T)$ ($300 \leq T/K \leq 1500$) are determined by B3LYP/6-31G(d,p) optimized geometries and frequencies. The isomer with hydroxyl H oriented to Cl has lower energy than the isomer with hydroxyl H oriented to H in 2-chlorophenol, due to the possible H bonding between hydroxyl H atom and Cl atom.

CHAPTER 5

TRENDS IN KINETIC PARAMETERS FOR ASSOCIATION REACTIONS BETWEEN CHLOROMETHYL RADICALS, ASSOCIATION REACTIONS OF CL AND CHLOROALKYL RADICALS, ADDITION OF CHLORINE ATOMS TO CHLOROETHYLENES, AND ABSTRACTION REACTIONS OF CL OR H ATOM WITH HYDRO OR CHLOROCARBON SPECIES

The trends in the rate constants of several types of reactions between two chloro hydrocarbons, and a chloro hydrocarbon and a Cl (or H) atom are developed in this chapter. The major literature source upon which the trends are obtained is the NIST Kinetic Database version 2Q98 (commercially available from NIST, see NIST website at http://www.nist.gov/srd/nist17.htm).

5.1 Chemically Activated Association Reaction of Chloromethyl and Chloromethyl Radicals

Part of this work has been contributed by a former member of this group, Dr. Hong-Ming Chiang, [84] and Dr. Yang Soo Won. [85]

Association reactions of methyl and chloromethyl radicals are the important formation pathways of chlorinated ethylenes (C_2H_3Cl, CH_2CCl_2, CHClCHCl, and C_2HCl_3). These combination reactions form an energized chloroethane adduct, which can be stabilized, react to new products, or dissociate back to reactants. Analysis of stabilization and dissociation of the adduct is therefore a function of both temperature and pressure. The important reaction pathways for these chlorinated methyl radicals are included in Figure 5.1.

$$\begin{tikzcd}
\mathrm{CH_3 + CH_2Cl} \arrow[r, leftrightarrow] & \mathrm{(C_2H_5Cl)^*} \arrow[r] \arrow[dr] \arrow[dd] & \mathrm{C_2H_4 + HCl} \\
 & & \mathrm{C_2H_5 + Cl} \\
 & \mathrm{C_2H_5Cl} &
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{CH_3 + CHCl_2} \arrow[r, leftrightarrow] & \mathrm{(CH_3CHCl_2)^*} \arrow[r] \arrow[dr] \arrow[dd] & \mathrm{C_2H_3Cl + HCl} \\
 & & \mathrm{CH_3CHCl + Cl} \\
 & \mathrm{CH_3CHCl_2} &
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{CH_2Cl + CH_2Cl} \arrow[r, leftrightarrow] & \mathrm{(CH_2ClCH_2Cl)^*} \arrow[r] \arrow[dr] \arrow[dd] & \mathrm{C_2H_3Cl + HCl} \\
 & & \mathrm{CH_2ClCH_2 + Cl} \\
 & \mathrm{CH_2ClCH_2Cl} &
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{CH_2Cl + CHCl_2} \arrow[r, leftrightarrow] & \mathrm{(CH_2ClCHCl_2)^*} \arrow[r] \arrow[dr] \arrow[ddr] \arrow[dddr] \arrow[dddd] & \mathrm{CH_2CCl_2 + HCl} \\
 & & \mathrm{CHClCHCl + HCl} \\
 & & \mathrm{CH_2ClCHCl + Cl} \\
 & & \mathrm{CHCl_2CH_2 + Cl} \\
 & \mathrm{CH_2ClCHCl_2} &
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{CHCl_2 + CHCl_2} \arrow[r, leftrightarrow] & \mathrm{(CHCl_2CHCl_2)^*} \arrow[r] \arrow[dr] \arrow[dd] & \mathrm{C_2HCl_3 + HCl} \\
 & & \mathrm{CHCl_2CHCl + Cl} \\
 & \mathrm{CHCl_2CHCl_2} &
\end{tikzcd}$$

Figure 5.1 Important Reaction Pathways for the Combination of Chlorinated Methyl Radicals.

The relatively small adduct - 8 atoms and the availability of low energy product channels (relative to initial of the adduct) with a tight TST (HCl elimination) as well as mid energy products with loose TST's (Cl elimination) make the fall-off analysis of these important reaction systems both complex and interesting. [86-90]

H atom elimination from the energized adduct is higher in energy and less important, and therefore not included above. H atom addition to chloromethyl radicals is however very important as it forms a C-H bond which is stronger than the existing C-Cl bond, and often results in fast decomposition of the adduct, loss of Cl or HCl plus the corresponding radical (diradical).

Methyl and chlorine-substituted methyl radicals CH_2Cl, $CHCl_2$ and CCl_3 are the initial products from pyrolysis, oxidation, combustion, or photochemical reaction of chlorinated methanes. The reactions of these radicals play a major role in the initial oxidation and pyrolysis chemistry of reaction systems in which they are participating. The chloromethyl radical addition reactions with O_2 have low rate constants to products and thus, the combination reactions are the important formation pathways to C_2 compounds, chlorinated ethanes, ethylenes, and acetylenes. These chlorinated C_2 compounds are precursors to formation of higher molecular weight species, chlorinated-aromatics, dibenzofurans, and dioxins and ultimately soot + Cl_2 in pyrolysis and fuel rich oxidation of chlorinated hydrocarbons (CHCs). An understanding of these combination and molecular weight growth (MWG) reactions is also important in combustion of chlorinated hydrocarbons, which has received significant attention due to the important role incineration plays in the treatment of hazardous chemical wastes. [91] The presence of known or suspected toxic/carcinogenic chlorocarbon or chloro-oxy carbon species in the effluent from waste and resource recovery incinerators may result from these chloromethyl radical combination reactions in the combustion which persist due to the relatively low reactivity of the chloromethyl peroxy radicals. [92]

The importance of combination reactions for methyl and chloromethyl radicals is further amplified by the relative slow abstraction reaction rates of these C1 radicals relative to H, OH, and Cl combined with the low reactivity of their respective peroxy radicals. These C1 radicals do not react rapidly with O_2 to form stable new products relative to higher carbon number hydrocarbon and chloro hydrocarbon radicals. The C_1 radicals do react rapidly with O_2 to form peroxy species, but dissociation of the adduct back to reactants is its primary reaction under combustion conditions. Because for isomerization or dissociation of the methyl or chloromethyl peroxy radicals are 6 or more kcal/mol greater than dissociation of the adduct back to reactants. The low E_a and relatively high A (~ 10^{15} sec^{-1}) of the reverse reactions to dominate at even moderate temperature of 500 K and above.

Accurate temperature and pressure analysis of these reactions is critical to reliable modeling of the C2 formation and further molecular weight growth in chloro hydrocarbon pyrolysis and oxidation. Accurate input parameters, and high-pressure limit rate constants, are important for estimation of the apparent rate constants of the chemical activation and dissociation reactions.

Table 5.1 Rate Constants (in cm^3/mol.sec) of Chloromethyl + Chloromethyl Association Reactions[a]

Reaction	No. of Cl	k	Literature source (method)
$CH_3 + CH_3$	(0 + 0)	2.40E+13	[93]
		2.50E+13	[94]
		2.67E+13	[95]
		3.61E+13	[96]
		3.56E+13	[97]
		3.78E+13	[98]
$CH_3 + CH_2Cl$	(0 + 1)	**5.01E+13**	[99]
$CH_3 + CHCl_2$	(0 + 2)	**2.83E+13**	[100] for iso-C3H7 + ·CH3 = iso-C4H10
		1.58E+13	[94] for iso-C3H7 + ·CH3 = iso-C4H10
$CH_3 + CCl_3$	(0 + 3)	3.61E+12	[101]
		2.51E+13	[102] for CH3 + CF3
$CH_2Cl + CH_2Cl$	(1 + 1)	1.00E+13	[99]
		1.69E+13	[91]
$CH_2Cl + CHCl_2$	(1 + 2)	**1.57E+13**	[100] for iso-C3H7 + ·C2H5 = iso-C5H12
$CH_2Cl + CCl_3$	(1 + 3)	**9.64E+12**	[103] for tert-C4H9 + ·C2H5 = (CH3)3CCH2CH3
$CHCl_2 + CHCl_2$	(2 + 2)	**5.60E+12**	[91]
		3.16E+13	[104]
$CHCl_2 + CCl_3$	(2 + 3)	**4.92E+12**	Calculated, from reverse C2HCl5 dissociation [105]
$CCl_3 + CCl_3$	(3 + 3)	6.02E+12	[106]
		3.56E+12	[107]
		4.68E+12	[108]

a: values in bold are used to obtain the trend.

5.1.1 $C{\bullet}H_nX_{3-n}$ + $C{\bullet}H_nX_{3-n}$ Association Reactions in the Literature

There are a number of literature values for these types of reactions, and are summarized in Table 5.1.

A computational study of the recombination kinetics of CH_3 + CH_3 uses a direct transition state theory by Klippenstein and Harding in 1999. [98,109] They also compared their results with some experimental or computational values.

Cody et al. [110] report the rate of the reaction $CH_3 + CH_3\ (+ M) \rightarrow C_2H_6\ (+ M)$ (k_1) at the low temperatures and pressures in 2002. The absolute rate constant for the self-reaction of CH_3 is measured using the discharge-flow kinetic technique coupled to mass spectrometric detection at T = 202 and 298 K and P = 0.6-2.0 Torr nominal pressure (He). CH_3 was produced by the reaction of F with CH_4, with CH_4 in large excess over F, and detected by low energy (11 eV) electron impact ionization at m/z = 15. The results were obtained by graphical analysis of plots of the reciprocal of the CH_3 signal vs reaction time. At T = 298 K, $k_1(0.6\ \text{Torr}) = (2.15 \pm 0.42) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ and $k_1(1\ \text{Torr}) = (2.44 \pm 0.52) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$. At T = 202 K, the rate constant increased from $k_1(0.6\ \text{Torr}) = (5.04 \pm 1.15) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ to $k_1(1.0\ \text{Torr}) = (5.25 \pm 1.43) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ to $k_1(2.0\ \text{Torr}) = (6.52 \pm 1.54) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$, indicating that the reaction is in the fall-off region. Klippenstein and Harding had previously calculated rate constant falloff curves for this self-reaction in Ar buffer gas. Transforming these results for a He buffer gas suggest little change in the energy removal per collision, $-\langle E \rangle_d$, with decreasing temperature and also indicate that $-\langle E \rangle_d$ for He buffer gas is approximately half of that for Ar. Since the experimental results seem to at least partially affirm the validity of the Klippenstein and Harding calculations, Cody et al. suggest that, in atmospheric models of the outer planets, use of the theoretical results for k_1 is preferable to extrapolation of laboratory data to pressures and temperatures well beyond the range of the experiments.

Several strategies are used when there is no data in the literature: (i) For types of 0+2, 1+2, 1+3, CH_3 group is used to replace Cl. (ii) For type of 0+3, CF_3 group is used to replace CCl_3. (iii) For type of 2+3: the reverse reaction and microscopic reversibility <mr> is used. It is also assumed Ea = 0 kcal/mol for all association reactions, although some literature show that this type of reaction has negative Ea up to 0.6 kcal/mol.

5.1.2 Trend of the C•H_nX_{3-n} + C•H_nX_{3-n} Association Rate Constants

The relationship between the association rate constants and the number of Cl substituents in two chloromethyl radicals, is shown in Figure 5.2.

0 + 0 here means CH_3 + CH_3 association reaction;

0 + 1 means CH_3 + CH_2Cl association reaction;

……

3 + 3 means CCl_3 + CCl_3 association reaction.

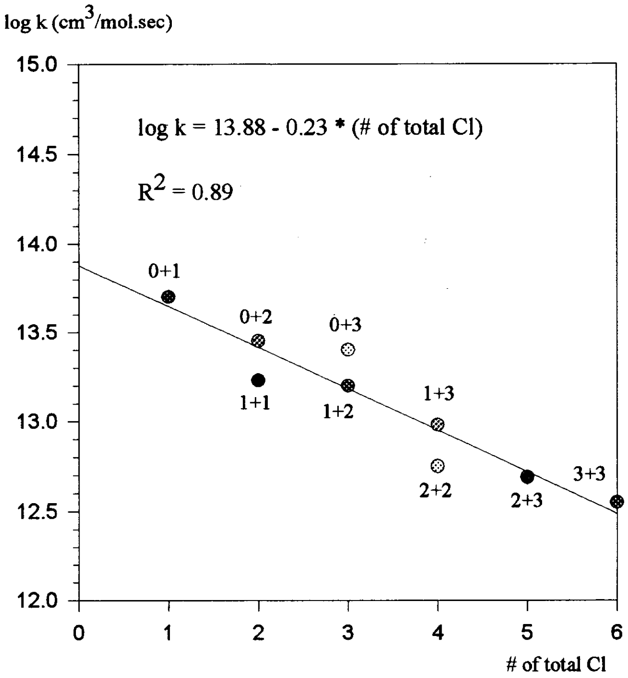


Figure 5.2 High-Pressure Limit Rate Constant for Association Reaction between Chloromethyl and Chloromethyl Radicals.

5.1.3 Conclusion for $C{\bullet}H_nX_{3-n}$ + $C{\bullet}H_nX_{3-n}$ Association

It is seen from Figure 5.2 that there is good linear relationship between rate constant and the number of Cl substitution in a chloromethyl combination reaction, the regression factor (R) is 0.943.

When the total number of Cl atoms in reactants is the same, the reaction which has a bigger difference in the charge of two combined central carbon atoms (no split) seems to be always faster, such as 0+2 is faster than 1+1, 0+3 is faster than 1+2, 1+3 is faster than 2+2.

Bimolecular rate constants of the association reactions are lower than 1.0E+14 and higher than 3.0E+12 $cm^3mol^{-1}sec^{-1}$.

The geometric mean rule of Garland and Bayes [101] is not used.

This trend which is shown in Figure 5.2 may be useful to estimate association reactions of heavier halo radicals.

5.2 Association Reaction of Chlorine Atom with Chloroalkyl Radicals

It is seen from Figure 5.1 that the C-Cl bond fission reaction is the second low energy channel for the dissociation of an ethyl chloride or vinyl chloride. It is slightly higher than the HCl molecular elimination channel. A compilation of the HCl elimination is summarized in an article about Cl_2 molecular elimination from CH_2ClCH_2Cl. [111]

5.2.1 Cl + Chloroalkyl Radical Reactions in the Literature

There have been a number of literature values for this type of reactions; they are summarized in Table 5.2.

Table 5.2 Rate Constants of Cl + Chloromethyl / Chloroethyl Association Reactions[a]

Reaction	k	Literature source (method)
$Cl + CH_3$	**1.54E+13**	[112]
	6.41E+13	[99]
$Cl + CH_2Cl$	**7.60E+13**	Calculated from reverse reaction [113]
$Cl + CCl_3$	**3.92E+13**	[107]
	3.01E+13	[114]
$Cl + C_2H_5$	**2.74E+14**	[112]
$Cl + C{\bullet}HClCCl_3$	**7.08E+13**	[115]
$Cl + C_2H_3$	**7.04E+13**	Calculated from reverse reaction [116]
$Cl + C{\bullet}H{=}CCl_2$	**1.74E+13**	Calculated from reverse reaction [117]
$Cl + C_2Cl_3$	**7.21E+11**	Calculated from reverse reaction [118]

a: values in bold are used to get trend.

Rate constants are taken from literature which have the same forward reaction or reverse reactions when forward is not available. Reverse reaction is used with <MR> to obtain the forward reaction. We assume Ea = 0 kcal/mol, although some literature show that this type of reaction has a slight negative barrier of ca. 0.6 kcal/mol.

5.2.2 Trend of Cl + Chloroalkyl Radicals

The relationship between the rate constant and the number of Cl substitution on the associated site in a chloroalkyl radical, is shown in Figure 5.3.

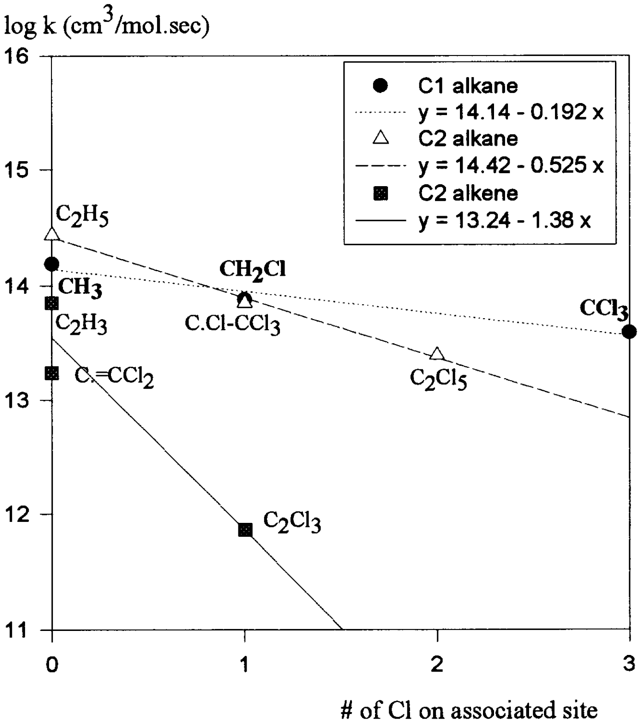


Figure 5.3 High-Pressure Limit Rate Constant for Association Reaction of Cl and Chloroalkyl Radicals.

5.2.3 Conclusion for Trend of Cl + R•

It is seen from Figure 5.3 that there is a linear relationship between rate constant and the number of Cl substitution on the associated site. The more Cl substitutes, the lower the association rate constant.

The Cl + R• Association rate constant for is $10^{14.14 - 0.192\times(\#\text{ of Cl in R}\bullet)}$ cm^3/mol.sec, when R• is a C1 alkane.

The Cl + R• Association rate constant for is $10^{14.42 - 0.525\times(\#\text{ of Cl on associated site})}$ cm^3/mol.sec, when R• is a C2 alkane.

The Cl + R• Association rate constant for is $10^{13.24 - 1.38\times(\#\text{ of Cl on associated site})}$ cm^3/mol.sec, when R• is a C2 alkene.

The trend shown in Figure 5.3 is useful in estimation of association reactions of Cl to heavier halo radicals.

5.3 Addition Reactions of Cl Atom to Chloroethylenes

This is another important type of reaction that occurs in the atmosphere and in combustion. The activation energy is usually low, close to zero. And the A factor is moderate, ~ 10^{13} cm^3/mol.sec. It is of importance to have an estimation for these addition rate constants of Cl + unsaturated alkyl hydrocarbons reactions, because these rate constants are relatively high; this is especially when building a relatively bigger mechanism where computational methods are expensive.

5.3.1 Cl + Vinyl Chloride Reactions in the Literature

There have been a number of literature values for this reaction, and these are summarized in Table 5.3. This type of reactions, from Cl + C_2H_3Cl to Cl + C_2Cl_4, is studied by Grosjean and Williams [119] and Atkinson and Aschmann [120] systematically.

Table 5.3 Rate Constants of Cl + Vinyl Chlorides Addition Reactions[a]

Reaction	k	A	Ea	Literature source
Cl + C_2H_4	6.38E+13	6.38E+13	0	[121]
	1.81E+14	1.81E+14	0	[122]
	1.84E+14	1.84E+14	0	[123]
Cl + C_2H_3Cl	**8.79E+13**	**8.79E+13**	0	[119]
	7.66E+13	**7.66E+13**	0	[120]
	9.27E+13	**9.27E+13**	0	[124]
	7.05E+13	7.05E+13	0	[125]
Cl + E-$C_2H_2Cl_2$	**5.61E+13**	**5.61E+13**	0	[119]
	5.77E+13	**5.77E+13**	0	[120]
Cl + Z-$C_2H_2Cl_2$	5.53E+13	5.53E+13	0	[119]
	5.78E+13	5.78E+13	0	[120]
Cl + $CH_2{=}CCl_2$	**5.92E+13**	**5.92E+13**	0	[119]
	8.43E+13	**8.43E+13**	0	[120]
	7.53E+13	**7.53E+13**	0	[125]
	3.16E+13	3.16E+13	0	[126]
Cl + C_2HCl_3	**4.24E+13**	**4.24E+13**	0	[119]
	4.86E+13	**4.86E+13**	0	[120]
	4.70E+13	**4.70E+13**	0	[125]
	3.47E+13	3.47E+13	0	[126]
Cl + C_2Cl_4	**3.56E+13**	**3.56E+13**	0	[119]
	2.49E+13	**2.49E+13**	0	[120]
	2.41E+13	(2.24E+16) × $T^{-1.2}$	0	[127]
	1.85E+13	5.89E+13	0.7	[128]
	3.16E+12	3.16E+12	0	[126]
average		6.30E+13	0	

a: values in bold are used to get trend.

It is assumed that Ea = 0 kcal/mol, although some literature show that this type of reaction has low barrier, -0.5 [129] to 0.7 kcal/mol. All values in the above table are collected in NIST Kinetics Database 2Q98.

5.3.2 Trend of Cl + Vinyl Chlorides

The relationship between the rate constant and the number of Cl substitution on the addition site in vinyl chloride, and shown in Figure 5.4.

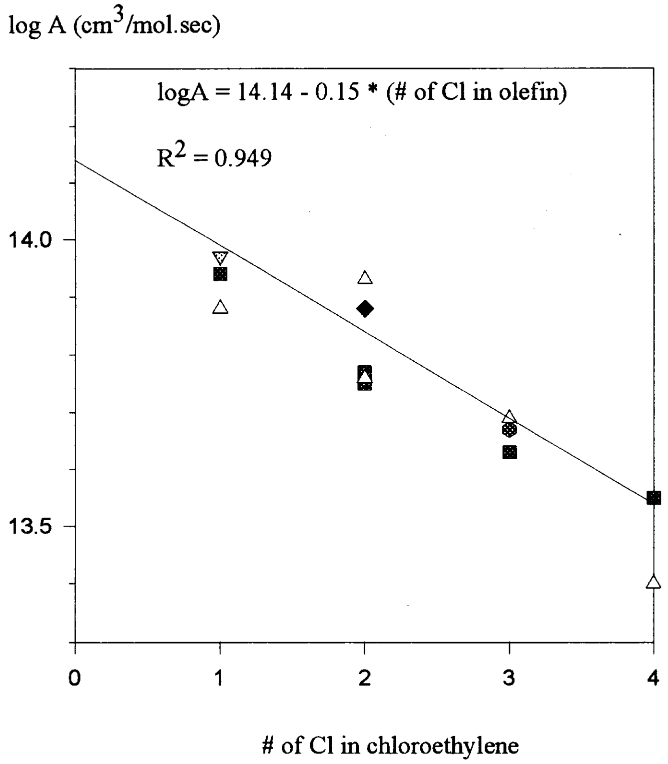


Figure 5.4 Chemically Activated Addition Reaction of Cl and Vinyl Chlorides.

5.3.3 Conclusion for Trend of Cl + Vinyl Chlorides

It is seen from Figure 5.4 that there is reasonable linear relationship between rate constant and the number of Cl substitution in an olefin with some scatter. The addition rate constants clearly decrease with the increasing of Cl substitute.

A factors for Cl addition to three types of central carbon atoms are derived as follows (Ea is assumed to be zero):

Cd/H_2 = CH_2CCl_2 – 0.5 × C_2Cl_4 = 4.14E+13 (92GRO/WIL [119])

= 0.5 × C_2H_4 = 3.19E+13 (87ATK/ASC [120])

Cd/Cl/H = 0.5 × CHClCHCl = 2.79E13 (92GRO/WIL [119])

= 2.89E13 (87ATK/ASC [120])

$Cd/Cl_2 = 0.5 \times C_2Cl_4$ = 1.78E13 (92GRO/WIL [119])
=1.25E13 (87ATK/ASC [120])

The trend shown in Figure 5.4 is useful in estimation of addition reactions of Cl to heavier halogenated unsaturated compounds.

5.4 A Few Types of Abstraction Reaction for Hydrohalocarbons

A few types of abstraction reaction will be investigated here.

5.4.1 $Cl + RX \rightarrow HCl + R\bullet X$

There has been a number of literature studies for this type of reactions. These data are summarized in Table 5.4.

The Evans-Polanyi relation says that there is a linear relationship between the activation energies and the enthalpies changes of reaction for one certain series of abstraction reactions. This relationship is plotted in Figure 5.4 for $Cl + RX \rightarrow HCl + R\bullet X$. All data in Table 5.4 are used.

Table 5.4 Literature Activation Energies of $Cl + RX \rightarrow HCl + R\bullet X$ Abstraction Reactions

Reaction	Ea (kcal/mol)	Literature source	ΔHrxn (kcal/mol)
$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$	2.484	[127]	-3.46
$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$	2.683	[127]	-4.720
$Cl + CHCl_3 \rightarrow HCl + CHCl_2$	2.464	[122]	-7.460
$Cl + C_2H_5Cl \rightarrow HCl + CH_3C\bullet HCl$	1.498	[130]	-5.740
$Cl + C_2H_5Cl \rightarrow HCl + C\bullet H_2CH_2Cl$	2.297	[131]	-1.860
$Cl + CH_2ClCH_2Cl \rightarrow HCl + C\bullet HClCH_2Cl$	2.160	[132]	-5.260
$Cl + CH_3CHCl_2 \rightarrow HCl + CH_3C\bullet Cl_2$	1.133	[131]	-9.800
$Cl + CH_3CHCl_2 \rightarrow HCl + C\bullet H_2CHCl_2$	3.603	[131]	0.300
$Cl + CH_3CCl_3 \rightarrow HCl + C\bullet H_2CCl_3$	3.557	[133]	-0.010
$Cl + CH_2ClCHCl_2 \rightarrow HCl + CH_2ClC\bullet Cl_2$	2.250	[131]	-8.380
$Cl + CH_2ClCHCl_2 \rightarrow HCl + C\bullet HClCHCl_2$	3.472	[131]	-4.500
$Cl + CHCl_2CHCl_2 \rightarrow HCl + CHCl_2C\bullet Cl_2$	2.448	[130]	-8.860
$Cl + CH_2ClCCl_3 \rightarrow HCl + C\bullet HClCCl_3$	2.448	[130]	-4.750
$Cl + C_2HCl_5 \rightarrow HCl + C_2Cl_5$	3.301	[105]	-7.190
$Cl + HCl \rightarrow Cl + HCl$	4.700	[134]	0.000

Cl + CH_3F → HCl + CH_2F	2.957	[131]	-1.860
Cl + $CHClF_2$ → HCl + $CClF_2$	4.829	[127]	-1.670
Cl + $CHCl_2F$ → HCl + $CFCl_2$	3.329	[135]	-4.560
Cl + CH_3CF_3 → HCl + $CH_2{\bullet}CF_3$	5.974	[136]	3.560
Cl + CH_3CHF_2 → HCl + $CH_3C{\bullet}F_2$	2.979	[137]	-3.650
Cl + CH_3CHF_2 → HCl + $C{\bullet}H_2CHF_2$	4.817	[138]	1.560
Cl + CH_3CH_2F → HCl + $CH_3C{\bullet}HF$	1.949	[137]	-3.150
Cl + CH_3CH_2F → HCl + $C{\bullet}H_2CH_2F$	2.943	[137]	-0.160
Cl + CHF_2CHF_2 → HCl + $C{\bullet}HFCHF_2$	4.829	[127]	-1.240
Cl + CH_2FCHF_2 → HCl + $C{\bullet}HFCHF_2$	4.747	[131]	-0.040
Cl + CH_2FCHF_2 → HCl + $CH_2FC{\bullet}F_2$	2.856	[131]	-2.540
Cl + CH_2FCH_2F → HCl + $CH_2FC{\bullet}HF$	2.490	[131]	-2.160
Cl + CH_2FCF_3 → HCl + $CH_2FC{\bullet}HF$	4.571	[139]	1.780

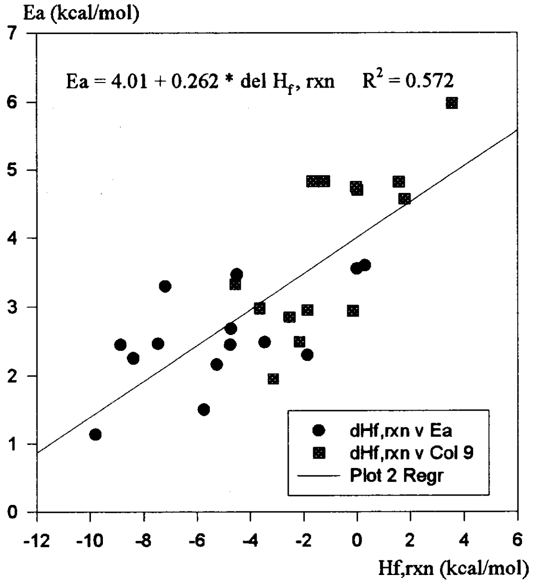


Figure 5.5 Evans-Polanyi Relation for Cl + RX → HCl + R•X Abstraction Reactions.

5.4.2 Cl + R → HCl + R•

There has been a number of literature values for this type of reactions, and are summarized in Table 5.5.

Table 5.5 Literature Activation Energies of Cl + RH → HCl + R•X Abstraction Reactions

Reaction	Ea (kcal/mol)	Literature source	ΔHrxn (kcal/mol)
$Cl + CH_4 \rightarrow HCl + CH_3$	0.765	[140]	1.590
$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	0.189	[122]	-1.750
$Cl + n\text{-}C_3H_8 \rightarrow HCl + n\text{-}C_3H_7$	0.421	[138]	-5.140
$Cl + i\text{-}C_3H_8 \rightarrow HCl + i\text{-}C_3H_7$	0.171	[138]	-5.010
$Cl + n\text{-}C_4H_{10} \rightarrow HCl + n\text{-}C_4H_9$	0.799	[141]	-5.410
$Cl + n\text{-}C_4H_{10} \rightarrow HCl + sec\text{-}C_4H_9$	0.298	[141]	-8.130
$Cl + i\text{-}C_4H_{10} \rightarrow HCl + i\text{-}C_4H_9$	0.580	[136]	-5.610
$Cl + i\text{-}C_4H_{10} \rightarrow HCl + t\text{-}C_4H_9$	0.020	[142]	-6.880
$Cl + neo\text{-}C_5H_{12} \rightarrow HCl + (CH_3)_3CC{\bullet}H_2$	0.070	[143]	-9.250
$Cl + n\text{-}C_3H_6 \rightarrow HCl + C{\bullet}H_2CH{=}CH_2$	0.179	[144]	-14.860

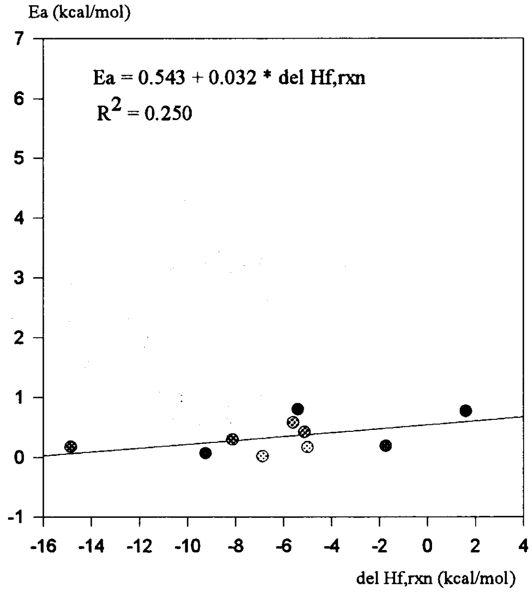


Figure 5.6 Evans-Polanyi Relation for Cl + R → HCl + R• Abstraction Reactions (Hydrocarons Only).

The Evans-Polanyi relationship is plotted in Figure 5.6 for Cl + R → HCl + R•. All data in Table 5.5 are used.

5.4.3 H + RCl → HCl + R• (or R•X)

There also have been a number of literature values for this type of reactions, and are summarized in Table 5.6.

Table 5.6 Literature Activation Energies of H + RCl → HCl + R• (or R•X) Abstraction Reactions

Reaction	Ea (kcal/mol)	Literature source	ΔHrxn (kcal/mol)
$H + Cl_2 \rightarrow HCl + Cl$	1.172	[145]	-45.170
$H + CH_3Cl \rightarrow HCl + CH_3$	9.300	[146]	-19.490
$H + CH_2Cl_2 \rightarrow HCl + CH_2Cl$	6.099	[147]	-23.340
$H + CF_3Cl \rightarrow HCl + CF_3$	8.795	[148]	-26.150
$H + C_2H_3Cl \rightarrow HCl + C_2H_3$	9.298	[149]	-7.600
$H + C_2Cl_4 \rightarrow HCl + C_2Cl_3$	8.404	[150]	-20.110

The Evans-Polanyi relationship is plotted in Figure 5.7 for H + RCl → HCl + R• (or R•X). All data in Table 5.6 are used.

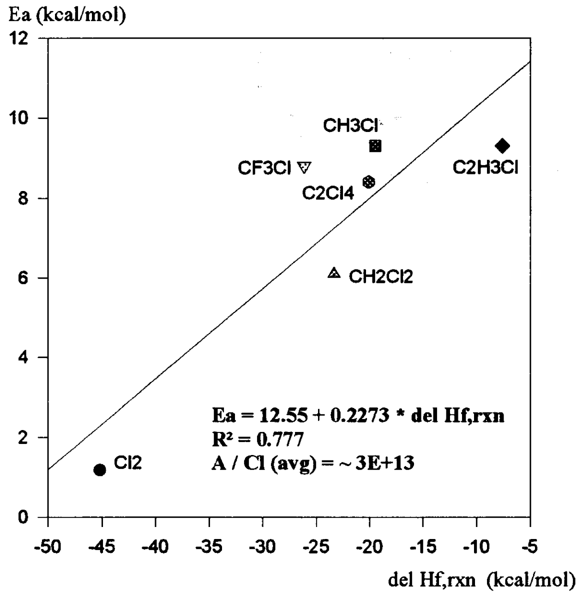


Figure 5.7 Evans-Polanyi Relation for H + RCl → HCl + R• (or R•X) Abstraction Reactions.

CHAPTER 6

CHLOROFORM PYROLYSIS AND OXIDATION: EFFECTS OF ADDED O_2

6.1 Overview

Hazardous waste incineration involving chlorine compounds merits attention because the behavior of chlorine is unique among the halogenated compounds. Organic chlorine compounds serve as a source of chlorine atoms, because the C—Cl bond is about 20 kcal/mol weaker than C—H bonds and 10 kcal/mol weaker than C—C bonds. Chlorine atoms readily abstract H atoms from other organic hydrocarbons accelerating the onset reactions. Chlorine, as HCl, can inhibit the initial stages of combustion through reactions like $OH + HCl \rightarrow H_2O + Cl$, which depletes OH needed for CO burnout. [151]

The mechanism for the pyrolysis and oxidation of $CHCl_3$ is investigated and the effects of concentration of O_2 in the system are also discussed. Four paths for chloroform initial decomposition are:

$CHCl_3 \rightarrow {}^1CCl_2 + HCl$ $\Delta H_{rxn,298} = 56.78$ kcal/mol (a)

$CHCl_3 \rightarrow CHCl_2 + Cl$ $\Delta H_{rxn,298} = 74.29$ (b)

$CHCl_3 \rightarrow CCl_3 + H$ $\Delta H_{rxn,298} = 93.78$ (c)

$CHCl_3 \rightarrow {}^1CHCl + Cl_2$ $\Delta H_{rxn,298} = 100.57$ (d)

A number of researchers have considered the pathways of chloroform decomposition. Semeluk and Bernstein [152,153] investigated the decomposition kinetics of chloroform where they estimated a 72 kcal/mol upper limit for the activation energy of $CHCl_3 \rightarrow CHCl_2 + Cl$. Shilov and Sabirova measured the rate constant for $CHCl_3 \rightarrow CCl_2 + HCl$ as $2.6\times10^{11}\exp(-47 \text{ kcal mol}^{-1}/RT)\ s^{-1}$ in 1957. [154] Schug et al. [155] point out that the molecular elimination of HCl is the dominant path of $CHCl_3$ pyrolysis, and the high pressure limit rate constant is determined to be $1.82\times10^{14}\exp(-54.5 \text{ kcal mol}^{-1} / RT) \text{ s}^{-1}$. A recent study by Kumaran et al. [156] report the rate constant $k_1 = 3.98\times10^{16}\exp(-44.7 \text{ kcal mol}^{-1} / RT) \text{ s}^{-1}$ based on their study on the thermal decomposition of $CHCl_3$ in Kr bath at T = 1282 – 1878 K. Their experimental results agree with RRKM theory calculations provided $Ea_1(0 \text{ K}) = 56$ kcal/mol, suggesting that the barrier for back reaction at 0 K is 3.8 kcal/mol.

Benson and Spokes [157] favor an Arrhenius A factor of $5.0\times10^{13} \text{ s}^{-1}$ with an Ea greater than 56 kcal/mol for HCl elimination from chloroform which is studied in a very low-pressure pyrolysis reaction. They also reported that when oxygen was added to reaction system, the products yielded a pair of mass peaks at 63 and 65 amu, possibly due to COCl from phosgene, CCl_2O, which is an expected product from the reaction of dichlorocarbene with O_2: $CCl_2 + O_2 \rightarrow CCl_2O + O$. The photolysis experiments on chloroform by Herman *et al.* [158] examined the pulsed CO_2 laser (11 μm) multiple-photon dissociation of deuterated chloroform ($CDCl_3$) in a molecular beam. The only observed dissociation pathway was hydrogen chloride (DCl) elimination (>99.1%), with no evidence of simple chloride atom cleavage (<0.9%).

The reaction of chloroform in hydrogen and water vapor has been studied in the temperature range 550 – 1200°C by Chuang and Bozzelli. [159] The major products of chloroform pyrolysis in H_2 at temperatures above 1100°C were HCl, C(s) and CH_4. The most stable chlorocarbon products observed were chloromethane and C_2H_3Cl for the reaction of chloroform with excess hydrogen. This study also demonstrated that selective formation of HCl can result from thermal reaction of chloroform under an atmosphere of hydrogen.

The experiments which will be modeled in this study have been previously described in detail. [160] and are only summarized here. The thermal reactions of $CHCl_3$ in both oxidative and pyrolytic reaction environments were studied in a tubular flow reactor at 1 atm pressure (Ar bath). The thermal decompositions of three reactant ratio sets were studied to determine important chlorocarbon reaction pathways before initiating development of the detailed reaction mechanism. Each reaction ratio set is studied at 8 temperatures: 808, 828, 848, 873, 908, 958, 1008, 1073 K.

Condition 1: $CHCl_3 : Ar = 1 : 99$,

Condition 2: $CHCl_3 : O_2 : Ar = 1 : 1 : 98$,

Condition 3: $CHCl_3 : O_2 : Ar = 1 : 3 : 96$.

Small amounts of O_2 (0 – 3%) were added to the $CHCl_3$/Ar flow. A quartz reactor tube, 10.5 mm ID, was housed within a three-zone electric tube furnace 46 cm length. Temperature profiles were obtained using a type K thermocouple probe moved coaxially within the reactor under representative flows. The reactor effluent stream was analyzed by an on-line gas chromatograph with flame ionization detector (FID). A catalytic converter was employed to increase the accuracy of quantitative analysis for CO and CO_2. The 5% ruthenium on alumina (30/40 mesh) at 315°C was used to catalyze CO and CO_2 reduction to CH_4 with H_2 (10 ml/min).

Quantitative analysis of HCl was performed for each run; reactor effluent was diverted through a dual bubbler train containing 0.01 M NaOH before being exhausted to a fume hood. The HCl was then calculated based upon titration of the combined bubbler solutions with 0.01 M HCl to the phenolphthalein endpoint. The NaOH solution also collected CO_2 and the CO_2/FID results were used to correct for this.

The study of chloroform pyrolysis and an elementary mechanism were reported by Won and Bozzelli, [160] where the enthalpy value, $\Delta_f H°_{298}(^1CCl_2) = 39$ kcal/mol, adapted from the work by Lias *et al.* [161] is used. This research group has since learned that the accurate value of $\Delta_f H°_{298}(^1CCl_2)$ is 54.33 kcal/mol [162]. A revised mechanism for both pyrolysis and oxidation is therefore required. This new mechanism has several major changes: (1) Reactions for $^1CCl_2$ are all re-evaluated; (2) Thermochemical properties for some oxychloro hydrocarbons are computed by density functional calculation; (3) Some important rate constants, such as $CHCl_3 \rightarrow CCl_2 + HCl$, $CHCl_3 + HCl \rightarrow C_2HCl_5$, $C_2HCl_5 \rightarrow C_2Cl_4 + HCl$, and $CCl_3OO \rightarrow CCl_2O + ClO$, are calculated at various levels of theory; (4) The chemical activated reactions for recombination, abstraction, and addition are of particular importance, such as $CCl_3 + CHCl_2$, $CCl_3 + Cl$, $CHCl_3 + Cl$, $C_2Cl_4 + Cl$. These chemical activated reactions are recalculated using trends in rate constants of chlorocarbons (more detail will be shown).

The variations in chloroform decay rates and product distributions in presence and absence of added oxygen, but with no added hydrogen fuel source, are the focuses in the present study. Future research will incorporate H_2O, H_2, CH_4 and supplemental hydrogen sources, which are most important to obtain quantitative HCl formation as well as application to actual incineration conditions.

6.2 Calculations Methods for Kinetic Modeling

6.2.1 Thermochemical Properties

The dissociation and recombination reactions and subsequent unimolecular isomerization or dissociation or addition reactions are first analyzed by construction of potential energy diagrams for the systems based on existing experimental data, theoretical calculations with isodesmic work reactions, or group additivity estimation techniques. Enthalpies of formation of radicals are either calculated from density functional theory or are adopted from evaluated literature on C-H and C-Cl bond energies and ($\Delta_f H°_{298}$ of the stable molecule that corresponds to the radical with a H atom at the radical site. Entropies and heat capacities values are from use of Hydrogen Bond Increments (HBI). [163]

Thermochemical parameters for all species in this study are listed in Table 6.1. Thermochemical data are required to determine the energy balance in chemical reactions and in determining the Gibbs Free Energy of a reaction as a function of temperature. The thermochemicals also provide a convenient way to determine reverse reaction rate constants from the calculated equilibrium constant of the reaction and the known forward rate [164] and play a very important role in determination of rate constants (A factors and activation energies).

"THERM" in Table 6.1 means that these thermochemical parameters are estimated using Group Additivity [68] incorporated in "THERM" computer code. [19,165] The groups in THERM, including interaction groups [166] and HBI groups [163] for radicals database are either form literature [68,77] or from *ab initio* or density functional calculations on respective species. [29-31,33-35]

Table 6.1 Thermochemical Properties ($\Delta_f H^\circ_{298}$ in kcal/mol, S°_{298} and Cp° in cal/mol.K)

SPECIES	$\Delta_f H^\circ_{298}$	S°_{298}	Cp° (K)							Note
			300	400	500	600	800	1000	1500	
$CHCl_3$	-24.52	70.66	15.76	17.83	19.34	20.44	21.91	22.86	24.20	[54], [62]
C_2Cl_4	-5.78	81.48	22.71	25.09	26.71	27.84	29.26	30.05	30.96	[54] and DFT calc.[a]
CO	-26.42	47.21	6.97	7.01	7.12	7.28	7.62	7.93	8.42	[46]
CCl_4	-22.85	74.09	19.96	21.94	23.12	23.83	24.62	25.10	25.50	[54], [41]
HCl	-22.07	44.60	6.89	6.95	7.03	7.12	7.32	7.54	8.06	[62]
CO_2	-94.05	51.07	8.90	9.88	10.67	11.31	12.29	12.98	13.95	[46]
C_2Cl_2	53.89	65.92	15.96	16.88	17.53	18.03	18.76	19.28	20.01	[167]
C_2HCl_5	-37.26	91.25	28.25	31.99	34.55	36.38	38.75	40.21	42.03	[39], [168]
C_2Cl_3	54.37	78.31	18.62	20.45	21.69	22.57	23.70	24.35	25.11	[43] + DFT calc.[a]
C_2HCl_3	-4.18	77.73	19.24	21.80	23.68	25.07	26.95	28.16	29.83	[39], [168]
$CHCl_2CCl_2$	4.64	90.65	23.88	26.74	28.78	30.23	32.15	33.31	34.89	[39] [169] [41]
C_2Cl_6	-35.42	95.33	32.76	36.22	38.39	39.80	41.55	42.13	43.25	[39] [168]
H	52.10	27.39	4.97	4.97	4.97	4.97	4.97	4.97	4.97	[46]
O	59.56	38.47	5.24	5.14	5.08	5.05	5.02	5.00	4.98	[46]
OH	8.89	43.88	7.17	7.08	7.06	7.06	7.15	7.33	7.87	[170] [46]
O_2	0.00	49.00	7.02	7.20	7.43	7.67	8.06	8.34	8.74	[46]
HO_2	5.00	54.38	8.35	8.91	9.48	9.98	10.77	11.37	12.35	[46]
H_2O	-57.80	45.11	8.03	8.19	8.42	8.68	9.25	9.85	11.23	[46]
H_2O_2	-32.53	55.66	10.33	11.58	12.56	13.31	14.30	15.02	16.33	[46]
H_2	0.00	31.21	6.89	6.98	6.99	7.01	7.09	7.22	7.72	[46]
Cl	28.99	39.48	5.22	5.36	5.43	5.44	5.38	5.31	5.17	[41]
Cl_2	0.00	53.29	8.12	8.44	8.62	8.74	8.88	8.96	9.07	[46]
CH_2Cl_2	-22.73	64.63	12.23	14.20	15.90	17.31	19.33	20.73	22.92	[39] [168]
CH_2Cl	27.07	57.08	9.04	10.00	10.84	11.55	12.70	13.62	15.24	Chap 2
$CHCl_2$	20.82	64.98	11.03	12.20	13.10	13.77	14.71	15.37	16.38	Chap 2
CCl_3	17.20	70.92	15.25	16.66	17.56	18.16	18.83	19.18	19.56	Chap 2, [46]
$^1CCl_2$	54.33	63.51	11.21	12.09	12.63	12.97	13.35	13.54	13.74	[162] DFT calc.[a]
HOCl	-17.80	56.50	8.90	9.50	10.10	10.50	11.10	11.60	12.40	[68]
ClO	24.34	54.21	7.37	7.72	8.05	8.29	8.54	8.70	8.90	[41]
ClOO	23.00	63.00	11.60	12.10	12.70	13.10	14.00	14.60	15.70	[68]
ClOCl	21.00	64.02	11.45	12.28	12.78	13.09	13.42	13.59	13.77	[46]
$CHCl_2CHCl_2$	-37.45	84.86	23.62	27.62	33.42	37.69	37.41	36.55	41.18	[39] [168]
$CHCl_2CHCl$	10.90	84.50	21.47	24.55	26.86	28.54	30.57	32.00	34.02	[39] [169] [41]
C_2Cl_5	6.39	95.83	27.16	30.18	32.05	33.17	34.35	35.36	35.97	[39] [169] [41]
C_2HCl	53.80	57.79	12.95	14.33	15.23	15.89	16.88	17.64	18.90	[167]
$CHCCl_2$	59.60	68.39	15.88	18.03	19.48	20.50	21.88	22.79	24.10	THERM
CH_2ClCCl_2O	-28.19	83.39	25.15	29.48	32.62	34.74	37.11	38.29		THERM
CHClCCl	52.68	71.80	15.08	16.93	18.39	19.53	21.14	22.26	23.85	THERM
CHO	10.40	53.69	8.27	8.70	9.18	9.66	10.52	11.22	12.34	[46]
CHClO	-38.48	61.96	10.70	12.01	13.12	14.04	15.45	16.46	17.94	[47] + DFT calc.[a]
CClO	-6.48	63.54	10.78	11.30	11.69	12.02	12.54	12.91	13.39	[43] [46]
$^3CCl_2OO$	38.70	84.13	19.94	21.23	21.80	21.93	22.33	22.59		DFT[b] + THERM
$CHCl_2OCl$	-26.14	81.04	21.18	23.25	24.56	25.49	26.78	27.60	28.68	[33]
$CHClOCCl_2$	16.91	87.93	24.29	27.25	29.36	30.68	32.63	33.46		THERM
CCl_2CCl_2O	9.82	90.59	27.64	31.41	34.01	35.48	36.98	37.45		THERM
CCl_2O	-50.07	67.79	13.86	15.31	16.27	16.97	17.89	18.46	19.16	[42] and DFT calc.[a]
$CHCl_2O$	-7.65	72.17	15.58	17.71	19.27	20.40	21.93	22.90	24.23	[29]
CCl_3O	-9.05	79.03	19.80	21.65	22.80	23.56	24.44	24.90	25.40	[29]
$CHCl_2OH$	-65.88	71.00	16.91	20.21	22.55	24.03	25.64	26.55	28.04	[29]
CHClOH	-14.46	65.72	13.88	16.40	18.03	19.00	20.07	20.80	22.16	[29]
$CHCl_2OO$	-8.61	83.38	20.17	22.30	23.56	24.38	25.54	26.43	27.90	Calc. from [29]
$CHCl_2OOH$	-44.74	83.03	22.13	25.09	27.08	28.45	30.25	31.39	32.97	[29]

CCl_2OH	-22.54	74.64	16.66	18.24	19.33	20.13	21.20	21.91	23.01	[29]
CCl_2OOH	-3.71	85.29	21.99	24.07	25.35	26.02	27.05	27.56	0.00	Calc. from [29]
CCl_3OH	-65.96	77.43	20.64	22.95	24.47	25.51	26.84	27.67	28.90	[30]
CCl_3OO	-5.00	83.00	22.89	25.05	26.47	27.51	28.81	29.65		[171] + THERM
CCl_3OOH	-45.63	86.91	24.89	27.75	29.68	30.99	32.52	33.27	34.04	[29]
$CHClCCl_2OH$	-35.65	86.86	26.71	30.49	33.33	34.83	36.69	37.56		THERM
$CHClCClOH$	-43.40	76.06	21.42	24.32	26.25	27.64	29.64	31.05	33.28	[35]
$CHClCHCl$	-0.12	69.30	15.98	18.52	20.60	22.27	24.60	26.19	28.55	[39] [168]
CCl_2CCl_2OH	-42.14	92.05	28.62	32.71	35.62	37.37	39.36	40.25		THERM
C_2Cl_3OH	-44.03	82.84	24.66	26.99	28.65	29.91	31.64	32.78	34.42	[35]
CCl_2CClO	-24.26	83.02	21.85	24.26	25.96	27.20	28.79	29.71	30.78	[111]
CCl_2CO	-5.73	74.15	17.55	19.31	20.56	21.50	22.80	23.63	24.69	DFT^b
$CHCl_2CCl_2O$	-31.18	89.84	27.87	32.48	35.77	37.93	40.19	41.29	41.67	THERM
$CHCl_2CClO$	-57.70	87.07	21.85	24.70	26.78	28.32	30.41	31.74	33.56	[111]
Ar	0.00	37.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	[68]
$Cl_2C{*}CClOO$	13.68	90.85	26.48	29.71	31.80	33.11	34.46	35.04	35.53	DFT^b
$Cl_2C{*}CClO.$	-10.78	85.26	22.32	23.51	24.21	25.30	26.73	27.73		THERM
CCl_3OCl	-26.72	85.37	23.54	25.99	27.54	28.52	29.53	29.91	30.07	[33]
$CHClCCl_3$	13.94	88.26	25.57	28.51	30.38	31.62	33.13	34.03	35.25	[39] [169] [41]
$Cl_2C.COOCl$	25.42	97.92	27.07	30.52	32.53	34.49	36.22	36.71		THERM
$Cl_2CCOClO.$	-10.57	94.14	26.61	30.78	32.74	34.88	36.67	37.36		THERM
$O{*}CC{*}O$	-80.25	82.12	24.43	25.69	26.65	27.42	28.67	29.50		[41]
$Cl_2C.OCClO$	-81.49	95.40	25.37	28.10	29.99	31.28	33.33	34.38		THERM
$CO.Cl_2CClO$	-48.89	90.70	25.69	29.27	30.95	32.09	33.68	34.31		THERM
CH_2O	-25.94	52.29	8.49	9.38	10.44	11.51	13.39	14.80	17.05	[41]
$C.HClOOCl$	13.66	84.93	18.32	20.45	22.24	23.06	25.02	28.11		THERM
CCl_3CClOH	-27.06	92.43	27.25	29.45	31.31	32.68	34.95	36.40		THERM
CCl_3CClO	-57.31	90.58	26.27	28.89	30.56	31.69	33.10	33.92	34.86	[43] [111]
$CCl_2CHClOH$	-30.04	87.77	23.01	25.44	27.64	29.4	32.41	34.4		THERM
$CCl_2CHClO.$	-19.08	85.56	22.26	25.21	27.79	29.96	33.24	35.44		THERM
$CCl_2C.OHCl$	-26.54	89.03	23.82	26.22	28.50	30.05	32.82	34.71		THERM
$CCl_3C.HOH$	-25.44	88.31	26.40	30.14	32.57	34.21	36.36	37.38		THERM
$CHCl_2CHO$	-44.93	79.17	20.98	23.33	25.17	26.67	28.95	30.56	32.88	[111]
CCl_3CHO	-45.52	83.82	23.43	26.12	28.04	29.46	31.40	32.61	34.17	[111]
CCl_2CHOH	-40.51	75.01	19.93	23.63	26.44	28.44	30.77	32.06	33.85	[35]
$CHCl_2CClOH$	-30.04	89.15	23.01	25.44	27.64	29.40	32.41	34.40		THERM
$CH_2ClCClO$	-58.70	79.67	20.92	23.26	24.86	26.16	28.25	29.83	32.31	[111]
^1CHCl	76.05	56.19	8.83	9.50	10.07	10.54	11.28	11.83	12.70	[162] DFT calc.^{a}
$ClOCO$	-1.82	68.84	9.83	10.75	11.56	12.24	13.29	13.99	14.91	b
$CHCl_3 \rightarrow {}^1CCl_2 + HCl$										
TS-a1	33.42	76.71	15.36	17.09	18.48	19.55	21.00	21.85	22.87	G3
TS-a2	31.90	76.09	15.73	17.60	19.03	20.09	21.45	22.21	23.07	G3//MP2/6-311G(d,p)
TS-a3	31.21	77.13	16.14	18.17	19.64	20.65	21.87	22.52	23.23	G3//B3LYP/6-311G(d,p)
$CHCl_3 \rightarrow {}^1CHCl + Cl_2$ (b)										
TS-b	82.76	78.82	16.83	18.19	19.17	19.88	20.87	21.55	22.54	CBSQ//B3LYP/6-31G(d,p)
$^1CCl_2 + CHCl_3 \rightarrow C_2HCl_5$ (c)										
TS-c	40.10	102.92	29.54	32.53	34.55	25.99	27.84	38.96	40.33	CBSQ//B3LYP/6-31G(d,p)
$C_2HCl_5 \rightarrow C_2Cl_4 + HCl$ (d)										
TS-d	25.42	95.78	28.11	31.29	33.60	35.29	37.49	38.77	40.28	CBSQ//B3LYP/6-31G(d,p)
$CCl_4 \rightarrow {}^1CCl_2 + Cl_2$ (e)										
TS-e	105.81	87.76	20.46	21.57	22.25	22.58	23.15	23.39	23.64	CBSQ//B3LYP/6-31G(d,p)
$^1CCl_2 + {}^3O_2 \rightarrow {}^3C.Cl_2OO.$ (f)										
TS-f	59.45	82.36	18.53	19.87	20.79	21.46	22.30	22.78	23.33	B3LYP/6-31G(d,p)
$CCl_3OO. \rightarrow CCl_2O + ClO$ (h)										
TS-h	29.62	83.12	21.67	23.88	25.37	26.41	27.68	28.37	29.13	B3LYP/6-31G(d,p)

$CHCl_2OH \rightarrow CHClO + HCl$ (i)

TS-i	-28.13	71.22	15.48	17.74	19.57	21.03	23.20	24.70	26.91	CBSQ//B3LYP/6-31G(d,p)

a: From freq at B3LYP/6-31G(d,p) using SMCPS [48];

b: See Table 6.3;

c: Personal Communication with Prof. Louis for $\Delta_f H$ and S, plus Cp's from MOPAC6/PM3.

Table 6.2 Total Energies at 298 K[a]

	B3LYP/ 6-31G(d,p)	B3LYP/6-311+G(3df,2p)	QCISD(t)/ 6-31+G(d')	CBS-Q	ZPVE[b,c]	H_{298}-H_0[c]
Species	// B3LYP/6-31G(d,p)					
$^3O_2$	-150.31303	-150.37229	-149.97821	-150.16039	2.33	2.08
HCl	-460.79088	-460.82847	-460.20395	-460.34379	4.14	2.07
ClO	-535.28703	-535.35886	-534.54799	-534.76645	1.17	2.12
Cl_2	-920.34526	-920.41945	-919.20513	-919.45598	0.73	2.21
^1CHCl	-498.74738	-498.79891	-498.06919	-498.24212	6.88	2.43
$^1CCl_2$	-958.37477	-958.45962	-957.14528	-957.425	2.46	2.75
$^3CCl_2$	-958.34797	-958.43218	-957.11436	-957.39220	2.71	2.74
CH_3	-39.80968	-39.82454	-39.68299	-39.74016	18.30	2.54
CH_4	-40.47606	-40.48879	-40.34161	-40.40530	27.70	2.39
$CH_3OO.$	-190.17221	-190.24445	-189.68457	-189.95320	26.48	3.01
CH_3OOH	-190.79737	-190.87333	-190.29379	-190.58722	33.68	3.30
CHClO	-574.09540				11.81	2.63
$CHCl_3$	-1419.25545	-1419.37254	-1417.44351	-1417.86388	12.23	3.40
CCl_4	-1878.83854	-1878.99192	-1876.48155	-1877.01446	5.73	4.13
CCl_2O	-1033.69918	-1033.81401			6.46	3.07
$^1C.Cl_2OO.$	-1108.74345	-1108.89043	-1107.17625	-1107.65159	8.15	3.71
$^3C.Cl_2OO.$	-1108.71284	-1108.85389	-1107.13938	-1107.61012	7.04	3.94
$CCl_3OO.$	-1568.94997	-1569.12518			8.72	4.63
CCl_3OOH	1569.58684	-1569.76483		-1568.05909	16.23	4.90
C_2H_4	-78.53969	-78.56698	-78.27555	-78.41162	31.46	2.50
CH_2=CCl_2	-997.74030	-997.83537	-996.37542	-996.72964	20.72	3.28
C_2HCl_3	-1457.33659	-1457.46580	-1455.42223	-1455.88545	15.27	3.96
C_2Cl_3	-1456.66474	-1456.79511			7.59	4.00
C_2Cl_4	-1916.92692	-1917.09164	-1914.46518	-1914.44467	9.43	4.67
$CHCl_2OH$	-1034.91935	-1035.03410	-1033.48138	-1033.86521	20.96	3.40
CH_2=C=O	-152.56648	-152.62680			19.49	2.81
CCl_2=C=O	-1071.73924	-1071.86722			9.46	3.80
C_2H_3OOH	-228.87622	-228.96480			36.57	3.73
CCl_2=CClOO•	-1607.03177	-1607.21968			12.31	5.23
C_2Cl_3OOH	-1607.66671	-1607.85684			19.54	5.58
C_2HCl_5	-2377.72654	-2377.92453	-2374.69475	-2375.40569	17.62	5.61
TS-b	-1419.08864	-1419.21412	-1417.26424	-1417.69263	8.97	3.97
TS-c	-2377.61100	-2377.81172	-2374.57056	-2375.28240	13.36	6.24
TS-d	-2377.64579	-2377.84627	-2374.59285	-2375.30580	14.28	5.86
TS-e	-1878.66851	-1878.82106	-1876.28139	-1876.80943	3.67	4.75
TS-f	-1108.68341	-1108.82418	-1107.10871	-1107.57769	5.66	4.25
TS-g	-1108.62880	-1108.77284	-1107.07345	-1107.53852	5.43	4.46

TS-h	-1568.89355	-1569.07001	-1566.74828	-1567.34341	8.29	4.49
TS-i	-1034.83596	-1034.95099	-1033.38710	-1033.80505	18.39	3.35
Species	G3	G3//MP2/6-311G(d,p)	G3//B3LYP/6-311G(d,p)			
$CHCl_3$	-1418.82321	-1418.82333	-1418.82292			
TS-a	-1418.73088	-1418.73341	-1418.73410			
$^{1}CCl_2$	-958.08118	-958.08110	-958.08066			
HCl	-460.65121	-460.65110	-460.65123			

a: All calculations are based on B3LYP/6-31G(d,p) optimized structures;

b: Total energies (ZPVE and thermal corrections are included) in hartree, 1 hartree = 627.51 kcal/mol;

c: Scaled by 0.9806; [37]

d: In units of kcal/mol.

Table 6.3 Calculated $\Delta_f H^\circ_{298}$ (kcal/mol) Using Isodesmic Reactions ^{a,b}

Isodesmic Reactions	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	QCISD(T)/6-31+G(d')	CBS-Q	use
	//B3LYP/6-31G(d,p)				
$^{1}C{\bullet}Cl_2OO{\bullet}$ + $CH_4 \rightarrow CH_3OOH + {}^{1}CCl_2$	10.64	11.32	9.53	12.61	
$^{1}C{\bullet}Cl_2OO{\bullet}$ + $CH_3 \rightarrow CH_3OO{\bullet} + {}^{1}CCl_2$	17.81	14.81	15.36	13.44	13.02
$^{3}C{\bullet}Cl_2OO{\bullet}$ + $CH_4 \rightarrow CH_3OOH + {}^{1}CCl_2$	29.85	34.26	32.66	38.64	38.64
$CCl_2{=}C{=}O$ + $C_2H_4 \rightarrow CH_2{=}C{=}O + CH_2{=}CCl_2$	-5.82	-5.75			
$CCl_2{=}C{=}O$ + $CH_2{=}CCl_2 \rightarrow CH_2{=}C{=}O + C_2Cl_4$	-7.75	-6.50			-6.13
$CCl_2{=}CClOOH$ + $C_2H_4 \rightarrow C_2H_3OOH + C_2HCl_3$	-22.33	-22.10			
$CCl_2{=}CClOOH$ + $C_2H_3Cl \rightarrow C_2H_3OOH + C_2Cl_4$	-25.28	-23.59			
$CCl_2{=}CClOOH$ + $CH_3OOH \rightarrow C_2H_3OOH + CCl_3OOH$	-24.12	-23.82			-23.17
$CCl_2{=}CClOO{\bullet}$ + $CCl_3OOH \rightarrow CCl_2{=}CClOOH + CCl_3OO{\bullet}$	-16.24	-15.89			-15.89

a: $\Delta_f H^\circ_{298}$ of CH_3OOH, CH_3OO, CCl_3OOH, and CCl_3OO are from [29];
b: $\Delta_f H^\circ_{298}$ of C_2H_3OOH is from [172];

"Calc" in Table 6.1 means that the thermochemical parameters are calculated in this work using isodesmic reactions for $\Delta_f H^\circ_{298}$ and "SMCPS" [48] for S°_{298} and Cp° and computational chemistry techniques. The total energies calculated at various levels of theory for using in the isodesmic reactions are listed in Table 6.2. The obtained $\Delta_f H^\circ_{298}$ for $CCl_2{=}C{=}O$, $^{3}C{\bullet}Cl_2OO{\bullet}$, and $C_2Cl_3OO{\bullet}$, from isodesmic reactions are shown in Table

6.3. The average values form CBS-Q//B3LYP/6-31G(d,p) or B3LYP/6-311+G(3df,2p) // B3LYP/6-31G(d,p) calculations are used, which are considered as high level computations and give accurate results as noted in referenced - published journal manuscripts of this author.

The "SMCPS" computer program uses the rigid-rotor-harmonic-oscillator approximation from the frequencies along with moments of inertia. The $S°_{298}$ and $Cp°(T)$ are calculated from this "SMCPS" code which uses the rigid-rotor-harmonic-oscillator approximation from the frequencies along with moments of inertia, or from "THERM" when internal rotation is exist.

6.2.2 Quantum Rice-Ramsperger-Kassel (QRRK) Kinetic Analysis

The C_2 species (C_2Cl_4, C_2Cl_6, C_2HCl_3, C_2HCl_5, C_2Cl_2, etc.) observed in this reaction system are formed as a consequence of C_1 radicals ($CHCl_2$, CCl_3 and $^1CCl_2$) which undergo combination and insertion processes which lead to formation of chemically activated adducts. The reaction versus stabilization of these adducts are strongly pressure- and temperature-dependent. Quantum Rice-Ramsperger-Kassel (QRRK) statistical analysis [13] is used to analyze the rate constants as a function of pressure and temperature for chemically activated reactions, and unimolecular reactions.

Lennard-Jones parameters, σ_{LJ} (in Angstrom) and ε/k (in K), are obtained from tabulations. [22] Limitations resulting from the assumptions in the QRRK and fall-off calculations are often over-shadowed by uncertainties in high-pressure limit rate constants and thermochemical parameters.

The input parameters for QRRK calculations of $CHCl_3$ pyrolysis and oxidation are listed in Appendix A (total 23 complex reaction systems, set I to XXIII).

6.2.3 Reaction Mechanism

An elementary reaction mechanism describing $CHCl_3$ high temperature pyrolysis (Ar bath) and oxidation is developed to interpret the available experimental data. The elementary reaction mechanism describing $CHCl_3$ pyrolysis and oxidation at high temperature in argon bath is listed in Appendix B, together with the rate parameters for the forward reaction paths including references for all rate constants. Reverse reaction rates are calculated from the thermochemical properties and microscopic reversibility (MR).

The detailed pyrolysis / oxidative mechanism was constructed by systematically considering the elementary reactions of $CHCl_3/O_2/Ar$ and intermediate stable species consistent with experimental observations. Rate constants based on theoretical calculations, recent experimental data, or evaluations are used whenever available. Kinetic data do not, however, exist for some of the needed elementary reactions, consequently, kinetic parameters are estimated for these by using principles of thermochemical kinetics and microscopic reversibility (MR), Transition State Theory [68] and by generic analysis of the trends of homologous reactions, i.e. abstraction of Cl from chloro(fluoro)carbons by a Cl atom, [173] combination between chloro-methyl radicals, [174] combination of Cl atom with radicals, [175] addition of Cl atom to vinyl chlorides [176] ……

The CHEMKIN-II computer program package (Kee et al. [177]) is used in interpreting and integrating the detailed reaction mechanisms (Appendix B) of the systems studied.

6.3 Results and Discussion

6.3.1 $CHCl_3$

As noted earlier there are four initial pathways for chloroform decomposition (Figure 6.1):

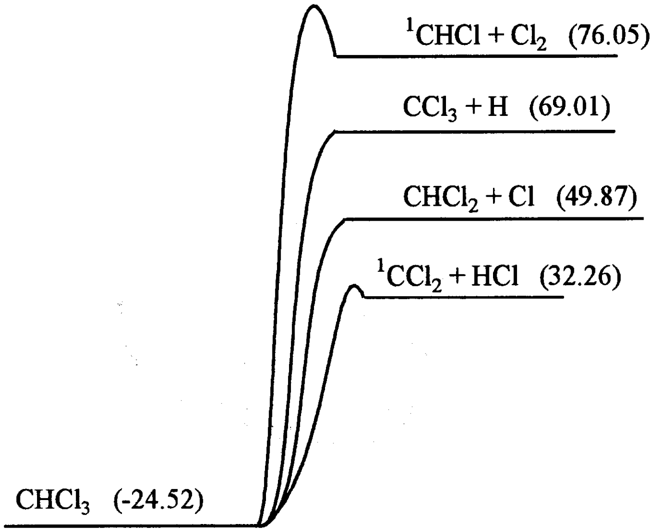
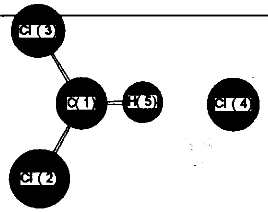
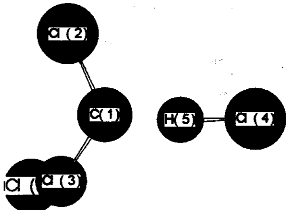
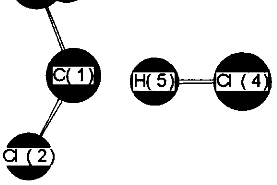
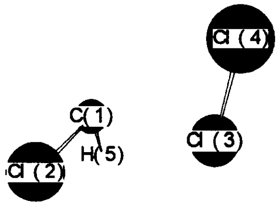


Figure 6.1 Potential Energy Diagram of $CHCl_3$ Dissociation.

The overall reaction rate of chloroform has high sensitivity to the single channel rate of $CHCl_3 \rightarrow {}^1CCl_2 + HCl$ product set, and the singlet diradical CCl_2 is the active intermediate of high importance in the pyrolysis and oxidation system. Adjustment of the pre-exponential A factor and the reaction barrier of this channel dramatically affect modeling results.

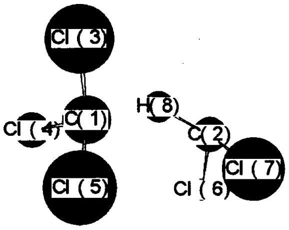
The HCl elimination for $CHCl_3$ is occurs via a three-center-elimination transition state and the geometries from several different level calculations are shown in Table 6.4. We have calculated the rate constant of $CHCl_3 \rightarrow {}^1CCl_2 + HCl$ using three different calculation methods. The three different composite calculations for the transition state geometry of $CHCl_3 \rightarrow CCl_2 + HCl$ are: G3 (TS-a1), G3//MP2/6-311G(d,p) (TS-a2), and G3//B3LYP/6-311G(d,p) (TS-a3), where the bond distances in the cleaving C-H and C-Cl bonds of the three TS's are 1.34, 1.32, 1.44, and 2.80, 2.71, 2.85 Å, respectively. The optimized geometries of these three TS's are shown in Table 6.4. The $\Delta_fH^\circ_{298}$ for transition states TS-a1, TS-a2, and TS-a3 are determined from $\Delta_fH^\circ_{298}$ of $CHCl_3$ plus the calculated total energy differences between the TS and $CHCl_3$ at the respective levels. S°_{298} and $Cp^\circ(T)$ of TS-a1, TS-a2, and TS-a3 are calculated from vibrational frequencies and moments of inertia at corresponding level using "SMCPS" program [48].

Table 6.4 Geometries of Transition States

TS's & Calculation levels	Structure	Bond length	(angstrom)	Bond angle	(degree)	Dihedral angle	(degree)
TS-a1: $CHCl_3 \rightarrow$		r21	1.645				
$^1CCl_2$ + HCl		r31	1.645	<312	119.88		
		r41	2.910	<412	118.37	<4123	-159.14
HF/6-31G(d),		r51	1.173	<512	119.78	<5123	-171.60
for G3							
TS-a2: $CHCl_3 \rightarrow$		r21	1.675				
$^1CCl_2$ + HCl		r31	1.675	<312	115.87		
		r41	2.711	<412	110.86	<4123	-127.35
MP2(FC)/6-311G(d,p)		r51	1.323	<512	117.44	<5123	-145.86
TS-a3: $CHCl_3 \rightarrow$		r21	1.702				
$^1CCl_2$ + HCl		r31	1.702	<312	114.50		
		r41	2.853	<412	115.01	<4123	136.79
B3LYP/6-311G(d,p)		r51	1.441	<512	118.63	<5123	148.36
TS-b: $CHCl_3 \rightarrow$		r21	1.754				
$^1CHCl + Cl_2$		r31	2.278	<312	107.53		
		r43	2.100	<431	99.66	<4312	-104.98
B3LYP/6-31G(d,p)		r51	1.115	<512	104.54	<5123	89.56

TS-c: $^1CCl_2$ + $CHCl_3 \rightarrow C_2HCl_5$

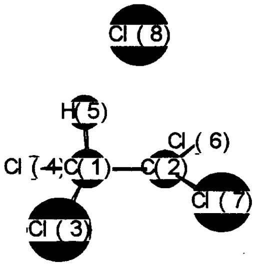
B3LYP/6-31G(d,p)



r21	2.591				
r31	1.774	<312	109.29		
r41	1.766	<412	106.12	<4123	121.92
r51	1.761	<512	102.15	<5123	-119.56
r62	1.725	<621	105.04	<6213	-151.58
r72	1.722	<721	103.46	<7213	88.20
r82	1.172	<821	21.39	<8213	-33.00

TS-d: $C_2HCl_5 \rightarrow C_2Cl_4 + HCl$

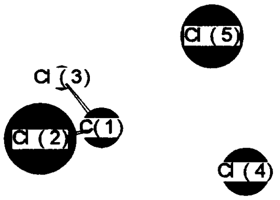
B3LYP/6-31G(d,p)



r21	1.481				
r31	1.780	<312	114.93		
r41	1.780	<412	114.94	<4123	-132.68
r51	1.172	<512	97.41	<5123	113.67
r62	1.687	<621	121.30	<6213	153.30
r72	1.687	<721	121.29	<7213	-20.74
r85	1.891	<851	142.88	<8512	0.07

TS-e: $CCl_4 \rightarrow$ $^1CCl_2 + Cl_2$

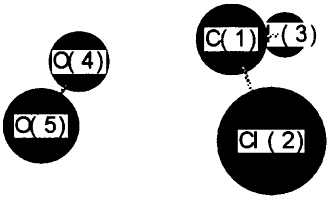
B3LYP/6-31G(d,p)



r21	1.713				
r31	1.714	<312	116.06		
r41	2.499	<412	120.73	<4123	173.88
r54	2.460	<541	61.41	<5412	-87.62

TS-f: $^1CCl_2 + {}^3O_2$ $\rightarrow {}^3C{\bullet}Cl_2OO{\bullet}$

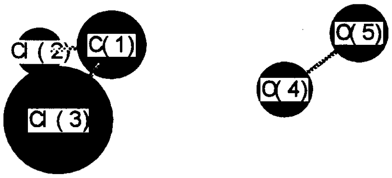
B3LYP/6-31G(d,p)



r21	1.732				
r31	1.732	<312	111.27		
r41	2.348	<412	111.16	<4123	124.38
r54	1.229	<541	125.74	<5412	117.81

TS-g: $^3CCl_2$ + $^3O_2 \rightarrow$ $^1C{\bullet}Cl_2OO{\bullet}$

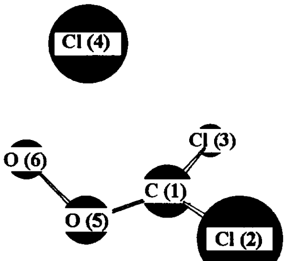
B3LYP/6-31G(d,p)



r21	1.734				
r31	1.737	<312	113.66		
r41	2.076	<412	105.70	<4123	113.94
r54	1.228	<541	113.01	<5412	15.36

TS-h: $CCl_3OO{\bullet}$ $\rightarrow CCl_2O + ClO$

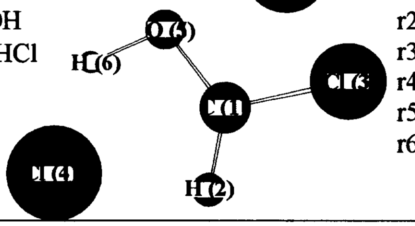
B3LYP/6-31G(d,p)



r21	1.704				
r31	1.703	<312	118.28		
r41	2.645	<412	114.34	<4123	-109.47
r51	1.285	<512	114.76	<5123	159.59
r65	1.406	<651	110.75	<6512	160.21

TS-i: $CHCl_2OH$ $\rightarrow CHClO + HCl$

B3LYP/6-31G(d,p)



r21	1.082				
r31	1.696	<312	116.41		
r42	2.453	<421	84.84	<4213	127.31
r51	1.276	<512	124.16	<5123	167.80
r65	1.045	<651	100.67	<6512	42.91

The high pressure limit rate constant of $CHCl_3 \rightarrow {}^1CCl_2 + HCl$ in three-parameter Arrhenius expression is then determined from above thermochemical parameters using canonical transition state analysis in a "THERMKIN" code [48]. The results over a temperature range of 300 to 2000 K are:

$1.20\times10^{13}\ T^{0.516}$ exp(-58.28 kcal mol^{-1} / RT) at the G3 level;

$1.95\times10^{12}\ T^{0.733}$ exp(-56.56 kcal mol^{-1} / RT) at G3//MP2/6-311G(d,p) level;

$8.70\times10^{11}\ T^{0.964}$ exp(-55.84 kcal mol^{-1} / RT) at G3//B3LYP/6-311G(d,p) level.

Application of these three rate constants separately in the mechanism shows that the three methods gave very similar results; the G3//MP2/6-311G(d,p) result is chosen. $CHCl_3 \rightarrow {}^1CCl_2 + HCl$ is determined to be the most important channel for decomposition of chloroform at low to moderate temperature; the barrier of 56 is at least 15 kcal/mol lower than the barrier for Cl atom elimination reaction.

The high-pressure limit Ea ($CHCl_3 \rightarrow {}^1CCl_2 + HCl$) = 56.56 kcal/mol is result from the G3//MP2/6-311G(d,p) calculation as shown above. It is known that ΔH_{rxn} is 56.42 kcal/mol at 300 K and 56.13 kcal/mol at 1500 K, which implies that the reverse reaction, insertion of singlet dichlorocarbene into HCl, has a barrier of only 0.1 to 0.4 kcal/mol at 298 to 1500 K. A study using *ab initio* MO calculation at the CCSD(T)/CC level results in this reaction barrier (E_0) 56.0 kcal/mol^{-1}, [156] and the reactions barrier for the back reaction is 3.8 kcal mol^{-1}. The Cl and H atoms produced from (R2) and (R3) can further have abstraction reactions with chloroform to generate more radicals (see R4 to R6 in Appendix B). Figure 6.2a compares and shows good agreement between the pyrolysis experimental data and model predictions for $CHCl_3$ decay versus reaction time at different temperature. The lines represent model prediction and the symbols are the experimental data. When reactor temperature increases, the rate constants of (1) to (3) increase, the decay rate of chloroform increases accordingly. Although the model over-estimates the decay rate of chloroform at 873 and 908 K, the estimations for the yields of three major products, HCl, CCl_4, and C_2Cl_4, at these two temperatures are reasonable (Figures 6.2b and 6.2c).

Figures 6.2b, 6.3a, and 6.3c show chloroform and other major product distribution changes with varied O_2 concentration at 873 K in the system. It can be seen from comparison of these three figures that O_2 has a significant effect on the decomposition of $CHCl_3$; higher O_2 results in faster $CHCl_3$ decay. For the same reason, the model predictions shown in Figure 6.4 indicate that chloroform is 100% depleted at 910 K under pyrolysis condition, whereas chloroform is 100% depleted at 890 K when 3% O_2 is present. The accelerated decomposition of $CHCl_3$ results from the bimolecular reactions of O_2, O and ClO with $CHCl_3$, CCl_2, $CHCl_2$, and CCl_3 (Figure 6.5).

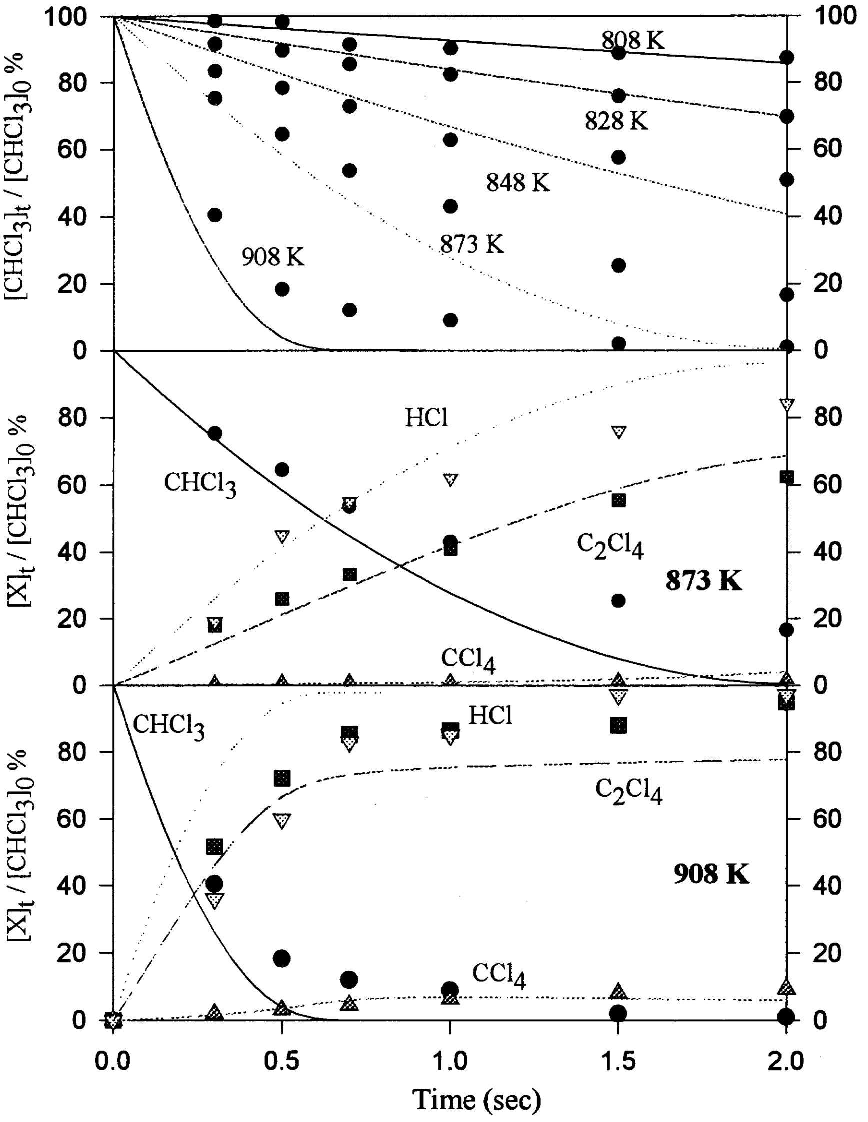


Figure 6.2 Pyrolysis of $CHCl_3$ vs. Time: Model vs. Experiments.

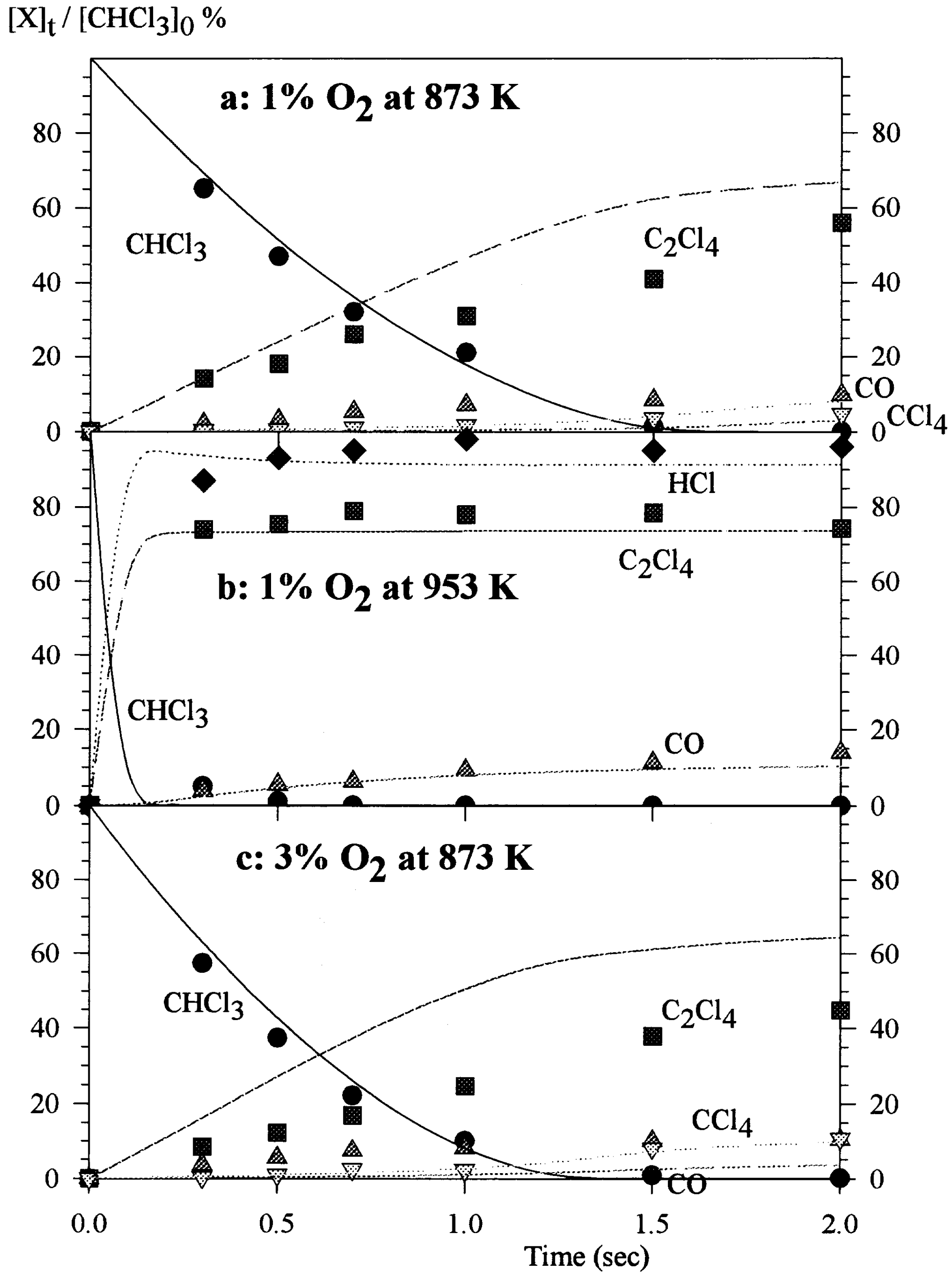


Figure 6.3 Oxidation of $CHCl_3$ at Different Conditions vs. Time: Model vs. Experiments.

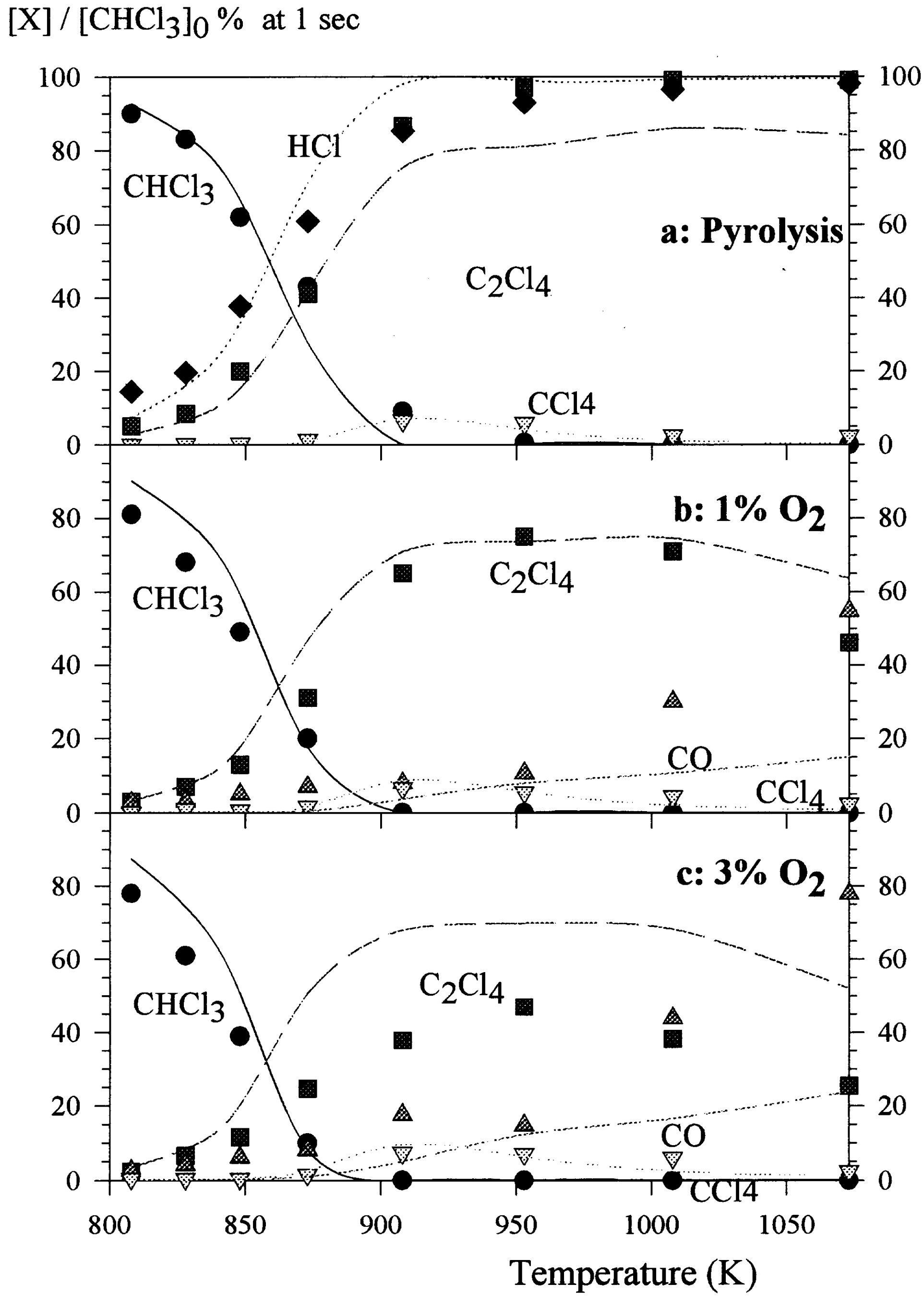
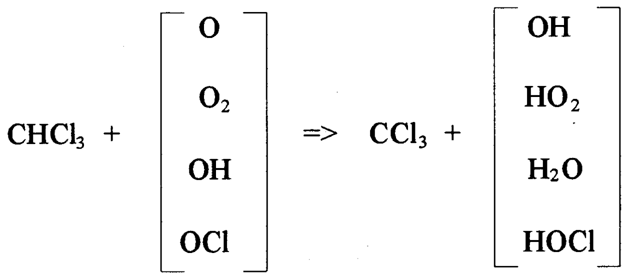


Figure 6.4 Oxidation of $CHCl_3$ at Different Conditions vs. Temperature: Model vs. Experiments.



$$CHCl_3 + \begin{bmatrix} O \\ O_2 \\ OH \\ OCl \end{bmatrix} \Rightarrow CCl_3 + \begin{bmatrix} OH \\ HO_2 \\ H_2O \\ HOCl \end{bmatrix}$$

Figure 6.5 $CHCl_3$ Decay is Faster When O_2 Presents.

6.3.2 The C_2Cl_4 Formation

C_2Cl_4 is the main product observed over a wide range of temperatures for all cases as shown in Figures 6.2, 6.3, and 6.4. C_2Cl_4 mainly results from recombination of two $^1CCl_2$ radicals, with a second formation path being insertion of CCl_2 into $CHCl_3$ followed by HCl elimination.

$$CCl_2 + CCl_2 \rightarrow C_2Cl_4 \quad (6\text{-}1)$$

$$CHCl_3 + CCl_2 \leftrightarrow [C_2HCl_5]^* \rightarrow C_2Cl_4 + HCl \quad (6\text{-}2)$$

$$CCl_2 + CCl_3 \leftrightarrow [C_2Cl_5]^* \rightarrow C_2Cl_4 + Cl \quad (6\text{-}3)$$

$$CCl_3 + CCl_3 \rightarrow [C_2Cl_6]^* \rightarrow C_2Cl_5 + Cl \quad (6\text{-}4)$$

$$\rightarrow C_2Cl_4 + Cl_2 \quad (6\text{-}5)$$

It is seen from Figure 6.2c that the C_2Cl_4 reaches a steady state value accounting for almost 85 % of the parent $CHCl_3$ carbon between 950 to 1073 K in pyrolysis experiments at 1 second reaction time, where C_2Cl_4 is under-estimated by the model to 77 %. C_2Cl_4 is apparently quite stable in the pyrolysis throughout this time and temperature regime. There is, in addition, limited hydrogen available to undergo reaction with this species and chlorine abstraction by Cl is unlikely, due to the large endothermicity. This indicates that chlorinated compounds, such as C_2Cl_4, have a relatively high degree of stability up to 800 °C in reaction systems, which are deficient of O_2 and hydrogen source. Tirey et al. [178] reported that C_2Cl_4 exhibited only minimal degradation at 800°C and 2.0 second reaction time in a C_2Cl_4/He system and further observed that poly-aromatic compounds were formed above 900 °C.

Analysis of Figures 6.2b, 6.3a, and 6.3c shows that there is less C_2Cl_4 formed when O_2 is added which implies that the reactions of $^1CCl_2 + O_2$ and $CCl_3 + O_2$ suppress the formation of C_2Cl_4. On the other hand more CCl_2 and CCl_3 radicals (C_2Cl_4 precursors) are produced under high O_2 conditions, which in some extent makes up some of the loss of these radicals to O_2. When O_2 is present in the system, the production of C_2Cl_4 increases with increasing temperature to a maximum near 953 K and then drops when CO begins to increase (Figure 6.4).

6.3.3 CCl_4 Formation

Higher CCl_4 yields are observed with higher temperature under pyrolysis condition (Figure 6.2). The experimental data show that at 1sec reaction time 1% $CHCl_3$ goes to CCl_4 at 873 K, whereas 6% goes to CCl_4 at 908 K. The model predicts these yields as 0.8% and 6.6% at these two temperature, respectively. CCl_4 are mostly from the CCl_3 radical by Cl atom recombination to CCl_3 and Cl abstraction by CCl_3, particularly from Cl_2.

$CCl_3 + Cl + M \rightarrow CCl_4 + M$,

$CCl_3 + RCl \rightarrow CCl_4 + R\bullet$,

$CCl_3 + Cl_2 \rightarrow CCl_4 + Cl$.

The amount of oxygen in reaction systems is shown to have little or no significant effect on the formation of CCl_4 (Figures 6.3 and 6.4). The peak value of CCl_4 yields is around 7% at 908 K in all three experimental condition sets. The model predicts the maximum yields of CCl_4 as 7%, 8%, and 9% at pyrolytic, 1% O_2, 3% O_2 conditions, respectively, at 908 K. These results are in good agreement with the experimental values. This is explained as the dual effects of O_2: On the one hand, the presence of O_2 results in faster decay of $CHCl_3$ and higher CCl_3 concentration, then CCl_4 concentration is higher consequently. On the other hand, O_2 can directly react (addition) to CCl_3 which reduces CCl_3 reaction to CCl_4.

6.3.4 CO Formation

The yield of CO increases slowly with the increase in both reaction time and temperature below 900 K (Figure 6.3);but the increases is faster with the increasing of O_2 and temperature above 900 K (Figure 6.4). CO is produced from decompositions of carbonyl-group-containing species.

$CHO \rightarrow CO + H$,

$CClO \rightarrow CO + Cl$......

Higher $[O_2]$ results in increased levels of carbonyl species and higher CO concentrations. The mechanism tends to under-predict CO formation, except at 953 K under 1% condition (Figures 6.3 and 6.4). The pathways of the important reactions are:

$^1CCl_2 + O_2 \leftrightarrow {}^3C.Cl_2OO. \rightarrow CClO + ClO$

$CCl_3OO. \rightarrow CCl_2O + ClO$

The parameters for rate constant of above reactions can be varied over small intervals to give a better fit to the experimental data. Density functional calculations at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level on the barrier for $CCl_3OO\bullet$ <<->

C•Cl_2OOCl (fast) → CCl_2O + ClO is 34.62 kcal/mol. This barrier is not adjusted to match the experiment results.

6.3.5 HCl Formation

The yield of HCl under pyrolytic condition increases with the increasing of reaction time and temperature below 900 K (Figure 6.2), and reaches a steady state to almost 100% above 900 K (Figures 6.2 and 6.4). Elimination of HCl from chloroform (R1) is the most important source of HCl formation. The presence of O_2 will result in faster decay of $CHCl_3$, HCl reaches a steady state at 0.2 sec, at 953 K under 1% O_2.

6.4 Summary

An elementary reaction mechanism is developed for chloroform pyrolysis and oxidation a in tubular flow reactor at 1 atm with a residence time 0.3 to 2.0 seconds in the temperature range 808 - 1073 K under three conditions: 1% $CHCl_3$ + 99% Ar, 1% $CHCl_3$ + 1% O_2 + 98% Ar, and 1% $CHCl_3$ + 3% O_2 + 96% Ar. The thermochemical data for the species in the reaction system are estimated from literature, modified group additivity method "THERM", or *ab initio* / density function calculations. High-pressure limit rate constants have been evaluated for the input of Quantum RRK calculations. Chemkin II is used to integrate the mechanism which consists of ~100 dissociation reactions, ~150 chemical activation reactions, and ~100 abstraction reaction, the model results show good agreement with the experimental product profiles.

Chloroform decay and product distributions are distinctly different in the absence and presence of added O_2. The presence of O_2 was observed to speed reagent loss, decrease C_2Cl_4 formation and increase CO production.

CHAPTER 7

THERMOCHEMICAL PROPERTIES, KINETIC PATH ANALYSIS ON THE THERMAL OXIDATION OF 1,3-HEXACHLOROBUTADIENE AT 773 - 1373 K

7.1 Overview

Waste feed to both municipal and hazardous waste incinerators is usually in solid or liquid form. Initial exposure of this feed to the incinerator environment results in thermal heating on surfaces of this material, where vaporization or polymer fragmentation occurs along with pyrolysis reactions. Once in the vapor phase these fragment molecules and radicals start to react in the oxidizing medium (air) before a uniform combustion environment is achieved. The initial reaction on and at the surface may be represented by pyrolysis. Initial reaction in the vapor, but near the solid or liquid surfaces may be described as oxidation of neat material, as opposed to well-mixed (with hydrocarbon co-fuel) combustion. It is of value to study reactions representative of these regimes in order to obtain knowledge about products that may enter subsequent incinerator processes.

The presence of polychloro-1,3-butadiene congeners in the aquatic environment has been observed worldwide in surface- and groundwater, treated and wastewater, sediments of streams, and aquatic organisms. [179]

Taylor et al. have reported the high-temperature pyrolysis of trichloroethylene, tetrachloroethylene, hexachloropropene, [180] and 1,3-hexachlorobutadiene [181] using flow reactors with on-line GC-MS. More or less detailed mechanisms are also given. The effects of reactor surface-area-to-volume (S/V) ratio were evaluated. In the case of C_4Cl_6 pyrolysis, under low S/V ratio, [181] initial decomposition is observed at 1023 K with formation of tetrachlorovinyl acetylene (C_4Cl_4), C_2Cl_4, CCl_4, and Cl_2.

Hexachlorobenzene and other aromatic species, such as C_6Cl_6, C_8Cl_8, $C_{12}Cl_8$, are observed as products at high temperature of pyrolysis of C_3Cl_6 and C_4Cl_6. They also revised previous C_2HCl_3 and C_2Cl_4 mechanism model to achieve agreement of model with hexachlorobutadiene pyrolysis experiment under low S/V ratio.

Over the last decade, several laboratory studies also have focused on the thermal degradation processes of chlorinated compounds. Most studies were devoted to chlorinated methanes [151,182-186] and ethanes [178, 182,183,187-193] because of their industrial interest and the relative simplicity of their pyrolysis and oxidation processes. Very few experimental investigations or modeling studies were performed on the higher molecular weight chlorinated hydrocarbons (CHCs) due to the complexity of their chemical processes and the lack of kinetic and thermochemical data to characterize or evaluate elementary reactions involved in their decomposition, pyrolysis and oxidation. Four investigations were reported on the more complex thermal degradation processes of chlorobenzenes. [184,194-196]

The purpose of this work is to contribute a better understanding on high temperature oxidation processes of chlorinated species without the presence of hydrogen. 1,3-hexachlorobutadiene was selected for several reasons: (i) its identification as a pyrolysis byproduct of trichloroethene, [188,193] tetrachloroethene, [178,189] and 1,2-dichlorobenzene; [196] (ii) the lack of experimental data related to its thermal degradation processes; (iii) as an unsaturate chlorinated species, the potential production of chlorinated aromatics and other toxic components such as phosgene by thermal oxidation or combustion.

Oxidation was investigated for thermal degradation of 1,3-hexachlorobutadiene in liquid phase over the temperature range 393-483 K for residence times between 1 and 7 hours. [197] Gas phase thermal decomposition data, including temperatures required for 99.9% and 99.99% conversion of 1,3-hexachlorobutadiene at 2 seconds with an equivalence ratio of 3 yielded empirical kinetic parameters and conversion data relative to other hazardous organic compounds. [198] An incinerability ranking was developed based on the type of mechanism which generally dominates compound decomposition. [199] Here 1,3-hexachlorobutadiene has been ranked in the family corresponding to stable species with dominant destruction by unimolecular bond fission or concerted molecular elimination. [199]

Thermochemical parameters of major and minor chlorinated intermediates and products (stable molecules) generated by pyrolysis and/or oxidation of 1,3-hexachlorobutadiene are estimated and an elementary reaction mechanism is developed for mineralization and conversion to lower molecular weight products (decomposition and oxidation reactions) under fuel rich conditions. Important reaction pathways and bond energies are analyzed.

7.2 Modeling

A detailed chemical kinetic model is presented, and evaluated by comparing the computed profiles of major products with the corresponding experimental profiles. It consists of 230 reversible reactions and 90 species, with the Chemkin Kinetics code [177,200] for integration. Since most of rate parameters and thermochemical properties characterizing these reactions are unknown, a consistent set of procedures for estimating their values is developed and reported.

Unimolecular dissociation and isomerization reactions of the chemically activated and stabilized adducts resulting from addition or combination reactions are analyzed by first evaluating thermochemical properties and constructing potential energy diagrams. Thermochemical parameters, $\Delta_f H°_{298}$, $S°_{298}$, $Cp°(T)$ ($300 \leq T/K \leq 1500$), are estimated based on existing experimental or theoretical data and on Group Additivity estimation techniques. High-pressure limit rate constants for each channel are obtained from literature or referenced estimation technique. Kinetic parameters for unimolecular and bimolecular (chemical activation) reactions are calculated using a modified multi-frequency QRRK analysis for k(E). [13] The modified strong collision formalism of Gilbert et al. is used for fall-off (β collision) with the steady-state assumption on the energized adduct(s). [16,17,201] It is shown to yield reasonable results and provides a framework by which the effects of temperature and pressure can be evaluated in complex reaction systems.

7.2.1 Thermochemical Property Estimation

Thermochemical parameters, $\Delta_f H°_{298}$, $S°_{298}$, $Cp°(T)$ ($300 \leq T/K \leq 1500$), for species in the reaction schemes are listed in Table 7.1 along with appropriate references. Molecules are calculated primarily by several means:

Table 7.1 Thermochemical Properties (Enthalpies in kcal/mol, Entropies and Heat Capacities in cal/mol.K)

Species	$\Delta_f H°_{298}$	$S°_{298}$	Cp(T)								
			300K	400K	500K	600K	800K	1000K	1500K	ref	Elements
O	59.56	38.47	5.24	5.14	5.08	5.05	5.02	5.00	4.98	[46]	O
O_2	0.00	49.00	7.02	7.20	7.43	7.67	8.06	8.34	8.74	[46]	O2
N_2	0.00	45.77	6.96	6.99	7.07	7.20	7.51	7.82	8.33	[46]	N2

CO	-26.42	47.21	6.97	7.01	7.12	7.28	7.62	7.93	8.42	[46]	C1 O1
CO_2	-94.05	51.07	8.90	9.88	10.67	11.31	12.29	12.98	13.95	[46]	C1 O2
Cl	28.99	39.48	5.22	5.36	5.43	5.44	5.38	5.31	5.17	[41]	Cl1
Cl_2	0.00	53.29	8.12	8.44	8.62	8.74	8.88	8.96	9.07	[46]	Cl2
CCl	120.00	53.63	7.72	8.03	8.28	8.46	8.68	8.81	8.98	[46]	C1 Cl1
ClO	24.34	54.21	7.37	7.72	8.05	8.29	8.54	8.70	8.90	[41]	Cl1 O1
CClO	-3.83	63.54	10.78	11.30	11.69	12.02	12.54	12.91	13.39	[46,47]	C1 O1 Cl1
CCl_2O	-52.70	67.82	13.82	15.28	16.27	16.98	17.92	18.49	19.19	[43,46]	C1 O1 Cl2
CCl_2	54.33	63.51	11.21	12.09	12.63	12.97	13.35	13.54	13.74	[162], a	C1 Cl2
CCl_2T	71.15	65.29	10.95	11.80	12.37	12.76	13.21	13.44	13.69	[162], a	C1 Cl2
C_2Cl_2	53.89	65.92	15.96	16.88	17.53	18.03	18.76	19.28	20.01	[167]	C2 Cl2
C_2Cl_3	53.18	79.69	18.62	20.45	21.69	22.57	23.70	24.35	25.11	a, b	C2 Cl3
C_2Cl_4	-5.78	81.41	22.43	24.86	26.66	27.95	29.40	29.95	30.78	[39,62]	C2 Cl4
C_2Cl_5	9.32	95.83	27.16	30.18	32.05	33.17	34.35	35.36	35.97	[41,47]	C2 Cl5
C_2Cl_6	-35.42	95.33	32.76	36.22	38.39	39.80	41.55	42.13	43.25	[39,41]	C2 Cl6
CCl_3	17.20	72.06	15.38	16.78	17.66	18.23	18.88	19.22	19.57	Chap. 2	C1 Cl3
CCl_4	-22.85	74.12	20.08	22.04	23.28	24.07	25.00	25.52	0.00	[39,41]	C1 Cl4
1,3-C_4Cl_6	2.91	109.02	38.55	42.80	45.82	47.97	50.68	52.23		[41],b	C4 Cl6
C4Cl5.N	61.42	106.51	34.00	37.87	40.57	42.51	45.00	46.44	48.11	THERM,a	C4 Cl5
C4Cl5.S	49.02	107.66	34.49	38.31	40.94	42.81	45.19	46.56	48.16	THERM,a	C4 Cl5
C4Cl7.P	22.19	122.27	43.84	48.69	51.11	53.05	55.21	57.03		THERM,a	C4 Cl7
C4Cl7.S	13.20	118.02	43.12	47.28	49.36	51.50	55.36	57.12		THERM,a	C4 Cl7
LC3Cl6	-5.85	104.49	36.04	38.96	40.83	42.60	44.38	45.69		THERM,a	C3 Cl6
LC3Cl4	39.41	88.96	27.31	29.82	31.66	33.06	35.06	36.36	38.76	THERM,a	C3 Cl4
CCl2CO	-6.75	70.98	18.57	20.71	22.55	23.22	24.06	24.72	25.28	THERM,a	C2 O1 Cl2
C6Cl8TE	12.50	141.71	53.81	59.32	63.76	67.52	71.94	75.35		THERM	
C2Cl3CClO	-39.09	96.56	30.74	33.17	34.53	36.03	37.59	38.45		THERM,a	C3 O1 Cl4
C4Cl4	52.63	98.95	30.63	33.21	34.25	36.97	38.69	39.76		THERM,a	C4 Cl4
C4Cl4A	52.15	90.79	29.74	33.64	36.06	37.84	39.86	41.02	42.28	THERM,a	C4 Cl4
C4Cl2	102.01	76.84	22.42	24.72	26.16	27.14	28.52	29.42	30.66	THERM,a	C4 Cl2
C4Cl3NV.	113.68	90.53	24.65	28.43	29.93	32.44	34.40	35.52	0.00	THERM,a	C4 Cl3
C4Cl3.S	99.27	89.17	25.86	29.29	30.75	33.18	34.88	35.93	37.23	THERM,a	C4 Cl3
C.#CC2Cl3	129.43	89.89	24.77	28.64	30.21	32.80	34.84	35.85		THERM,a	C4 Cl3
C4Cl3A	128.13	87.92	25.79	28.80	30.79	32.40	34.09	35.15	36.31	a, b	
NC4Cl5Q.	24.35	127.63	41.21	44.22	46.57	48.97	52.37	55.02		THERM,a	C4 O2 Cl5
L3VLC.YOO	26.01	124.81	42.32	47.14	49.37	52.36	56.36	57.83		THERM,a	C4 O2 Cl5
L3VVL2O.	-13.77	112.68	38.22	42.38	45.43	47.98	50.84	53.02		THERM,a	C4 O1 Cl5
O*COC.L4V	-52.96	120.00	38.80	42.47	45.23	47.91	51.36	53.82		THERM,a	C4 O2 Cl5
SC4Cl5Q.	24.95	124.48	41.26	45.32	48.28	50.55	53.39	55.10		THERM,a	C4 O2 Cl5
L3VYOOC.L	33.69	118.02	39.95	45.85	49.47	51.84	54.62	55.66		THERM,a	C4 O2 Cl5
L2VO.VL3	-4.61	112.65	39.55	43.61	46.70	48.78	51.05	52.32		THERM,a	C4 O1 Cl5
L5VO*COC.	-42.03	121.33	42.05	47.24	50.44	52.61	54.57	55.61		THERM,a	C4 O2 Cl5
C2Cl3C.*O	9.71	87.08	26.92	29.72	31.00	32.25	33.47	33.96		THERM,a	C3 O1 Cl3
L3VLC*C*O	-3.03	102.77	34.64	38.26	41.37	43.17	45.25	46.69		THERM,a	C4 O1 Cl4
LC.*ClKT	57.31	95.64	29.99	34.20	36.86	38.23	40.14	41.38		THERM,a	C4 O1 Cl3
L2V.LKT	49.44	93.92	30.45	34.60	37.45	38.89	40.67	41.94		THERM,a	C4 O1 Cl3
L3VK.T	30.89	96.00	30.20	34.49	37.36	38.69	40.40	41.55		THERM,a	C4 O1 Cl3
Cl2C*CClOO	15.89	97.51	25.67	27.11	28.05	29.14	31.04	32.38		THERM,a	C2 O2 Cl3
Cl2C*CClO.	-24.26	83.02	21.85	24.26	25.96	27.20	28.79	29.71	30.78	[36]	C2 O1 Cl3
Cl2C.COOCl	21.29	97.92	27.07	30.52	32.53	34.49	36.22	36.71		THERM,a	C2 O2 Cl3
Cl2C.OCClO	-40.18	93.65	26.52	29.70	31.97	33.14	34.44	35.03		THERM,a	C2 O2 Cl3
ClC*OQ.	-30.63	80.70	16.79	18.86	20.11	20.96	22.25	22.86		THERM,a	C1 O3 Cl1
CCl3OO	-3.30	83.00	22.89	25.05	26.47	27.51	28.81	29.65		[29,202] HBI	C1 O2 Cl3
CCl2OO	38.64	84.13	19.94	21.23	21.80	21.93	22.33	22.59		THERM,a	C1 O2 Cl2
ClCO2.	-30.89	68.21	13.32	14.89	16.04	16.88	17.95	18.55	19.24	THERM,a	C1 O2 Cl1
CCl_3O	-9.05	79.03	19.80	21.65	22.80	23.56	24.44	24.90	25.40	[30]	C1 O1 Cl3
LC3Cl5N	34.46	97.76	31.06	33.88	35.58	37.19	39.00	39.75		THERM	C3 Cl5
CYC6Cl7	-38.61	125.81	44.70	53.24	57.14	60.92	66.05	67.84		THERM	C6 Cl7
CYC6Cl6	-0.60	104.81	41.89	47.91	52.34	55.61	59.82	62.23	65.00	Chap 3	C6 Cl6
CYC6Cl5	54.93	101.54	40.50	46.23	49.85	52.02	55.35	57.33		THERM	C6 Cl5
C6Cl7N	43.78	135.14	49.60	55.32	59.39	62.30	66.18	69.27		THERM	C6 Cl7
C6Cl7S	49.10	135.05	50.29	55.75	59.99	63.05	66.74	69.80		THERM	C6 Cl7

C6Cl6N	34.06	124.74	44.67	50.97	54.21	58.02	61.68	63.95		THERM	C6 Cl6
C6Cl6S	27.52	124.96	42.32	50.00	53.06	58.08	61.88	63.58		THERM	C6 Cl6
C6Cl5N	90.04	118.87	40.49	46.10	48.93	52.49	55.88	58.08		THERM	C6 Cl5
C6Cl5S	97.90	119.14	41.93	46.99	49.76	53.32	56.39	58.61		THERM	C6 Cl5
C6Cl4N	89.13	108.33	36.14	41.52	44.03	47.32	50.34	51.85		THERM	C6 Cl4
STYRENE	-0.01	139.50	60.09	67.64	73.13	76.78	81.93	85.30		THERM	C8 Cl8
C6Cl4S	80.32	107.09	35.56	41.75	43.75	48.21	51.38	52.76		THERM	C6 Cl4
C2Cl	135.66	57.40	10.54	11.38	11.95	12.40	13.06	13.53	14.17	[167]	C2 Cl1
ClC.*C*O	33.90	68.28	15.05	16.44	17.88	18.35	18.75	19.21	19.51	THERM	C2 O1 Cl1
C2Cl3OO	12.66	96.81	26.02	27.75	28.44	29.58	31.00	31.98		THERM	C2 O2 Cl3
C.Cl2Cl*O	-21.05	84.76	23.25	24.97	25.83	26.39	27.76	28.21		THERM	C2 O1 Cl3
C.*OLKT	-22.16	76.40	23.16	25.41	26.85	27.69	28.26	28.62		THERM	C3 O2 Cl1
CCl*OLKT	-68.72	85.27	26.75	28.91	30.55	31.59	32.56	33.29		THERM	C3 O2 Cl2
LC#CCClO	3.27	82.00	20.57	22.90	23.90	26.23	28.02	28.83		THERM	C3 O1 Cl2
LC#CCJ*O	58.37	74.35	17.09	19.28	20.06	22.20	23.72	24.27		THERM	C3 O1 Cl1
LC#CCO2.	14.07	79.90	18.93	21.77	23.08	25.55	27.53	28.52		THERM	C3 O2 Cl1
SC4L5PXO.	-9.89	115.61	39.49	46.11	49.68	52.23	55.07	56.31		THERM	C4 O2 Cl5
NC4L5EPO.	-8.96	125.85	43.32	48.39	51.34	54.50	56.99	58.31		THERM	C4 O2 Cl5
Cl2CCOClO.	-10.57	94.14	26.61	30.78	32.74	34.88	36.67	37.36		THERM	C2 O2 Cl3
CO.Cl2CClO	-48.89	90.70	25.69	29.27	30.95	32.09	33.68	34.31		THERM	C2 O2 Cl3
C2Cl5O	-17.60	96.43	31.29	35.86	38.15	39.56	41.17	42.05		THERM	C2 O1 Cl5
CJ#CCClO	87.01	75.33	18.00	18.87	19.73	20.49	21.88	22.64		THERM	C3 O1 Cl1
CJ*CCClO	4.58	90.08	26.33	28.35	29.42	30.62	31.97	32.74		THERM	C3 O1 Cl3
C*CJCClO	-8.24	85.79	25.23	28.77	31.00	32.42	34.14	35.00	0.00	THERM	C3 O1 Cl3
L2C*C*C*O	10.44	76.98	22.47	25.11	27.25	28.22	29.36	30.22	30.98	THERM	C3 O1 Cl2
C#CCCl2O	46.79	90.14	26.04	29.86	31.72	32.99	34.64	35.34	0.00	THERM	C3 O1 Cl3
O*C*C*O	-23.76	70.98	18.57	20.71	22.55	23.22	24.06	24.72	25.28	THERM	C2 O2
C2Cl3CO2.	-43.14	95.14	28.12	31.63	33.65	35.39	37.33	38.37		THERM	C3 O2 Cl3
VL3C*OC.	-12.54	114.12	37.69	41.80	44.03	45.84	48.26	49.44		THERM	C4 O1 Cl5
V.L2C*OC.	43.86	116.63	36.81	40.18	41.79	43.12	44.82	45.48		THERM	C4 O1 Cl4
CYC4Cl4O	-21.78	92.04	30.85	36.40	38.94	41.27	43.39	44.70	0.00	THERM	C4 O1 Cl4
C2Cl2C.*O	43.49	108.74	33.36	37.63	39.59	41.20	43.03	44.07		THERM	C4 O1 Cl4
C*CCJC*O	-35.67	112.01	36.87	40.73	42.72	44.78	48.79	50.29		THERM	C4 O1 Cl5
CJC*CC*O	-36.87	107.46	38.16	41.64	43.32	45.53	47.67	48.96		THERM	C4 O1 Cl5
O*CC*O	-80.25	81.93	19.47	20.68	21.59	23.34	24.75	26.13		[42], THERM	C2 O2 Cl2
CYC4Cl5O	14.02	98.90	38.28	44.13	46.58	48.72	50.30	51.20		THERM	C4 O1 Cl5
C*C*CC*O	-22.28	100.45	34.02	37.44	39.36	41.21	43.06	44.09		THERM	C4 O1 Cl4
C*C*C	22.68	84.79	25.84	29.24	31.36	32.84	34.56	35.52	36.58	THERM	C3 Cl4
CJ*C*C	62.14	82.08	22.32	24.97	26.69	27.97	29.25	30.01	30.81	THERM	C3 Cl3
CJCC*O	-41.02	106.60	34.31	38.88	41.27	42.74	44.93	46.04	0.00	THERM	C3 O1 Cl5
CCl3C.*O	-5.18	85.63	22.68	24.77	26.14	27.10	28.28	28.94	29.61	[36]	C2 O1 Cl3
CCl3CClO	-57.31	90.58	26.27	28.89	30.56	31.69	33.10	33.92	34.86	[36]	C2 O1 Cl4

a: S and Cp from DFT freq calc.; [36]

b: Enthalpy from DFT and isodesmic reaction calculations in this work.

Group Additivity method [68] using "THERM" computer code, [19,165]. The groups in THERM are derived from experimental data, or *ab initio* and density functional methods and isodesmic reactions for the chlorocarbons and oxychlorocarbons in this NJIT thermochemical kinetics research group. Thermochemical properties of radicals are obtained using

(i) Hydrogen Bond Increments (HBI) method. [163]

(ii) or from evaluation of literature when available;

(iii) or from direct *ab initio* and density functional methods and isodesmic reactions.

Total energies for the species calculated in this study are listed in Table 7.2, and the enthalpies calculated by isodesmic reactions are shown in Table 7.3.

Table 7.2 Calculated Total Energies of Oxy- or Chloro-Oxy- Species at 298 K^{a,b}

Species	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	ZPVE^{c,d}	H_{298}-H_0^{d}
C4H6DE13	-155.91242	-155.96271	52.49	3.51
C4Cl6DE13	-2913.4872	-2913.7444	18.21	7.64
C4Cl5S	-2453.2463	-2453.4683	15.98	7.01
TC4Cl7xCC	-3373.5752	-3373.8703	16.91	8.84
C4Cl7n	-3373.6251	-3373.9173	18.32	8.58
TC4Cl7PS	-3373.6184	-3373.9107	18.05	8.38
C2Cl3CClO	-2030.248	-2030.4539	15.29	5.86
LC3Cl6	-2875.3857	-2875.6314	14.58	6.95
C4Cl7S	-3373.6402	-3373.9316	18.25	8.71
C4HCl7S	-3374.2804	-3374.571	26.55	8.50
C4HCl7P	-3374.2698	-3374.5604	26.47	8.45
C2H3-C2Cl3	-1534.7056	-1534.8583	35.67	5.39
COCl2	-1033.6992	-1033.814	6.46	3.07
COCl-COCl	-1147.0082	-1147.1631	12.23	4.31
L3Cl4	-1954.9636	-1955.1442	11.81	5.57
C6Cl8TE	-3910.0454	-3910.3957	26.96	10.65
C2H3OH	-228.87622	-228.9648	36.57	3.73
C2H3OO	-228.25107	-228.33583	29.39	3.33
C2Cl3OOH	-1607.6667	-1607.8568	19.54	5.58
C2Cl3OO	-1607.0318	-1607.2197	12.31	5.23
CCl2=C=O	-1071.7392	-1071.8672	9.46	3.80
Cl2CJCYOOCl	-1607.0249	-1607.2111	12.13	5.15
C4HCl5S	-2453.8947	-2454.1164	24.13	6.80
C4Cl4	-1993.0582	-1993.2501	15.59	6.05
C4Cl4A	-1993.0605	-1993.2493	15.56	6.01
Allene	-116.60512	-116.64488	34.03	2.95
C4Cl3NV.	-1532.7921	-1532.9502	13.72	5.36
C4Cl3S	-1532.8158	-1532.9732	13.08	5.10
C3Cl4A	-1954.9899	-1955.1657	12.44	5.39
C4Cl5N	-2453.2259	-2453.4486	16.40	6.90
C4HCl5N	-2453.896	-2454.1177	24.14	6.86
C2Cl3C.=O	-1570.0021	-1570.1741	13.28	5.19
C4Cl2	-1072.6286	-1072.7563	13.11	4.73
C=C-C=C=C (VA)	-2951.5477	-2951.8162	21.21	8.33
CClO	-573.45319	-573.53274	4.04	2.72
C.#CC2Cl3	-1532.77	-1532.9251	12.82	5.48
TC4Cl5NXCC	-2453.1416	-2453.3709	14.27	7.54
TC4Cl4	-1992.974	-1993.1642	13.79	5.97
NC4Cl5OO.	-2603.5924	-2603.8724	21.13	8.17
SC4Cl5OO.	-2603.5914	-2603.8714	21.16	8.19
CCl3OO	-1568.95	-1569.1252	8.72	4.63
C2Cl3C(=O)CCl3	-2988.6985	0.0456458	20.37	8.27
C4Cl3A	-1532.8158	-1532.9732	13.07	5.09
L3VYOOC.L	-2603.5785	-2603.8575	20.85	8.11

O*COC.L4V	-2603.7119	-2603.9956	21.45	8.09
Cl2CJOCClO	-1607.1448	-1607.3359	12.86	5.23
ClC*OQ.	-723.80341	-723.94054	9.43	3.57
L2VOJVl3	-2528.4871	-2528.7401	19.04	7.52
L3VVL2OJ	-2528.502	-2528.7547	19.07	7.49
L3VLCJYOO	-2603.5915	-2603.8697	20.75	7.95
Styrene C8Cl8	-3986.2874	-3986.6559	35.00	10.86
TC4Cl3PS	-1532.7742	-1532.9335	12.76	5.55
CYC6Cl5	-2529.4593	-2529.6996	24.36	7.11
CYC6Cl7	-3449.8667	-3450.1778	26.06	9.00
L3VLC*C*O	-2068.3079	-2068.5279	18.30	6.63
L2V.LKT	-1608.0573	-1608.2417	15.88	6.06
L3VK.T	-1608.0858	-1608.2713	16.51	5.77
LC.*CLKT	-1608.0427	-1608.2292	16.40	5.96
CCl2*CJCClO	-1569.989	-1570.1601	13.18	5.32
C.*CCClO	-1569.9957	-1570.1674	13.56	5.17
CO.Cl2CClO	-1607.1257	-1607.3145	11.93	5.37
ClCO2.	-648.67101	-648.7801	6.40	3.01
TCOClOOXClO	-723.74148	-723.87935	7.94	3.75

a: All calculations are based on B3LYP/6-31G(d,p) optimized structures;

b: Total energies (ZPVE and thermal corrections are included) in hartree, 1 hartree = 627.51 kcal/mol;

c: Scaled by 0.9806; [37]

d: In units of kcal/mol.

Table 7.3 Calculations for $\Delta_f H^\circ_{298}$ (kcal/mol) by Isodesmic Reactions [a,b]

Isodesmic Reactions (all atoms not shown = Cl)	B3LYP/6-31G(d,p)	B3LYP/6-311+G (3df,2p)	use
C=C-C=C + 2 × C_2H_4 → 2 × C_2HCl_3 + CH_2=CH-CH=CH_2	4.84	2.91	2.91
C_2Cl_3 + C_2H_4 → C_2HCl_3 + C_2H_3	53.86	53.97	
C_2Cl_3 + CH_4 → C_2HCl_3 + CH_3	52.18	52.79	53.18
C=C-C•=C + C_2Cl_4 → C=C-C=C + C_2Cl_3	48.49	49.02	49.02
C=C-C=C• + C_2Cl_4 → C=C-C=C + C_2Cl_3	61.33	61.42	61.42
C=C-C + C_2Cl_4 → C=C-C=C + CCl_4	-5.91	-5.85	-5.85
C=C-C-CH + C_2Cl_4 → C=C-C=C + C_2HCl_5	-17.89	-18.02	
C=C-C-CH + C_2H_4 + CH_4 → CH_2=CH-CH_3 + C_2HCl_3 + $CHCl_2CHCl_2$	-14.80	-16.55	
C=C-C-CH + $CHCl_3$ → C=C-C + $CHCl_2CHCl_2$	-17.02	-17.24	
C=C-C-CH + CCl_4 → C=C-C + C_2HCl_5	-17.83	-18.02	-17.46
C=C-C-C• + C_2H_6 → C=C-C-CH + C_2H_5	21.60	21.77	
C=C-C-C• + CH_4 → C=C-C-CH + CH_3	21.85	22.26	
C=C-C-C• + C_2H_4 → C=C-C-CH + C_2H_3	23.03	22.54	22.19
C=C-CH-C + C_2Cl_4 → C=C-C=C + C_2HCl_5	-24.56	-24.65	
C=C-CH-C + C_2H_4 + CH_4 → CH_2=CH-CH_3 + C_2HCl_3 + CH_2ClCCl_3	-21.69	-23.17	
C=C-CH-C + $CHCl_3$ → C=C-C + CH_2ClCCl_3	-23.90	-23.86	
C=C-CH-C + CCl_4 → C=C-C + C_2HCl_5	-24.50	-24.65	-24.08
C=C-C•-C + C_2H_6 → C=C-CH-C + C_2H_5	12.14	12.79	
C=C-C•-C + CH_4 → C=C-CH-C + CH_3	12.39	13.27	
C=C-C•-C + C_2H_4 → C=C-CH-C + C_2H_3	13.57	13.55	13.20
C-C≡C + CH_4 → CH_3-C≡CH + CCl_4	38.45	39.31	

C-C≡C + C_2H_4 → CH_3-C≡CH + C_2Cl_4	40.67	39.51	39.41
C=C-C≡C + C=C-C → C=C-C=C + C-C≡C	52.50	52.63	52.63
C=C=C=C → C=C-C≡C	54.04	52.15	52.15
C•=C-C≡C + C_2Cl_4 → C=C-C≡C + C_2Cl_3	114.07	113.68	113.68
C=C•-C≡C → C•=C-C≡C	98.86	99.27	99.27
C=C-C≡C• → C•=C-C≡C	127.59	129.43	129.43
C=C=C=C• → C•=C-C≡C	128.53	128.13	128.13
C≡C-C≡C + C=C-C=C → 2 × C=C-C≡C	102.81	102.01	102.01
C=C-OOH + C_2H_4 → C_2H_3OOH + C_2HCl_3	-22.33	-22.10	
C=C-OOH + C_2HCl_3 → C_2H_3OOH + C_2Cl_4	-25.28	-23.59	
C=C-OOH + CH_3OOH → C_2H_3OOH + CCl_3OOH	-24.12	-23.82	-23.17
C=C-OO• + CCl_3OOH → C=C-OOH + CCl_3OO•	16.24	15.89	15.89
C=C-C=C-OO• + CCl_4 → C=C-C=C + CCl_3OO•	24.66	24.08	
C=C-C=C-OO• + C_2Cl_4 → C=C-C=C + C_2Cl_3OO•	24.36	24.63	24.35
C=C-C=O + CH_4 → CCl_4 + CH_3CH=O	-40.65	-39.09	-39.09
C=C-C•=O + C_2Cl_4 → C=C-C=O + C_2Cl_3	10.78	10.56	
C=C-C•=O + CCl_2O → C=C-C=O + CClO	9.66	8.86	9.71
C=C=O + C_2H_4 → ketene + CH_2=CCl_2	-5.82	-5.75	
C=C=O + CH_2=CCl_2 → ketene + C_2Cl_4	-7.75	-6.50	-6.13
C=C-C=C-O• + C_2Cl_4 → C=C-C=C + C=C-O•	-13.82	-13.77	-13.77
C=C-C•-Y(C-O-O) → C=C-C=C-OO•	24.94	26.01	26.01
C=C-C•-O-C=O → C=C-C=C-OO•	-50.66	-52.96	-52.96
C=C-C(OO•)=C + CCl_4 → C=C-C=C + CCl_3OO•	25.29	24.68	
C=C-C(OO•)=C + C_2Cl_4 → C=C-C=C + C_2Cl_3OO•	24.99	25.23	24.95
C=C-C(O•)=C + C_2Cl_4 → C=C-C=C + C=C-O•	-4.46	-4.61	-4.61
C=C-Y(C-O-O)-C• → C=C-C(OO•)=C	33.04	33.69	33.69
C=C-C(-O-C•)=O → C=C-C(OO•)=C	-40.48	-42.03	-42.03
C=C-C=C=O + C_2Cl_4 → C=C-C=C + C=C=O	-3.98	-3.65	-3.65
C•=C-C=C=O + C_2Cl_4 → C=C-C=C=O + C_2Cl_3	57.84	57.31	57.31
C=C•-C=C=O + C_2Cl_4 → C=C-C=C=O + C_2Cl_3	48.72	49.44	49.44
C=C-C•=C=O + C_2Cl_4 → C=C-C=C=O + C_2Cl_3	30.79	30.89	30.89
C•-Y(C-O-O) → C=C-OO•	20.21	21.29	21.29
C•-O-C=O + CH_4 → C•Cl_2OH + CH_3CClO	-41.36	-40.18	-40.18
O=CCl-OO• + CCl_4 → CCl_2O + CCl_3OO•	-30.33	-30.63	-30.63
CCl(=O)-O + CCl_4 → CCl_2O + CCl_3OO•	-30.61	-30.89	-30.89

a: All based on B3LYP/6-31G(d,p) geometries;

b: Values or average values at B3LYP/6-311+G(3df,2p) are used.

7.2.2 Input Data Requirements for the QRRK Calculation

High-pressure limit pre-exponential factors (Arrhenius A-factors, A(T)) for bimolecular addition and combination reactions are obtained from the literature (see individual tables), and from trends in homologous series of reactions [68,94,203] as described below.

Three reduced vibration frequency sets and their associated degeneracies are computed from fits to heat capacity data, as described by Ritter. [19,204] These have been shown by Ritter to accurately reproduce molecular heat capacities, Cp(T), and by Bozzelli et al. [20] to yield accurate density of state to partition coefficient ratios, p(E)/(Q). Lennard-Jones parameters, σ (angstrom) and e/k (K), are from tabulations [22] and a calculation method based on molar volume and compressibility. [205]

7.2.3 Kinetic Parameters

Pre-exponential A factors for isomerization reactions — intramolecular Cl atom transfer to radical sites, are obtained from transition-state theory, usually from the estimated entropies of transition-state structures. Activation energies come from the endothermicity of reactions plus ring strain energy when cyclic TSTs are present.

Detailed estimations on each reaction channel are shown in the tables for QRRK calculations.

7.2.3.1 Abstraction Reactions. Chlorine atom is the species present in highest concentration and the abstraction of Cl by free Cl atoms is a major chain propagation sequence in this reaction system. A review of the literature produced very little in the way of consistent rate parameters for Cl abstraction of Cl from RCl. There were however, a significant number of abstraction rate constant data for R abstraction of a Cl atom from

Cl_2, where R-Cl bonds (75-100 kcal/mol) are significantly stronger than the Cl-Cl bond (57.8 kcal/mol). Review [173] of the abstraction rate constant on a number of RCl + Cl $\leftrightarrow$ R. + Cl_2 reactions with the use of thermochemical properties of relative species and microscopic reversibility <mr> yields an modified Evans-Polanyi relation that Ea_{fwd} (in kcal/mol) = $0.64 \times \Delta_f H°_{rxn} + 9.7$. Literature combined with <mr> yield the pre-exponential Arrhenius A factor (per Cl atom) of 4.44E+13 $cm^3mol^{-1}s^{-1}$. No temperature dependence is evaluated for the reverse direction of RCl + Cl $\rightarrow$ R• + Cl_2.

7.2.3.2 Addition Reactions of Cl Atom to Vinyl Chlorides. Analysis of literature rate constants for Cl atom addition to chlorinated and non-chlorinated olefinic, carbonyl (at carbon) and acetylenic bonds show Ea's of 0.0 or in some cases slightly negative Ea's in NIST Kinetics Database 2Q98. Ea for Cl addition was set to 0.0 kcal/mol. Pre-exponential terms (in $cm^3mol^{-1}s^{-1}$) for Cl atom addition to the above bonds were evaluated (high-pressure limit values) as:

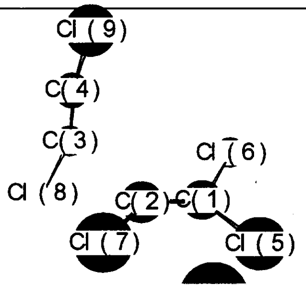
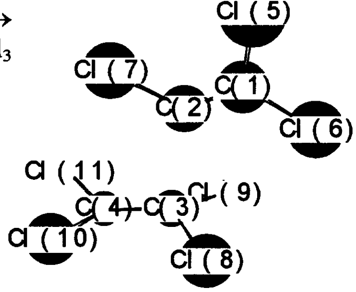
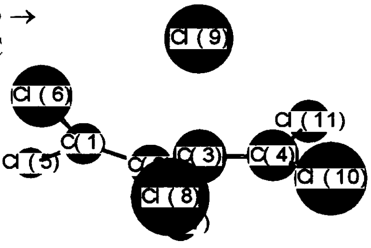
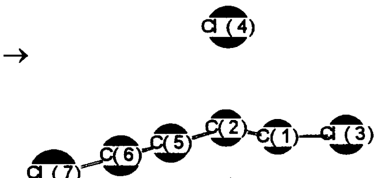
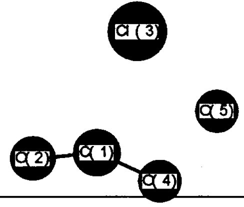
A = 1.25E+13 for Cl + CD/Cl_2 and carbonyl (at carbon) groups.

A = 2.89E+13 for Cl + CT/CD, CT/Cl, CD/Cl/C, CD/Cl/H groups.

7.2.3.3 Combination Reactions. Association reactions of Cl with varied degree of substituted chlorinated alkyl and vinyl radicals are treated with Ea of 0.0 and with high-pressure limit pre-exponential A-factors decreasing with increasing degree of chlorine substitution (see also chapter 5).

7.2.3.4 DFT for Some Transition States. The transition states calculated for several important addition, isomerization, and elimination reactions at B3LYP/6-31G(d,p) level. The geometries of these TS's are listed in Table 7.4.

Table 7.4 Geometries of Transition States at B3LYP/6-31G(d,p) Calculation Level

TS's	Structure	Bond length	(angstrom)	Bond angle	(degree)	Dihedral angle	(degree)
TS1:		r21	1.322				
C=C-C=C• →		r32	2.411	a321	119.52		
$C_2Cl_2 + C_2Cl_3$		r43	1.225	a432	102.85	d4321	-83.44
		r51	1.756	a512	123.55	d5123	-178.17
		r61	1.743	a612	121.86	d6123	1.26
		r72	1.691	a721	130.93	d7213	179.29
		r83	1.664	a832	101.01	d8321	97.83
		r94	1.642	a943	166.40	d9432	3.85
TS2:		r21	1.328				
C=C-C-C• →		r32	2.345	a321	122.37		
$C_2Cl_4 + C_2Cl_3$		r43	1.388	a432	100.22	d4321	179.98
		r51	1.756	a512	122.69	d5123	-179.99
		r61	1.737	a612	123.44	d6123	0.00
		r72	1.700	a721	127.03	d7213	-180.00
		r83	1.749	a832	99.22	d8321	58.40
		r93	1.749	a932	99.22	d9321	-58.43
		r104	1.719	a1043	122.04	d10432	-87.02
		r114	1.719	a1143	122.04	d11432	87.04
TS3:		r21	1.355				
C=C-C-C• →		r32	1.497	a321	126.92		
C=C-C•-C		r43	1.421	a432	120.88	d4321	-154.10
		r51	1.732	a512	122.01	d5123	-175.95
		r61	1.719	a612	124.56	d6123	2.31
		r72	1.757	a721	117.97	d7213	169.55
		r83	1.760	a832	112.74	d8321	62.41
		r93	2.314	a932	107.67	d9321	-50.91
		r104	1.709	a1043	122.53	d10432	-154.09
		r114	1.711	a1143	121.39	d11432	34.35
TS4:		r21	1.243				
C=C-C=C• →		r31	1.628	a312	168.18		
C=C-C•=C		r42	2.386	a421	98.34	d4213	0.00
		r52	1.368	a521	155.43	d5214	179.88
		r65	1.214	a652	179.15	d6521	-179.57
		r76	1.638	a765	179.52	d7654	179.97
TS5:		r21	1.166				
CCl(=O)OO• →		r31	2.307	a312	113.53		
CO_2 + ClO		r41	1.242	a412	149.52	d4123	179.92
		r54	1.635	a541	103.62	d5412	-179.90

7.2.4 Chemkin II for Modeling

Chemkin II program [177] is used for mechanism interpretation, calculation of reverse reaction rates from thermochemical parameters, at reaction time of 2 seconds and at constant pressure and temperature.

7.3 Modeling Results and Sensitivity Analysis

The complete mechanism for pyrolysis and oxidation of 1000 ppmV 1,3-hexachlorobutadiene at 773 to 1373 K and 1 atm air, is listed in Appendix D.

7.3.1 The 1,3-Hexachlorobutadiene

The thermal degradation of 1,3-hexachlorobutadiene is initiated by the breaking of C-Cl bonds which are weaker than the C-C bonds, to generate primary and secondary hexachlorobutadienyl radicals (C_4Cl_5.N and C_4Cl_5.S, respectively) via two unimolecular reactions:

C=C-C=C ↔ C=C-C.=C + Cl ΔHrxn = 73.93

C=C-C=C ↔ C=C-C=C. + Cl ΔHrxn = 83.60

All ΔHrxn's are listed for 298 K in units of kcal/mol. Formation of secondary radicals (C_4Cl_5.S) is energetically favored. Unimolecular reaction of 1,3-C_4Cl_6 to C_4Cl_5.S + Cl is the most sensitive reaction for overall conversion in early to mid stages of reaction. The similar mechanism is also proposed by Taylor et al. [181]

Other reactions important to 1,3-C_4Cl_6 loss include abstraction of Cl by Cl atoms (k_4 and k_5), and addition of Cl (k_8), ClO, and O (k_{222} and k_{223}) in order of importance.

As noted above the abstraction reactions RCl + Cl ↔ R. + Cl_2 are significantly endothermic, but occur in this system due to the relatively high concentrations of Cl atoms and the high temperature. An example of the addition is:

C=C-C=C + Cl ↔ C=C-C-C. (C_4Cl_7.N) ΔHrxn = -13.83

C=C-C=C + Cl ↔ [C=C-C-C.*] ↔ C_2Cl_3 + C_2Cl_4 slow ΔHrxn = +24.09

The rate of Cl addition to 1,3-C_4Cl_6 (k_8) is large compared to that of ClO and O (k_{222} and k_{223}) and to the abstractions by Cl atoms (k_4 and k_5). The reverse beta scission reaction is, however, very fast under the temperature conditions, so this addition reaction's overall effect is small. The C_4Cl_7.N exists in low steady state concentration through the early stages of the reaction and does undergo loss via addition / C_4Cl_7O-Cl, then bond cleavage and disproportionation reactions with ClO.

7.3.2 The C_4Cl_5.S and C_4Cl_5.N

Loss of these initial chlorinated vinylic radicals C_4Cl_5.S and C_4Cl_5.N occurs via O_2 combination to the radical site; a chemical activation reaction that results in rapid formation of chlorinated phosgene and aldehydic species:

C=C-C.=C + O_2 ↔ (overall) C=C-C.=O + $COCl_2$

C_2Cl_3 + O_2 ↔ (overall) COCl + $COCl_2$

The reactions occur through the corresponding vinyl peroxy radicals, their cyclization to an oxetane ring, unimolecular isomerization to an oxirane ring with an oxy radical on one carbon. This oxirane further reacts to form a carbonyl and either an oxy, or alkyl radical adjacent to an oxygen atom. Bond cleavage then occurs at a C-C or C-O bond and formation of a second carbonyl, as previously reported for the oxidation of vinyl radical. [9] (see the reaction path diagram 12, 13, and 17)

7.3.3 Chlorinated Aldehydes and Aldehyde Radicals

Reaction of the aldehydic radicals occurs through relatively low Ea elimination (beta scission), for example:

C=C-C.=O ↔ C_2Cl_3 + CO $\qquad \Delta Hrxn = 27.94$

Loss of the chlorinated aldehydes occurs through Cl addition and subsequent C-C bond cleavage, where the overall reactions are ca. thermoneutral, for example:

$C{=}C{-}C{=}O + Cl \leftrightarrow C{=}C{-}C{-}O. \rightarrow C_2Cl_3 + COCl_2$ ΔHrxn = 21.86

$C{=}C{-}C{=}O + Cl \leftrightarrow C.{-}C{-}C{=}O \rightarrow C_2Cl_4 + CClO$ ΔHrxn = 15.18

C_2Cl_3 is a vinylic radical and reacts rapidly with O_2 to form $COCl_2$ + COCl in a similar reaction as C_4Cl_5.S and C_4Cl_5.N. A reaction path diagram is illustrated in Appendix C.17.

$COCl_2$ (Phosgene) is one of the major chlorinated intermediates produced by the overall oxidation of 1,3-hexachlorobutadiene. Its formation occurs primarily via chemical activation reactions of penta-chlorobutadienyl (C_4Cl_5), trichlorovinyl (C_2Cl_3, see above) and trichloromethyl (CCl_3) radicals with O_2. (Appendix C.12, C.13, C.17, and C.21)

For CCl_3 plus O_2, the CCl_3OO peroxy radical undergoes a Cl atom shift, through transition state which is higher in energy than the reactants. The tight transition state and high isomerization barrier makes the reverse dissociation of CCl_3OO the primary reaction of this adduct.

$CCl_3 + O_2 <\!<\!-\!> CCl_3OO^* \rightarrow$ (slow) $COCl_2 + CO$

The barrier of the above shift is very important to the CCl_4 concentration profiles in this reaction system. CCl_3 will react with Cl and ClO to form CCl_4. (k_{39}, k_{214}) Phosgene is also formed by:

$CCl_3 + ClO \rightarrow CCl_3OCl^* \rightarrow CCl_3O + Cl$ ΔHrxn = -28.87

where CCl_3O rapidly dissociates to Cl + phosgene.

Destruction of phosgene occurs via reaction with O or Cl atoms; the O atom reactions occur by chemical activation addition / elimination and the Cl atom reactions occur by both abstraction and addition / elimination of Cl_2.

$COCl_2 + O \rightarrow COCl + ClO$

$COCl_2 + O \rightarrow CClO_2 + Cl$

$COCl_2 + Cl \rightarrow COCl + Cl_2$

7.3.4 C_2Cl_4 and CCl_4

Tetrachloroethene and tetrachloromethane are the main non-oxygenatd organic intermediates produced in this overall thermal degradation of 1,3-hexachlorobutadiene. C_2Cl_4 is generated to some extent by Cl addition to the C_2Cl_3 moiety and then cleavage of the stronger C-C single bonds. These reactions are slightly endothermic and occur primarily on: 1,3-C_4Cl_6, Cl_2C=CCl-CCl=C=O (C_2Cl_3CClCO), and Cl_2C=CCl-CCl=O (C_2Cl_3CClO):

$C{=}C{-}C{=}C + Cl \rightarrow C_2Cl_4 + C_2Cl_3$ $\Delta Hrxn = 24.09$

$C{=}C{-}C{=}C{=}O + Cl \rightarrow C_2Cl_4 + C.{=}C{=}O$

$C{=}C{-}C{=}O + Cl \rightarrow C_2Cl_4 + COCl$ $\Delta Hrxn = 15.18$

Tetrachloroethylene is also formed by decomposition of C_2Cl_6 and C_2Cl_5 that are formed by $CCl_3 + CCl_3$ combination and by $C_2Cl_3 + Cl_2 \rightarrow C_2Cl_4 + Cl$. It is also formed by Cl addition to Cl_2=CCl-CCl=O as discussed above.

Tetrachloroethene removal occurs by addition of Cl to the double bond; but the reverse reaction is also fast due to the low Ea, ca. 24 kcal/mol, so C_2Cl_5 is present in equilibrium with $Cl + C_2Cl_4$. As with C_4Cl_7 radical, C_2Cl_5 is lost by reactions with ClO, O, and Cl.

$C_2Cl_4 + Cl \rightarrow C_2Cl_5$ $\Delta Hrxn = -23.79$

$Cl + C_2Cl_5$ results in an energized C_2Cl_6 moiety, which dissociates to CCl_3 + CCl_3, $\Delta Hrxn = -4.39$ kcal/mole nearly thermoneutral.

Tetrachloromethane is formed by the reactions involving CCl_3 radical as a precursor species. Important reactions are:

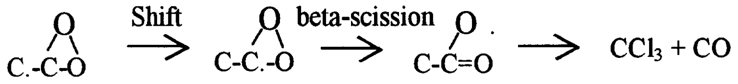
$CCl_3 + Cl \rightarrow CCl_4$ $\Delta Hrxn = -69.59$

$CCl_3 + Cl_2 \rightarrow CCl_4 + Cl$ $\Delta Hrxn = -35.95$

$CCl_3 + ClO \rightarrow CCl_4 + O$ $\Delta Hrxn = -5.38$

The loss of CCl_3 by reactions with O_2 and the dissociation of the CCl_3OO peroxy adduct are critical to the CCl_4 profile versus temperature. The reaction barrier of ClO elimination from CCl_3OO through a ring type transition state to form $COCl_2$) is calculated to be 34.62 kcal/mol at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level. The chemical activation reaction of $CCl_3 + O_2$ are important for conversion of CCl_3 with O_2.

The above reactions are also responsible for the consumption of CCl_4. Other reactions leading to CCl_3 formation are 1,2-Cl atom shift on the oxetane intermediates formed in the chlorovinylic radical reactions with O_2, (see Appendix C.12, C.13 and 1.17):



which is a minor component, ca. 10%, of the C_2Cl_3 radical reactions with O_2. Please note that this is also a "prompt CO_2" formation route and:

C.C=O → CC.=O → CCl_3 + CO ΔHrxn = 11.23

where the rate is controlled by the rate of isomerization, which is ca 11 kcal/mole endothermic plus a 15 kcal/mol barrier.

7.3.5 The CO and CO_2

Carbon monoxide represents the major inorganic intermediate formed by oxidation of 1,3-hexachlorobutadiene. Its production is primarily through thermal decomposition of species containing a carbonyl group, such as C_2Cl_3CClCO, $C_2Cl_3C.O$ and COCl via the following beta scission reactions:

C=C-C=C=O + Cl → C=C-C. + CO ΔHrxn = -48.33

C=C-C.=O → C=C. + CO ΔHrxn = 27.94

COCl → Cl + CO ΔHrxn = 6.40

In absence of source of hydrogen (to form OH), oxidation of CO to CO_2 is essentially due to the reactions with ClO, O and O_2:

$CO + O_2 \rightarrow CO_2 + O$

$CO + O + M \rightarrow CO_2 + M$

$CO + ClO \leftrightarrow C.OCl(=O) \rightarrow CO_2 + Cl$

These oxidation processes are quite slow in comparison with the oxidation of CO by OH radical as usually occur in oxidation of hydrocarbons.

7.3.6 The Cl_2

Molecular chlorine as a final product is generated via recombination of Cl atoms:

$Cl + Cl + M \rightarrow Cl_2 + M$

This is due to the high concentration of Cl atoms released in the thermal degradation of 1,3-hexachlorobutadiene. Cl_2 is also formed by reaction of $Cl + ClO \rightarrow Cl_2 + O$ (k-160) which is thermoneutral, only 3.3 kcal/mol endothermic. O atom is, however, quite reactive and loss of O to form the relatively more stable carbonyls shifts this reaction toward Cl_2.

The calculated concentration of Cl_2 decreases above 1150K due to its unimolecular decomposition (k-45). $Cl + ClO \rightarrow Cl2 + O$ is in equilibrium with the small O atom concentration, controlling the Cl_2/ClO ratio.

7.3.7 The ClO Reactions

ClO reactions play an important role in these reaction systems of carbon, oxygen and chlorine. Chain propagation reactions include ClO combination with a radical site to form an energized R-OCl* moiety, then the breaking of the weaker O-Cl bond, and the formation of a stronger C-O bond (RO.) plus Cl atom. The chloro-alkoxy radical (RO.) will undergo rapid reaction to Cl + a carbonyl with the alkoxy formation have barriers of only several kcal/mole.

R.Cl + ClO → (overall) R'C=O + 2Cl

ClO will also react with alkyl radicals, in a disproportion like reaction, which effectively loses one radical moiety, which is exothermic by 5 to 30 kcal/mol.

R. + ClO → RCl + O

Example

$CCl_3 + ClO \rightarrow CCl_4 + O$ Hrxn = -5.38

The O atoms can add to double bonds to generate carbonyls plus Cl atoms.

$$\mathrm{C{=}C + O \rightarrow C.\text{-}C\text{-}O. \rightarrow COCl_2 + CCl_2}$$

$$\mathrm{\rightarrow C.\text{-}C{=}O + Cl}$$

ClO can add to an unsaturated bond forming C.COCl radicals which can then cleave a C-C or C-Cl bond and the ROCl can undergo unimolecular dissociation to RO. + Cl. — chain branching.

Some C6 to C8 species are detected by GC/MS, and we include them in the mechanism. A C_2Cl_3 radical addition to a vinyl acetylene (C=CC≡C) forms a secondary C_6Cl_7 linear adduct (k178) that can undergo unimolecular isomerization to a primary C_6Cl_7 radical then cyclization (k181) to form a highly reactive cyclic-C_6Cl_7-2,4-diene radical. This radical will undergo beta scission by loss of a Cl atom (k182) and/or under go further addition reaction to form higher molecular weight chlorocarbons.(k195). We show an example here, which illustrates molecular weight growth and formation of chlorobenzenes from small, low molecular weight chlorocarbons.

7.4 Comparison of Elementary Reaction Model with Experimental Profiles

Figure 7.1a shows the computed concentration profiles of 1,3-C_4Cl_6, CO, CO_2 and Cl_2 and the experimental data. The modeling result of the Cl_2 concentration profile shown in Figure 7.1a is the concentration of Cl_2 plus one half of Cl atom. Figure 7.1b shows the comparisons for the other three major products, $COCl_2$, CCl_4, and C_2Cl_4. where relative good agreement is obtained for CCl_4 and C_2Cl_4, but the calculated $COCl_2$ levels are almost twice the experimental values.

7.5 Summary

Modeling on the thermal reaction of 1,3-hexachlorobutadiene in air at 773-1373 K is presented for the reactant, intermediate and product profiles. Elementary kinetic parameters governing the destruction of 1,3-C_4Cl_6 have been determined between 773-1373 K for ninety stable intermediate and final products ranging from C1 to C8. Phosgene is the major chlorinated intermediate passing through a maximum concentration at around 973K. A detailed chemical kinetic model consisting of 230 reactions and 90 species is developed for the oxidation and pyrolysis reactions, and evaluated by comparing computed profiles with the corresponding experimental data. Important reactions responsible for the major species profiles as a function of temperature are identified. Relatively good agreement is obtained between computed and experimental profiles.

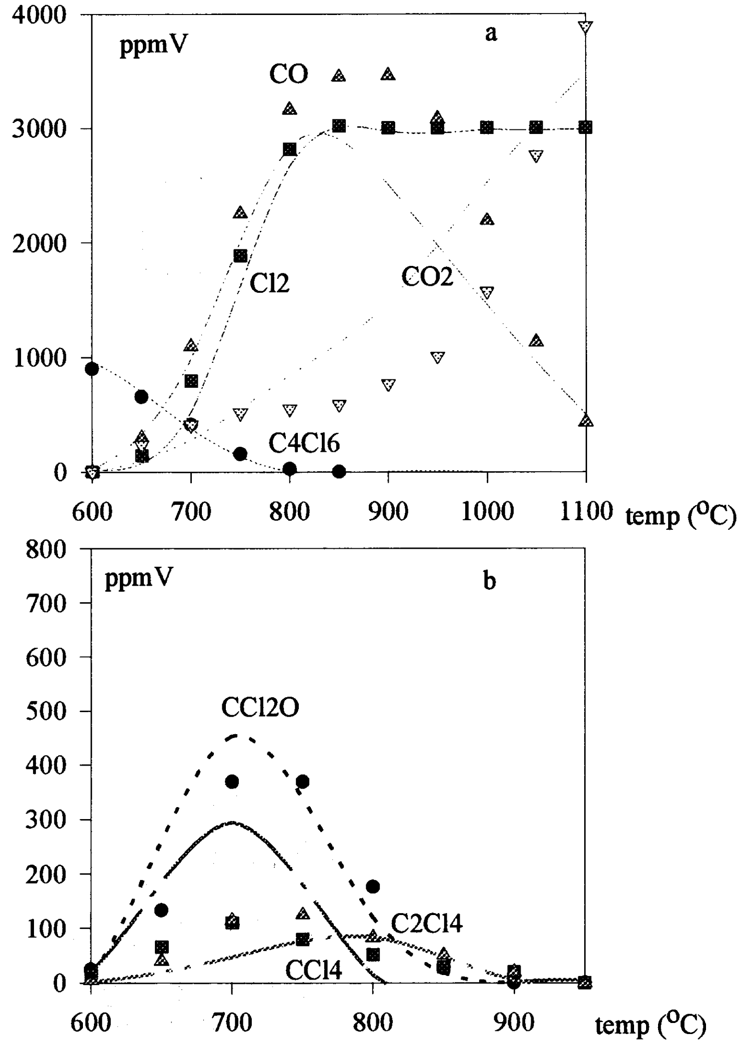


Figure 7.1 The Oxidation of 1000 ppmV 1,3-C_4Cl_6 in 1 atm Air: Expt vs Modeling.

CHAPTER 8

MODELING STUDY ON THE GAS-PHASE PYROLYSIS AND OXIDATION OF 2-CHLOROPHENOL AT 400-800°C AND 1 ATM (4% O_2 IN HE)

8.1 Overview

Yang et al. [206] has studied experimentally the formation of furans by gas-phase reactions of chlorophenols. They compared the product yields of phenol, 2-CP, 3-CP, 4-CP, 2,3-DCP, 2,4-DCP, 2,6-DCP, and 3,4-DCP, under pyrolysis (He) and oxidative pyrolysis (8% O_2 + 92% N_2) conditions at 400-850°C. They summarized three major reaction channels important for the formation of furan products from chlorophenol pyrolysis. (1) chlorophenoxy radical coupling reactions result in the formation of primary DD, DCDF, MCDF-ol (monochlorodibenzofuranol); (2) H substitution reactions that produce phenol and chlorobenzene, then secondary MCDF and DF; (3) CO elimination reactions result in naphthalene and then BNF (benzonaphthofurans). In the 3-CP experiments, the presents of oxygen did not affect the distribution of DF isomers. The total yield of dibenzofurans was affected, however, with the presence of oxygen resulting in higher yield and lower formation temperature. Their results support the hypothesis that the formation of PCDF in gas-phase flow reactor occurs by ortho-ortho carbon coupling of phenoxy radicals. It is also shows that the isomer distributions of PCDF are controlled by statistical factors and steric effects. Semi-empirical MNDO method was used to calculated standard enthalpies and entropies of PCDF. In the 2-CP experiments, the primary polychlorodibenzofuran (PCDF) product is 4,6-DCDF, and the secondary PCDF product is 4-MCDF and DF.

Weber and Hagenmaier studied the formation of PCDD/Fs from various chlorophenols pyrolysis in gas phase. [207] In the pyrolysis of ortho-chlorophenol the only DCDF formed is 4,6-DCDF in addition of 4-MCDF, 1-MCDD, DD, the chlorinated POP and DOHB, this result is very similar to Yang et al. [206]

The formation mechanism of polychlorinated dibenzo-*p*-dioxins (PCDDs) from 2,4,5-trichlorophenol has been studied for the first time by theoretical B3LYP/6-311++G(2d,2p)//B3LYP/6-31G(d',p') + ZPVE(B3LYP/6-31G(d',p')) calculations. [208] They examined twelve possible formation pathways from 2,4,5-TCP to three PCDD isomers (2,3,7,8-TCDD, 1,2,4,7,8-PeCDD, and 1,2,4,6,7,9-HxCDD). Four pathways by direct intermolecular condensation of two 2,4,5-TCP molecules and eight pathways via radicals were considered. H_2O elimination is not considered in this paper.

Fadli et al. have performed the experimental studies on the thermal oxidation of chlorobenzene at 575-825°C. [50] The major products are CO_2, HCl, Cl_2, CO, CH_4, C_2H_2, C_2H_4, C_2H_3Cl, vinylacetylene, furan, and benzene.

Lin et al. studied the oxidation of 2,4-dichlorophenol in supercritical water. [209] The properties of supercritical water, such as the complete miscibility in all proportions with oxygen, negligible surface tension, high diffusivity, low viscosity, and low solubility of inorganic salts, are unique in the destruction and removal of hazardous wastes. Hazard organic compounds are completely oxidized and converted to carbon dioxide and water in a reaction time of less than a few minutes. The development and rational design, control, optimization, analysis, and evaluation of the SCWO (supercritical water oxidation) processes require a knowledge of governing reaction kinetics and potential by-product formed from the oxidation of real pollutants, especially when one considers that incineration of wastes can produce undesired condensation products such as dioxins and furans. Ghorishi and Altwicker have studied the rapid formation of polychlorinated dioxins/furans during the heterogeneous combustion of 1,2-dichlorobenzene and 2,4-dichlorophenol. [51]

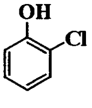
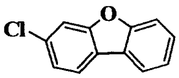
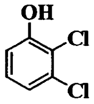
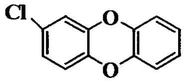
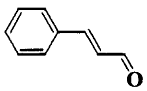
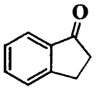
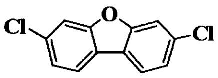
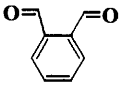
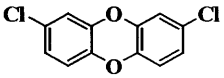
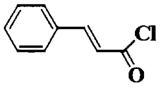
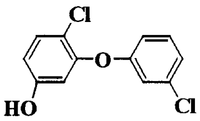
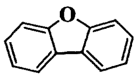
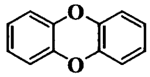
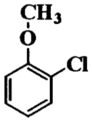
2-chlorophenol		**2-chlorodibenzofuran**	
dichlorophenol		**2-chlorodibenzo-p-dioxin**	
cinnomic aldehyde			
1-indanone		**2,8-dichlorodibenzofuran**	
phthalic anhydride		**2,8-dichlorodibenzo-p-dioxin**	
cinnomoyl chloride		**2,4'-dichloro-5-hydroxydiphenyl ether**	
dibenzofuran			
dibenzo-p-dioxin		**2-chloroanisole**	

Table 8.1 Reactant (2-CP, or 2-CA) and Other Products Detected in the Experiments.

8.2 Experimental Results

The experiments are conducted at University of Dayton, OH, by Dr. Sidhu's research group. All experiments were performed using a high-temperature flow reactor coupled with an in-line gas chromatograph/mass spectrometer (GC/MS) system designed to simulate the reaction conditions in a combustor post-flame zone. 4±1 ppmV 2-chlorophenol is presented in the temperature range 400-800 K and 4% O_2 in 1 atmosphere pressure He at 2 seconds residence time. The structure of reactant, 2-chlorophenol, and products of detected in the experiment are modeling is listed in Table 8.1.

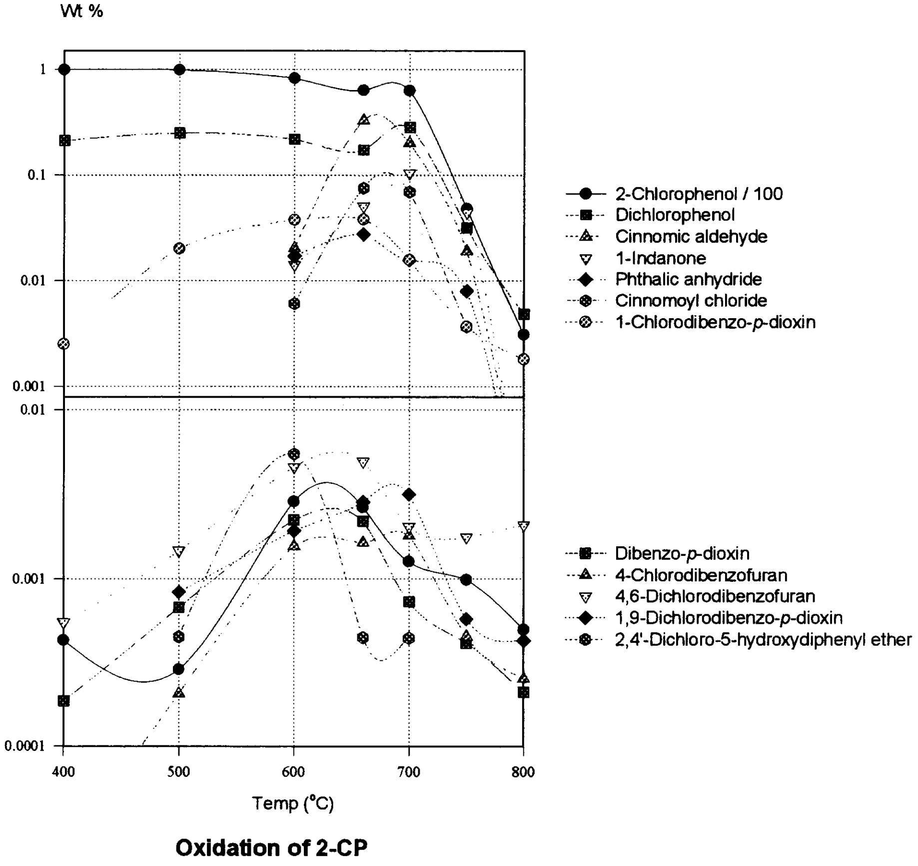


Figure 8.1 Product Profiles for 2-CP Oxidation.

8.3 Modeling

Thermochemical parameters of major and minor chlorinated intermediates and products (stable molecules) generated by pyrolysis and/or oxidation of 2-chlorophenol are estimated and an elementary reaction mechanism is developed for conversion to higher molecular weight products (dibenzo-*p*-dioxins and furans) under fuel rich conditions. Important reaction pathways and bond energies are analyzed.

A detailed chemical kinetic model is still in construction. It will be evaluated by comparing the computed profiles of major products with the corresponding experimental profiles. It consists of reversible reactions and species, with the Chemkin II Kinetics code [177,200] for integration. Since most of rate parameters and thermochemical properties characterizing these reactions are unknown, a consistent set of procedures for estimating their values is developed and reported.

Unimolecular dissociation and isomerization reactions of the chemically activated and stabilized adducts resulting from addition or combination reactions are analyzed by first evaluating thermochemical properties and constructing potential energy diagrams. Thermochemical parameters, $\Delta_f H°_{298}$, $S°_{298}$, $Cp°(T)$ ($300 \leq T/K \leq 1500$), are estimated based on existing experimental or theoretical data and on Group Additivity estimation techniques. High-pressure limit rate constants for each channel are obtained from literature or referenced estimation technique. Kinetic parameters for unimolecular and bimolecular (chemical activation) reactions are calculated using a modified multi-frequency QRRK analysis for k(E). The modified strong collision formalism of Gilbert et al. is used for fall-off (β collision) with the steady-state assumption on the energized adduct(s). [16,17,201] It is shown to yield reasonable results and provides a framework by which the effects of temperature and pressure can be evaluated in complex reaction systems.

8.3.1 Thermochemical Property Estimations

8.3.1.1 The $\Delta_f H°_{298}$ of 2-CP and Final Products. Standard enthalpies of formation of all major products are calculated by isodesmic reactions with total energies obtained at B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) levels of theory. Molecular structures and vibration frequencies are determined at B3LYP/6-31G(d,p) level of theory. Vibration frequencies are scaled for zero point energies and thermal corrections.

Table 8.2 Calculated Total Energies of Some Species in Table 8.1 at 298 K[a,b]

Species	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	ZPVE[c,d]	H_{298}-H_0[d]
2-chlorophenol	-766.9735878	-767.1092016	58.76	4.72
2,4-dichlorophenol	-1226.5740778	-1226.7432928	52.82	5.50
2,6-dichlorophenol	-1226.5716607	-1226.7409687	52.89	5.47
cinnomic aldehyde	-422.8381330	-422.9720671	88.24	6.00
1-indanone	-422.8687944	-422.9975325	89.58	5.37
phthalic anhydride	-532.8482864	-533.0285823	63.64	5.39
cinnomoyl chloride	-882.4567411	-882.6233916	82.78	6.67
Dibenzofuran	-537.1709796	-537.3315606	101.25	5.93
dibenzo-p-dioxin	-612.3648265	-612.5562978	103.38	6.64
4-chlorodibenzofuran	-996.7726770	-996.9668849	95.27	6.73
1-chlorodibenzo-p-dioxin	-1071.9631576	-1072.1883174	97.47	7.44
4,6-dichlorodibenzofuran	-1456.3683240	-1456.5965887	89.42	7.55
1,9-dichlorodibenzo-p-dioxin	-1531.5605090	-1531.8195715	91.53	8.25
2,4'-dichloro-5-hydroxydiphenyl ether	-1532.7511011	-1533.0146452	104.73	9.20
2-chloroanisole	-806.2443718	-806.3875239	76.21	5.63

a: All calculations are based on B3LYP/6-31G(d,p) optimized structures;

b: Total energies (ZPVE and thermal corrections are included) in hartree, 1 hartree = 627.51 kcal/mol;

c: Scaled by 0.9806; [37]

d: In units of kcal/mol.

Total energies, zero-point vibrational energies, and thermal contributions to enthalpy calculated by B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) are listed in Table 8.2. Please go to chapters of chlorophenols and mono- and di-chloro dibenzo-p-dioxins and furans for total energies and thermochemical properties of 2-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, dibenzofuran, dibenzo-p-dioxin, 4-chlorodibenzofuran, 1-chlorodibenzo-p-dioxin, 4,6-dichlorodibenzofuran, and 1,9-dichlorodibenzo-p-dioxin.

Table 8.3 The $\Delta_f H^o_{298}$ (kcal/mol) by Isodesmic Reactions

Isodesmic Reactions	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)[a]
	// B3LYP/6-31G(d,p)	
CH_2=CH-CH=O + CH_2=CH-CH_3 → CH_2=CH-CH=CH_2 + CH_3CHO	-16.21	-15.92
CH_2=CH-CH=O + C_2H_6 → CH_2=CH-CH=CH_2 + CH_3CHO	-17.12	-16.16
3-ph-2-propenal + CH_4 → toluene + CH_2=CH-CH=O	3.54	4.39
1-indanone + cyclohexane → indane + cyclohexanone	-16.81	-15.76
pathalan + 1,3-cyclohexadiene → naphthalene + tetrahydro furan	-4.02	-5.60
pathalic anhydride + 2 × C_2H_5OH → pathalan + 2 × $CH_3C(=O)OH$	-89.61	-90.34
cinnomoyl chloride + + CH_4 → 3-ph-2-propenal + CH_3Cl	-12.41	-11.84
2,4'-dichloro-5-hydroxydiphenyl ether + 4 × benzene → 2 × chlorobenzene + 2 × phenol + biphenyl	-45.11	-44.16
anisole + CH_3OH → phenol + CH_3-O-CH_3	-16.04	-16.90[b]
2-chloro anisole + benzene → chlorobenzene + anisole	-22.11	-22.10
2-chloro anisole + CH_3OH → 2-chlorophenol + CH_3-O-CH_3	-21.53	-22.12

a: values from or average values from B3LYP/6-311+G(3df,2p) are recommended;
b: this value is –18.33 by Pedley et al. [42]

Enthalpies of formation of these species are determined at these two levels by isodesmic reactions as listed in Table 8.3. The values at B3LYP/6-311+G(3df,2p)//B3LYP/6-31g(d,p) are used. $\Delta_f H^o_{298}$ of the references used in Tale 8.3 are listed in Table 8.4.

8.3.1.2 S^o_{298} and $C_p^o(T)$ ($300 \leq T/K \leq 1500$) of 2-CP and Final Products.

Contributions to S^o_{298} and $C_p^o(T)$ from translation, vibrations, and external rotation (TVR) of each species in Table 8.5 are obtained using the rigid-rotor-harmonic-oscillator approximation from the frequencies along with moments of inertia based on the optimized B3LYP/6-31G(d,p) structure, though the aids of "SMCPS" computer program.

[48] Harmonic vibrational frequencies and moments of inertia are calculated for at B3LYP/6-31G(d,p) level on the basis of optimized geometries at this same level of theory.

Table 8.4 The $\Delta_f H^\circ_{298}$ (kcal/mol) for Reference Species (and Literature Citations)

Species	$\Delta_f H^\circ_{298}$ (in kcal/mol)
CH_2=CH-CH_3	4.78±0.19(Pedley et al. [42])
CH_2=CH-CH=CH_2	25.38±0.22(Pedley et al. [42])
CH_3CHO	26.30(Prosen [212])
C_2H_6	-20.08±0.10(Manion [39])
CH_4	-17.38±0.07(Manion [39])
naphthalene	36.05±0.25(Cox et al. [55])
Toluene	12.05±0.14(Pedley et al. [42])
cyclohexane	-29.49±0.19(Pedley et al. [42])
Indane	14.51±0.41(Pedley et al. [42])
cyclohexanone	-55.23±0.21(Wiberg et al. [213])
1,3-cyclohexadiene	25.38±0.22(Pedley et al. [42])
tetrahydro furan	-44.02±0.17(Cox et al. [55])
C_2H_5OH	-56.24±0.07(Cox et al. [55])
$CH_3C(=O)OH$	-103.26±0.12(Cox et al. [55])
CH_3Cl	-19.57±0.12(Pedley et al. [42])
Benzene	19.74±0.17(Pedley et al. [42])
chlorobenzene	12.43±0.31(Pedley et al. [42])
Phenol	-23.04±0.22(Pedley et al. [42])
Biphenyl	43.36±0.48(Pedley et al. [42])
CH_3OH	-48.16±0.07(Pedley et al. [42])
CH_3-O-CH_3	-44.00±0.16(Pedley et al. [42])
2-chlorophenol	-31.51±2.23(Chapter 4)

Table 8.5 Ideal Gas-phase Thermochemical Properties for 2-Chlorophenol and All Major Products

		$\Delta_f H^\circ_{298}$	S°_{298}			C_p° (T)				
				300K	400K	500K	600K	800K	1000K	1500K
2-Chlorophenol	a	-31.51	79.86	27.76	35.76	42.18	47.10	53.76	58.01	64.07
2,4-Dichlorophenol	a	-37.40	86.64	31.62	39.40	45.53	50.14	56.28	60.08	65.34
2,6-Dichlorophenol	a	-35.94	86.07	31.15	38.57	44.45	48.99	55.27	59.32	65.00
cinnomic aldehyde	TVR	0.77	84.53	30.37	40.42	49.13	56.27	66.89	74.26	85.05
1-indanone		-18.17	86.49	32.26	42.89	52.02	59.46	70.42	77.97	88.93
Phthalic anhydride		-90.34	85.61	32.06	41.09	48.50	54.38	62.78	68.32	75.97
Pedley [42]		-88.77								
cinnomoyl chloride	TVR	-15.06	90.41	33.89	44.01	52.51	59.37	69.39	76.25	86.20
Dibenzofuran	b	13.19	89.36	38.64	51.98	63.11	71.99	84.76	93.32	105.48
Dibenzo-*p*-dioxin	b	-14.15	94.43	42.65	56.52	67.99	77.10	90.16	98.88	111.24
4-Chloro dibenzo furan	b	7.94	97.92	42.44	55.54	66.37	74.96	87.22	95.35	106.74
4,6-diChloro dibenzo furan	b	3.02	103.76	46.24	59.09	69.62	77.93	89.69	97.38	108.00
2-Chloro dibenzo-p-dioxin	b	-20.63	104.34	46.56	60.19	71.35	80.16	92.68	100.95	112.51

1,9-Dichloro dibenzo-p-dioxin		-23.22	110.13	50.28	63.67	74.54	83.08	95.11	102.96	113.76
2,4'-dichloro-5-hydroxydiphenyl ether	TVR	-44.16	103.07	49.33	63.33	74.72	83.70	96.48	105.00	117.13
2-chloroanisole	TVR	-21.67	80.25	28.41	37.00	44.42	50.50	59.55	65.85	75.10

a: Taken from Chapter 4;
b: Taken from manuscript of chlorodibenzo-p-dioxins and furans;
TVR: contribustion from IR have not been included, unfinished work.

Thermochemical parameters for all species in Table 8.1, including $\Delta_f H^\circ_{298}$, S°_{298}, and $Cp^\circ(T)$ ($300 \leq T/K \leq 1500$), are listed in Table 8.4 along with appropriate references.

8.3.1.3 Thermochemical Properties Estimation for Reaction Intermediates. Most molecules are calculated primarily by Group Additivity method [68] using "THERM" computer code, [19,165] or from evaluation of literature when available.

Some reaction intermediates, such as (chloro)biphenyl species, (chloro)biphenyl ether species, (chloro)phenyl radicals, chlorophenoxy radical, etc…, are calculated using the same DFT methods as that for 2-CP and other reaction products described above. Thermochemical parameters, $\Delta_f H^\circ_{298}$, S°_{298}, $Cp^\circ(T)$ ($300 \leq T/K \leq 1500$), for all intermediate species in Table 8.1 are also listed in Table 8.4 along with appropriate references.

8.3.1.4 Thermochemical Properties Estimation for Reaction Transition States. The geometries of transition states are optimized at B3LYP/6-31g(d) levels of theory using the Gaussian 98 and the frequencies are obtained at the same level. Transition state (TS) geometries are identified by the existence of only one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations are performed for some TSTs to verify the reaction path.

Forward reaction barrier is obtained from the calculated total energies (E, in hartree) of reactant(s), TS, and product(s); as well as the reported literature enthalpies of reactant(s) and product(s):

$$Ea_f = \frac{\{[E_{TS} - E_{reactant})] + [E_{TS} - E_{product}]\} \times 627.51 + \Delta H^0_{rxn}}{2}$$

Then $\Delta_f H^\circ_{298}$ of TS is the sum of $\Delta_f H^\circ_{298}$ of reactant(s) and Ea_f.

Calculations of S°_{298} and $C_p{}^\circ(T)$ for TS are the same as for stable molecules, except the first imaginary frequency is omitted.

8.3.2 Input Data Requirements for the QRRK Calculation

High-pressure limit pre-exponential factors (Arrhenius A-factors, A(T)) for bimolecular addition and combination reactions are obtained from the literature [68,203,214], and from trends in homologous series of reactions [68,94,203] as described below. Detailed estimations on each reaction channel are shown in the tables for QRRK calculations.

8.3.3 QRRK/Fall-off Kinetic Calculations

Unimolecular dissociation and branching ratios of the adduct formed from combination, addition or insertion reactions to various product channels are calculated using a quantum version of RRK theory (QRRK) to evaluate energy dependent rate constants, k(E), of the adduct. The QRRK calculation of k(E) is combined master equation for fall-off to compute rate constants over a range of temperature and pressure, for the chemical activated adducts as well as for unimolecular reactions of stabilized adducts and molecules.

8.3.4 Chemkin II for Modeling

Chemkin II program [177] is used for mechanism interpretation, calculation of reverse reaction rates from thermochemical parameters, at reaction time of 2 seconds and at constant pressure and temperature.

8.4 Results and Discussion

8.4.1 The 2-Chlorophenol Dissociation

The dissociation of 2-chlorophenol (Figure 8.2, Table 8.6) is initiated by the elimination of hydroxyl H atom to generate 2-chloro phenoxy radical. Two other paths for dissociation of 2-chlorophenol require higher energies.

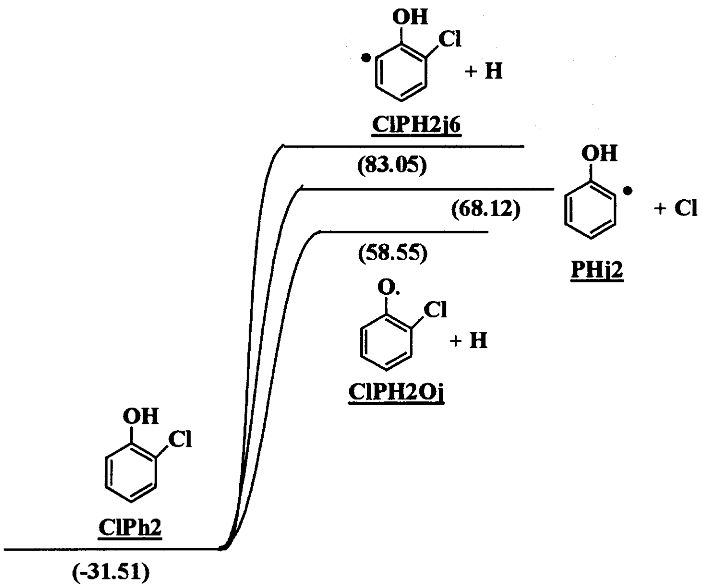


Figure 8.2 PE Diagram for Dissociation of 2-CP (in kcal/mol).

Table 8.6 Input Parameters of 2-CP Dissociation for the QRRK Calculation

Reaction		A	n	Ea
k_1	2-CP → Clph2oj + H	2.67E+16	0	89.74
k_2	2-CP → Phj2 + Cl	3E+15	0	99.39
k_3	2-CP → Clph2j6 + H	1E+15	0	113.49

k_1 A_1 = from phenol → phenoxy + H, [215] $Ea_{-1} = 0$.
k_2 A_2 = from chlorobenzene → phenyl + Cl, [204] $Ea_{-2} = 0$.
k_3 A_3 = from estimation in this work, $Ea_{-3} = 0$.
Lennard-Jones parameters: $\sigma = 5.45$Å; $\varepsilon/k = 643$ K. [22,205]
Reduced frequency sets (from CPFIT [19]) are:

2-CP	Vibration	Modes	Freq. (cm^{-1})
	1	11.808	457.3
	2	16.519	1165.2
	3	4.174	3546.1
	mean	32.5	956.9

Other reactions important to 2-chlorophenol loss include abstraction reactions with H, Cl, OH atoms (Figure 8.3, data in parenthesis are Ea calculated by Okamoto et al. [208]). Isomerization of 2-chlorophenol to its keto form is also considered.

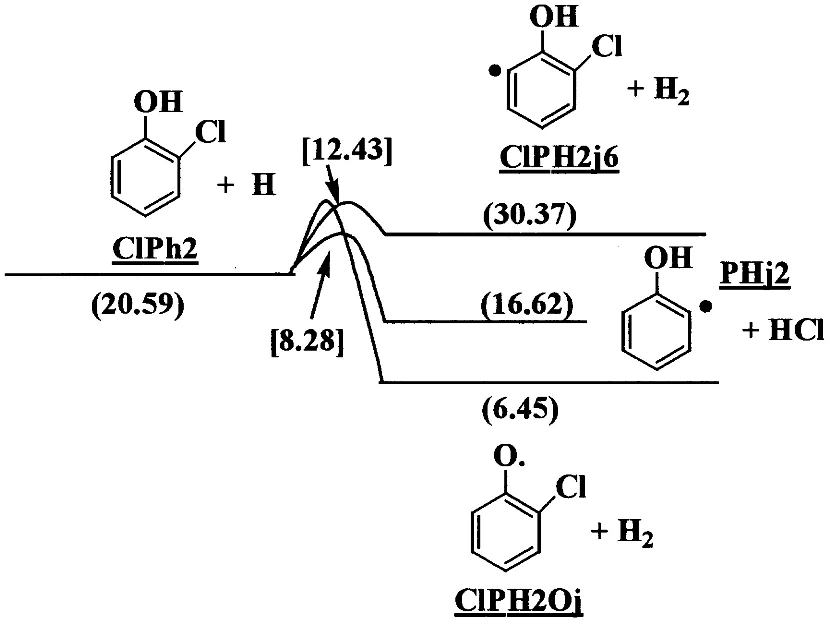


Figure 8.3 PE Diagram for Abstraction of 2-CP by H Atom (in kcal/mol).

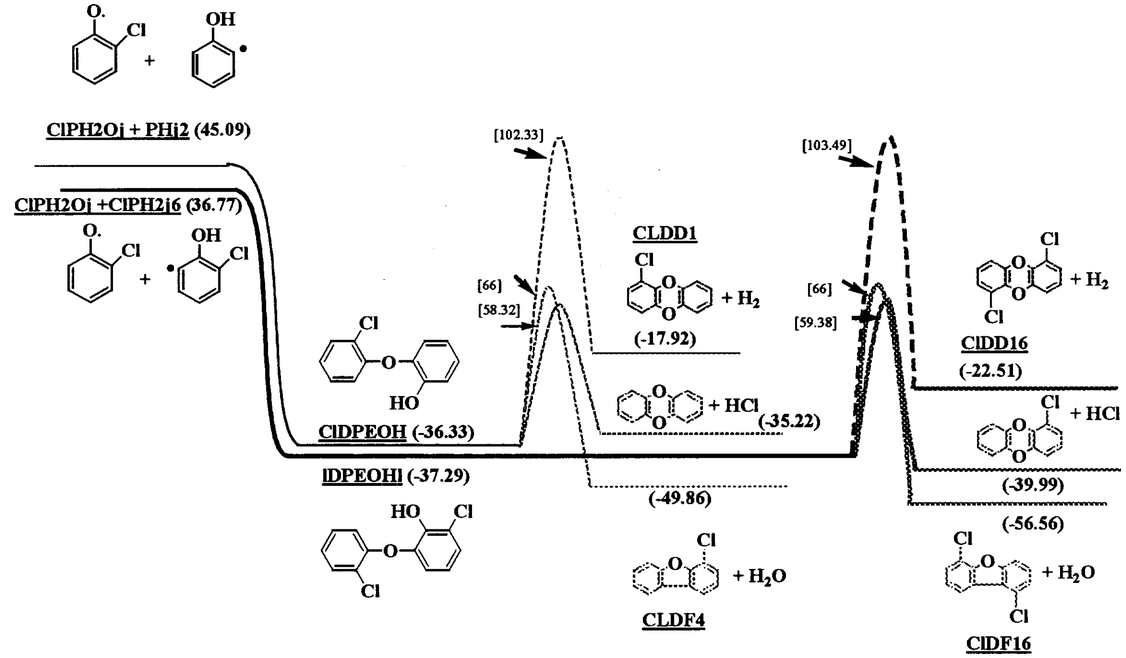


Figure 8.4 PE Diagram for Reactions from Radical + Radical: Lower or no Barrier to PCDD/Fs Formation (in kcal/mol).

8.4.2 Radical-Radical Association Reactions of Primary Radicals

Initial dissociation of 2-chlorophenol produces three primary radicals, chph2oj, phj2, and clph2j6 (see Table 8.3). Radical-radical association reactions occur for chph2oj + phj2, and chph2oj + clph2j6 rapidly since activation energies are zero. (Figure 8.4, Tables 8.7 and 8.8)

Table 8.7 Input Parameters of Chph2oj + Clph2j6 Radical-Radical Association for the QRRK Calculation

Reaction		A	n	Ea
k_1	Clph2oj + Clph2j6 → LDPEOHL	2.5E+13	0	0
k_{-1}	LDPEOHL → Clph2oj + Clph2j6	7.28E+15	0	69.98
k_2	LDPEOHL → CLDF16 + H2O	1E+13	0	60.40
k_3	LDPEOHL → CLDD1 + HCl	1E+13	0	55.98
K_4	LDPEOHL → CLDD16 + H2	1E+13		103.45

k_1 A_1 = from phenoxy + phenoxy → adduct, [216] $Ea_1 = 0$.

k_{-1} from k_1 and microscopic reversibility <MR>.

k_2 A_2 = from estimation in this work, Ea_2 = from p,p'-biphenol → (tphohphohxh2o) → dibenzofuran + H_2O, calculated in this work.

k_3 A_3 = from estimation in this work, Ea_3 = calculated in this work, (59.38 in ref. [208]).
K_4 A_4 = from estimation in this work, Ea_4 = from ref. [208].
Lennard-Jones parameters: $\sigma = 7.5Å$; $\varepsilon/k = 859$ K. [22,205]
Reduced frequency sets (from CPFIT [19]) are:

LDPEOHL	Vibration	Modes	Freq. (cm^{-1})
	1	35.260	492.2
	2	23.250	1298.0
	3	5.991	3386.2
	mean	64.5	835.1

Table 8.8 Input Parameters of Chph2oj + Phj2 Radical-Radical Association for the QRRK Calculation

Reaction		A	n	Ea
k_1	Clph2oj + phj2 → CLDPEOH	2.5E+13	0	0
k_{-1}	CLDPEOH → Clph2oj + phj2	2.2E+16	0	77.03
k_2	CLDPEOH → CLDF4 + H2O	1E+13	0	60.40
k_3	CLDPEOH → DD + HCl	1E+13	0	55.89
K_4	CLDPEOH → CLDD1 + H2	1E+13		102.29

k_1 A_1 = from phenoxy + phenoxy → adduct, [216] $Ea_1 = 0$.
k_{-1} from k_1 and microscopic reversibility <MR>.
k_2 A_2 = from estimation in this work, Ea_2 = from estimation in this work
k_3 A_3 = from estimation in this work, Ea_3 = calculated in this work, (58.32 in ref. [208]).
K_4 A_4 = from estimation in this work, Ea_4 = from ref. [208].
Lennard-Jones parameters: $\sigma = 7.5Å$; $\varepsilon/k = 859$ K. [22,205]
Reduced frequency sets (from CPFIT [19]) are:

CLDPEOH	Vibration	Modes	Freq. (cm^{-1})
	1	34.694	525.5
	2	23.273	1361.1
	3	6.533	3438.9
	mean	64.5	896.0

The reactions occur through the corresponding radical + radical association to activated adducts, the adducts can stabilized to biphenyl ether, or cyclization via intramolecular H_2O and HCl molecular eliminations to mono- and di-chloro dibenzo-p-dioxins and furans. The Ea for intramolecular H_2O molecular elimination is estimated as 60.40 kcal/mol from calculation on non-chlorinted species, p,p'-biphenol → dibenzofuran + H_2O at B3LYP/6-31G(d,p) level, and the two HCl molecular eliminations in Tables 4 and 5 are 55.98 and 55.89 kcal/mol from B3LYP/6-31G(d,p) calculations, these values are ~2.5 kcal/mol lower than the same data for 2,4,5-trichlorphenol. [208]). It is seen that the activation energies for H_2O and HCl molecular eliminations are much less than the Ea for dissociation of adducts back to radical + radical (> 75 kcal/mol), so these reaction are important for the formation of dibenzo-p-dioxins and furans in final products.

8.4.3 Molecule-Radical Addition Reactions of 2-CP with Primary Radical Clph2OJ

2-chlorophenol can have addition reactions with three primary radicals, chph2oj, phj2, and clph2j6, Figure 8.5 shows that PE diagram of 2-chlorophenol has addition reaction with the lowest energy primary radical, clph2oj. The activation energies are ~20 kcal/mol from Okamoto et al. [208] (Figure 8.5, Tables 8.9 and 8.10)

There are two kinds of adduct form this addition reaction in Figure 8.5. These two adducts then undergo H or Cl beta-scission to the chlorinted biphenyl ether (same as in Figure 8.4). The $\Delta_f H^\circ_{298}$ of M_c is estimated from Group Additivity, this species is not stable in B3LYP/6-31G(d,p) calculation. Further work is needed for this species.

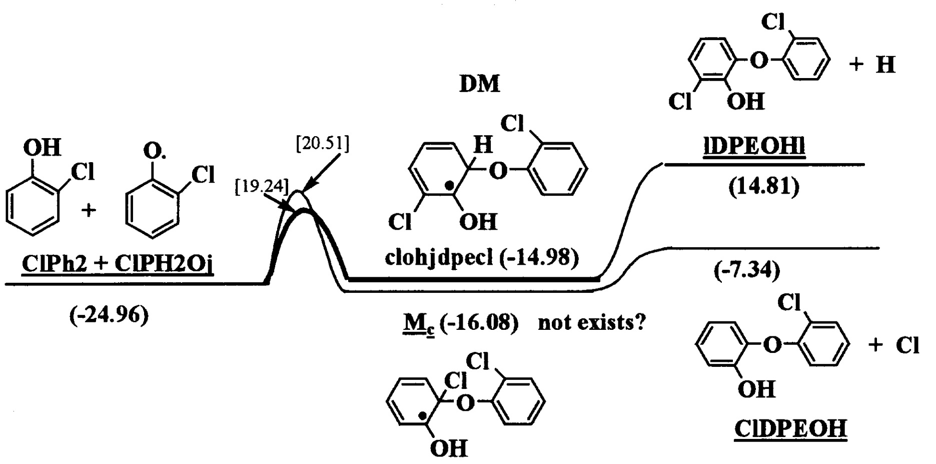


Figure 8.5 PE Diagram for Reactions from Molecule + Radical: Intermediate Barrier (ca. 20 kcal/mol).

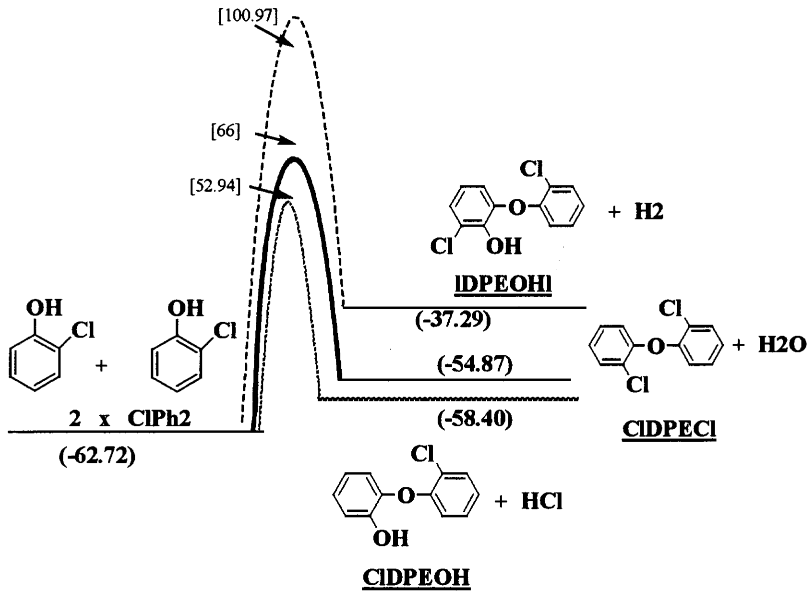


Figure 8.6 PE Diagram for Reactions from Two Stable Molecules: Relatively High Barriers (ca. 60 kcal/mol).

8.4.4 Molecule-Molecule Intermolecular Reactions Between 2-CP

The Ea's in Figure 6 are taken from Okamoto et al. [208]

8.4.5 Oxidation

The above radical (phj2) $+O_2$ has been studied by Zhong and Bozzelli. [217]

APPENDIX A

INPUT PARAMETERS FOR THE QRRK – MASTER EQUATION CALCULATIONS OF $CHCL_3$ PYROLYSIS AND OXIDATION

This appendix lists the input rate constants for the QRRK - master equation analysis for $CHCl_3$ pyrolysis and oxidation, as discussed in Chapter 6.

Set	No	Reactions	A_∞ (in cm^3, mol, s)	n	Ea (kcal/mol)
I	1	$CHCl_3 \rightarrow {}^1CCl_2 + HCl$	1.95E12	0.73	56.56
	2	$CHCl_3 \rightarrow CHCl_2 + Cl$	4.38E16	0	71.57
	3	$CHCl_3 \rightarrow CCl_3 + H$	1.76E15	0	93.13
	4	$CHCl_3 \rightarrow {}^1CHCl + Cl_2$	9.84E11	1.08	107.46
		b: 286.4 (×3.372), 931.3 (×4.449), 2836.6 (×1.179),			
		c: σ = 5.389 Å, e/k = 340.2 K			
II	1	${}^1CCl_2 + CHCl_3 \rightarrow C_2HCl_5$	6.35E+6	1.236	10.29
	-1	$C_2HCl_5 \rightarrow {}^1CCl_2 + CHCl_3$	2.20E+12	1.236	77.36
	2	$C_2HCl_5 \rightarrow C_2Cl_4 + HCl$	1.94E+11	1.005	62.68
	3	$C_2HCl_5 \rightarrow CHCl_2CCl_2 + Cl$	4.09E+16	0	65.53
	4	$C_2HCl_5 \rightarrow CHCl_2 + CCl_3$	7.24E+16	0	71.21
		b: 227.9 (×8.373), 401.0 (×3.613), 1500.2 (×5.514),			
		c: σ = 6.14 Å, e/k = 556.0 K			
III	1	$CCl_2 + CCl_2 \rightarrow C_2Cl_4$	9.12E+12	0	0
	-1	$C_2Cl_4 \rightarrow CCl_2 + CCl_2$	1.71E+17	0	111.12
	2	$C_2Cl_4 \rightarrow Cl + C_2Cl_3$	3.22E+14	0	87.27
		b: 316.2 (×8.203), 990.8 (×3.285), 1893.6 (×0.511)			
		c: σ = 5.64 Å, e/k = 541.9 K			
IV	1	${}^1CCl_2 + CCl_3 \rightarrow C_2Cl_5$	5.37E+12	0	0
	-1	$C_2Cl_5 \rightarrow {}^1CCl_2 + CCl_3$	3.70E+15	0	60.13
	2	$C_2Cl_5 \rightarrow Cl + C_2Cl_4$	5.99E+13	0	12.50
	3	$C_2Cl_5 \rightarrow Cl_2 + C_2Cl_3$	1.07E+14	0	93.40
		b: 100.7 (×4.510), 568.9 (×9.400), 1912.6 (×0.590)			
		c: σ = 6.14 Å, e/k = 556.0 K			
V	1	$CCl_3 + CCl_3 \rightarrow C_2Cl_6$	3.16E12	0	0
	-1	$C_2Cl_6 \rightarrow CCl_3 + CCl_3$	8.61E16	0	68.11
	2	$C_2Cl_6 \rightarrow Cl + C_2Cl_5$	6.70E16	0	69.73
	3	$C_2Cl_6 \rightarrow Cl_2 + C_2Cl_4$	1.07E+14	0	93.40
		b: 293.1 (×8.608), 518.5 (×6.799), 602.1 (×2.093)			
		c: σ = 6.45 Å, e/k = 554.4 K			
VI	1	$CCl_2 + CHCl_2 \rightarrow CHCl_2CCl_2$	9.12E12	0	0
	-1	$CHCl_2CCl_2 \rightarrow CCl_2 + CHCl_2$	2.07E15	0	66.43
	2	$CHCl_2CCl_2 \rightarrow Cl + C_2HCl_3$	1.48E14	0	18.31
	3	$CHCl_2CCl_2 \rightarrow H + C_2Cl_4$	3.82E8	0	44.12
		b: 320.7 (×8.809), 1063.4 (×4.721), 3102.8 (×0.970)			
		c: σ = 6.14 Å, e/k = 556.0 K			
VII	1	$CHCl_2 + CHCl_2 \rightarrow CHCl_2CHCl_2$	9.12E12	0	0
	-1	$CHCl_2CHCl_2 \rightarrow CHCl_2 + CHCl_2$	2.21E16	0	74.03
	2	$CHCl_2CHCl_2 \rightarrow Cl + CHCl_2CHCl$	1.02E17	0	74.90
	3	$CHCl_2CHCl_2 \rightarrow HCl + C_2HCl_3$	1.94E11	1.005	62.68
		b: 436.0 (×8.746), 1000.0 (×7.735), 1810.0 (×1.020)			
		c: σ = 5.91 Å, e/k = 525.9 K			
VIII	1	${}^1CCl_2 + {}^3O_2 \rightarrow {}^3CCl_2OO$	1.00E12	0	4.72
	-1	${}^3CCl_2OO \rightarrow {}^1CCl_2 + O_2$	5.14E12	0	18.13
	2	${}^3CCl_2OO \rightarrow CCl_2O + O$	1.38E13	0	3.5
	3	${}^3CCl_2OO \rightarrow CClO + ClO$	6.85E11	0.47	34.85
		b: 283.8 (×4.570), 431.3 (×3.400), 2000.0 (×0.530)			
		c: σ = 5.486 Å, e/k = 677.3 K			

IX	1	$^{1}CCl_{2} + OH \rightarrow CCl_{2}OH$	5.70E13	0	0
	-1	$CCl_{2}OH \rightarrow CCl_{2} + OH$	3.78E15	0	83.61
	2	$CCl_{2}OH \rightarrow CCl_{2}O + H$	3.82E12	0	26.14
	3	$CCl_{2}OH \rightarrow CClO + HCl$	2.87E12	0.313	38.13
	4	$CCl_{2}OH \rightarrow CHCl_{2}O$	4.12E12	0	48.67
	-4	$CHCl_{2}O \rightarrow CCl_{2}OH$	1.86E13	0	35.41
	5	$CHCl_{2}O \rightarrow CHClO + Cl$	4.00E13	0	9.141
	6	$CHCl_{2}O \rightarrow CHCl_{2} + O$	1.84E15	0	85.11
		b: 391.0 (×5.647), 1314.3 (×1.882), 3801.4 (×0.971)			
		c: σ = 4.70 Å, e/k = 376.0 K			
X	1	$^{1}CCl_{2} + H \rightarrow CHCl_{2}$	1.00E14	0	0.0
	-1	$CHCl_{2} \rightarrow {}^{1}CCl_{2} + O$	1.05E15	0	85.82
	2	$CHCl_{2} \rightarrow CHCl + Cl$	3.31E15	0	83.53
		b: 503.7 (×4.453), 973.3 (×0.676), 2005.3 (×0.870)			
		c: σ = 4.70 Å, e/k = 376.0 K			
XI	1	$^{1}CCl_{2} + O \rightarrow CCl_{2}O$	1.00E13	0	0.0
	-1	$CCl_{2}O \rightarrow CCl_{2} + O$	1.61E16	0	165.12
	2	$CCl_{2}O \rightarrow CClO + Cl$	5.71E15	0	72.41
	3	$CCl_{2}O \rightarrow CO + Cl_{2}$	1.45E14	0	82.46
		b: 503.7 (×4.453), 973.3 (×0.676), 2005.3 (×0.870)			
		c: σ = 4.70 Å, e/k = 376.0 K			
XII	1	$CCl_{3} + O_{2} \rightarrow CCl_{3}OO$	2.27E17	-2.1	0
	-1	$CCl_{3}OO \rightarrow CCl_{3} + O_{2}$	7.65E19	-2.1	19.5
	2	$CCl_{3}OO \rightarrow CCl_{3}O + O$	4.33E15	0	54.18
	3	$CCl_{3}OO \rightarrow CCl_{2}O + ClO$	6.85E11	0.47	34.85
		b: 214.0 (×5.537), 402.8 (×2.782), 1170.5 (×3.181)			
		c: σ = 5.842 Å, e/k = 697.2 K			
XIII	1	$CCl_{3} + O \rightarrow CCl_{3}O$	2.00E13	0	0
	-1	$CCl_{3}O \rightarrow CCl_{3} + O$	1.15E15	0	83.99
	2	$CCl_{3}O \rightarrow CCl_{2}O + Cl$	4.00E13	0	9.14
		b: 367.4 (×7.386), 1109.8 (×1.638), 1945.8 (×-0.024)			
		c: σ = 5.257 Å, e/k = 733.8 K			
XIV	1	$C_{2}Cl_{4} + O \rightarrow C_{2}Cl_{4}O$	5.90E11	0	4.5
	-1	$C_{2}Cl_{4}O \rightarrow C_{2}Cl_{4} + O$	4.71E12	0	47.35
	2	$C_{2}Cl_{4}O \rightarrow CCl_{2}O + CCl_{2}$	8.26E13	0	6.9
	3	$C_{2}Cl_{4}O \rightarrow CCl_{2}CClO + Cl$	6.07E15	0	5
		b: 307.0 (×7.161), 512.8 (×5.824), 601.6 (×1.515)			
		c: σ = 5.997 Å, e/k = 733.8 K			
XV	1	$C_{2}Cl_{3} + O_{2} \rightarrow CCl_{2}{=}CClOO.$	1.21E12	0	-0.829
	-1	$CCl_{2}{=}CClOO. \rightarrow C_{2}Cl_{3} + O_{2}$	2.25E14	0	35.32
	2	$CCl_{2}{=}CClOO. \rightarrow CCl_{2}{=}CClO. + O$	4.32E14	0	20.44
	3	$CCl_{2}{=}CClOO. \rightarrow CCl_{2}CO + ClO$	6.85E11	0.47	34.85
	4	$CCl_{2}{=}CClOO. \rightarrow C.Cl_{2}Y(COO)Cl$	6.41E9	1	23.5
		b: 469.3 (×13.938), 2500.0 (×0.551), 2403.8 (×0.011)			
		c: σ = 4.63 Å, e/k = 380 K			
	-4	$C.Cl_{2}Y(COO)Cl \rightarrow CCl_{2}{=}CClOO.$	5.19E7	1	10.66
	5	$C.Cl_{2}Y(COO)Cl \rightarrow CCl_{2}O + CClO$	6.41E9	1	5

		b: 298.3 (×7.136), 516.8 (×5.705), 601.0 (×1.658)			
		c: σ = 4.63 Å, e/k = 380 K			
XVI	1	$CHCl_2 + OH \rightarrow CHCl_2OH$	5.70E13	0	0
	-1	$CHCl_2OH \rightarrow CHCl_2 + OH$	2.44E16	0	92.25
	2	$CHCl_2OH \rightarrow CHClOH + Cl$	1.19E16	0	78.88
	3	$CHCl_2OH \rightarrow CHClO + HCl$	2.87E12	0.313	60.71
		b: 250.1 (×2.130), 860.6 (×7.903), 3994.2 (×1.467)			
		c: σ = 4.94 Å, e/k = 494.0 K			
XVII	1	$CHCl_2 + O_2 \rightarrow CHCl_2OO$	4.91E15	-1.4	0
	-1	$CHCl_2OO \rightarrow CHCl_2 + O_2$	4.22E17	-1.4	29.89
	2	$CHCl_2OO \rightarrow CHCl_2O + O$	6.46E13	0	54.33
	3	$CHCl_2OO \rightarrow CHClO + ClO$	4.12E12	0	31
	4	$CHCl_2OO \rightarrow CCl_2OOH$	4.12E12	0	42.32
		b: 448.3 (×8.978), 2329.0 (×1.040), 3999.3 (×1.482)			
		c: σ = 5.09 Å, e/k = 542.2 K			
	-4	$CCl_2OOH \rightarrow CHCl_2OO$	8.36E11	0	36.59
	5	$CCl_2OOH \rightarrow CCl_2O + OH$	3.37E15	-1.1	1
	6	$CCl_2OOH \rightarrow CCl_2 + HO_2$	7.26E14	0	59.53
		b: 379.6 (×9.118), 1049.5 (×1.141), 3999.5 (×0.742)			
		c: σ = 5.09 Å, e/k = 542.2 K			
XVIII	1	$CHCl_2 + HO_2 \rightarrow CHCl_2OOH$	5.70E13	0	0
	-1	$CHCl_2OOH \rightarrow CHCl_2 + HO_2$	4.50E15	0	66.20
	2	$CHCl_2OOH \rightarrow CHCl_2O + OH$	1.21E15	0	46.65
	3	$CHCl_2OOH \rightarrow CHClO + H_2O$	4.12E12	0	50
		b: 380.5 (×8.599), 1102.3 (×3.991), 3999.8 (×1.410)			
		c: σ = 5.49 Å, e/k = 677.3 K			
XIX	1	$CHCl_2 + ClO \rightarrow CHCl_2OCl$	5.70E13	0	0
	-1	$CHCl_2OCl \rightarrow CHCl_2 + ClO$	1.28E16	0	67.11
	2	$CHCl_2OCl \rightarrow CHCl_2O + Cl$	4.27E14	0	48.53
	3	$CHCl_2OCl \rightarrow CCl_2O + HCl$	4.12E12	0	50
		b: 381.9 (×8.130), 1110.0 (×2.884), 3997.3 (×0.486)			
		c: σ = 4.94 Å, e/k = 494.0 K			
XX	1	$CCl_3 + OH \rightarrow CCl_3OH$	3.66E13	0	0
	-1	$CCl_3OH \rightarrow CHCl_2 + ClO$	6.64E15	0	78.62
	2	$CCl_3OH \rightarrow CHCl_2O + Cl$	5.10E15	0	58.71
	3	$CCl_3OH \rightarrow CCl_2O + HCl$	1.24E13	0	40
		b: 301.0 (×6.733), 994.5 (×4.130), 4000.0 (×1.137)			
		c: σ = 5.26 Å, e/k = 520.0 K			
XXI	1	$CCl_3 + HO_2 \rightarrow CCl_3OOH$	3.66E13	0	0
	-1	$CCl_3OOH \rightarrow CCl_3 + HO_2$	1.65E16	0	64.52
	2	$CCl_3OOH \rightarrow CCl_3O + OH$	6.90E15	0	46.37
		b: 100.0 (×7.376), 650.3 (×3.968), 1951.7 (×2.657)			
		c: σ = 5.26 Å, e/k = 520.0 K			

XXII: C_2HCl_3 + OH α-addition is taken from Tichenor et al. [218]

XXIII: C_2HCl_3 + OH β-addition is taken from Tichenor et al. [219]

Notes:

a: ΔE_{down} = 1000 cal/mol; b: Reduced frequency sets (frequency in cm^{-1}, degeneracy) from CPFIT [19]; c: Lennard-Jones parameters [22].

I_1	A_{I1} from transition state study (TST) using G3//MP2/6-31G(d,p) calculation level. Ea_{I}, this study, see discussion in text;
I_2	Via I_{-2} and Microscopic Reversibility (MR); A_{I-2} = 5.70E13 from trend analysis for Cl + chloromethyl radical recombination, Ea_{I-2}= 0; [175]
I_3	Via I_{-3} and MR; A_{I-3} = 1.20E14, from trend of Arrhenius parameters for H + methyl and chloromethyl radical recombination, Ea_{I-3}=0; [84]
I_4	From transition state study (TST) using CBS-Q//B3LYP/6-31G(d,p) calculation levels, see text;
II_1	A_{II1} Via A_{II-1} and MR, Ea_{II1}, this study, see discussion in text;
II_{-1}	II_{-1} from TST using CBS-Q//B3LYP/6-31G(d,p) calculations, see text;
II_2	From TST using CBS-Q//B3LYP/6-31G(d,p) calculations;
II_3	Via II_{-3} and MR; A_{II-3} = 2.34E13, from trend analysis for Cl + chlorovinyl radical recombination, Ea_{II-3}= 0; [175];
II_4	Via II_{-4} and MR; II_{-4} from the trend analysis for chloromethyl + chloromethyl radical recombination; [174]
III_1	A_{III1} from trend analysis for chloromethyl + chloromethyl radical recombination ($CHCl_2$ + $CHCl_2$), Ea_{III1}= 0; [35]
III_{-1}	Via III_1 and MR;
III_2	Via III_{-2} and MR; A_{III-2} = 7.24E11 from trend analysis for Cl + chlorovinyl radical recombination, Ea_{III-2}= 0; [175]
IV_1	A_{IV1} from trend analysis for chloromethyl + chloromethyl radical recombination, Ea_{IV1}= 0; [35]
IV_{-1}	Via IV_1 and MR;
IV_2	Via IV_{-2} and MR; A_{IV-2}=3.47E13 from trend analysis for Cl + chloroethylene addition, Ea_{IV-2}= 0; [176]
IV_3	Taken from $CHCl_2CHCl_2 \rightarrow C_2H_4 + Cl_2$; [111]
V_1	A_{V1} from trend analysis for chloromethyl + chloromethyl radical recombination, Ea_{IV1}= 0; [35]
V_{-1}	Via V_1 and MR;
V_2	Via V_{-2} and MR; A_{V-2} = 2.34E13 from trend analysis for Cl + chloroethyl radical recombination Ea_{V-2}= 0; [175]
V_3	Ref. [220];
VI_1	$A_{VI\,1}$ from trend analysis for chloromethyl + chloromethyl radical recombination, $Ea_{VI\,1}$= 0; [35]
VI_{-1}	Via VI_1 and MR;
VI_2	Via VI_{-2} and MR; A_{VI-2} estimated from trend analysis for Cl + chloroethylene additions, Ea_{VI-2}= 0; [176]
VI_3	Via VI_{-3} and MR; A_{VI-3} = 3E9 and Ea_{VI-2}= 3 are estimated here;
VII_1	$A_{VII\,1}$ from trend analysis for chloromethyl + chloromethyl radical recombination, $Ea_{VII\,1}$= 0; [35]
VII_{-1}	Via VII_1 and MR;
VII_2	Via VII_{-2} and MR; A_{VII-2} =7.85E13 from trend analysis for Cl + chloroethyl radical recombination Ea_{VIII-2}= 0; [175]
VII_3	From C_2HCl_5 elimination of HCl (II_2);
$VIII_1$	A_{VII} estimated from the trend of Arrhenius parameters for O_2 + radical additions (literature review). Ea_{VII} is calculated in this study (see text). σ, e/k taken from critical properties for CCl_2OO; (Lydersen method by Won, ref. [85])
$VIII_{-1}$	Via $VIII_1$ and MR;
$VIII_2$	Via $VIII_{-2}$ and MR, A_{VIII-2}=3.50E12 taken from CH_2O + O, [221] $Ea_{VIII\,2}$ estimated in this work;
$VIII_3$	Take from $CCl_3OO \rightarrow CCl_2O + ClO$ (XI) in this study;

IX_1	Estimated from trend analysis for Cl + chloroethyl radical recombination for $CHCl_2$ + Cl; [175]
IX_{-1}	Via IX_1 and MR;
IX_2	Via IX_{-2} and MR; A_{X-2} = 1.23E13 taken from H + CH_3CHO [222], Ea_{IX-2} = 2.4 estimated.
IX_3	Take from $CHCl_2OH \rightarrow CHClO + HCl$ (XV),
IX_4	A_{X4} estimated using TST (loss of one rotor), Ea_{IX4} evaluated from ring strain (28) + ΔH_{rxn} + $Ea_{abstraction}$;
IX_{-4}	Via IX_4 and MR;
IX_5	estimated from $CCl_3O \rightarrow CCl_2O + Cl$; [122]
IX_6	Via IX_{-6} and MR. A_{IX-6} = 9.64E13 and Ea_{IX-6} = 0 are estimated from iso-C_3H_7 + O; [100]
X_1	estimated;
X_{-1}	Via X_1 and MR;
X_2	Via X_{-2} and MR, X_{-2} from trend analysis for Cl + chloroethyl radical recombination for $CHCl_2$ + Cl; [175]
XI_1	A_{VIII1} estimated from CF_2 + O recombination; [223]
XI_{-1}	Via XI_1 and MR;
XI_2	Ref. [224];
XI_3	Ref. [224];
XII_1	Ref. [127];
XII_{-1}	Via IX_1 and MR;
XII_2	Via XII_{-2} and MR, A_{XII-2}=1.27E13 evaluated from A(CH_3O + O) = 1.51E13; [222]
XII_3	Calculated in his work and fitted in THERMKIN, see text;
$XIII_1$	Estimated from $(CH_3)_3C$. + O recombination; [94]
$XIII_{-1}$	Via $XIII_1$ and MR;
$XIII_2$	Ref. [122]
XIV_1	A_{XIV1} from CH_2CCl_2 + O; [225] Ea_{XIV1} estimated;
XIV_{-1}	Via XIV_1 and MR;
XIV_2	Via XIV_{-2} and MR, A_{XIV-2} = 4.0E10 evaluated from CH_2O + C_3H_7 (A = 7.94E10 [226]), Ea_{XI-2} estimated in this work;
XIV_3	XI_3 via XIV_{-3} and MR, A_{XIV-3} = 6.92E13, estimated from trend of Arrhenius parameters for Cl + vinyl chloride additions, [176] Ea_{XIV-3} = 0 estimated.
XV_1	from Ref. [171];
XV_{-1}	Via XV_1 and <MR>;
XV_2	Via XV_{-2} and <MR>, A_{XV-2} = 2E13 (taken as O + CH_3O) [223], Ea_{XV-2}= 3 by estimation;
XV_3	From $CCl_3OO \rightarrow CCl_2O + ClO$, see XII;
XV_4	A_{XV4}, n_{XV4} from estimation, Ea_4 from ref. [227];
XV_{-4}	Via XV_4 and <MR>;
XV_5	A_{XV5}, n_{XV5} from estimation, Ea_5 from ref. [227];
XVI_1	Estimate from $CHCl_2$ + Cl; [176]
XVI_{-1}	Via XVI_1 and <MR>;
XVI_2	Via XVI_{-2} and <MR>, A_{XVI-2} estimated from $CHCl_2$ + Cl; [175]
XVI_3	From QCISD(T)/6-31G(d,p) // B3LYP/6-31G(d,p) calculation, see text;
$XVII_1$	from ref. [228];
$XVII_{-1}$	Via $XVII_1$ and <MR>;
$XVII_2$	Via $XVII_{-2}$ and <MR>, A_{XVII-2} = 2E13 (taken as O + CH_3O) [223], Ea_{XVII-2}= 3 by estimation;
$XVII_3$	From $CCl_3OO \rightarrow CCl_2O + ClO$, see XII;
$XVII_4$	A_{XVII4} from TST loss of one rotor, Ea $_{XVII4}$ evaluated from ring strain (26) + ΔH_{rxn} (5.73) + $Ea_{abstractioon}$ (12.5-5.73/3);
$XVII_{-4}$	Via $XVII_4$ and <MR>;
$XVII_5$	A_{XVII5} Via A_{XVII}-5 and <MR>, A_{XVII-5} = 3E15×$T^{-1.1}$ from CH_3CHO + OH, [229] Ea_{XVII5} from estimation;

$XVII_6$	Via X_{VII}-$_6$ and <MR>, X_{VII}-$_6$ from trend for $CHCl_2$ + Cl [175];
$XVIII_1$	Estimated from $CHCl_2$ + Cl; [175]
$XVIII_{-1}$	Via $XVIII_1$ and <MR>;
$XVIII_2$	Via $XVIII_{-2}$ and <MR>, $A_{XVIII-2}$ = 2E13 (taken as O + CH_3O) [223], $Ea_{XVIII-2}$= 3 by estimation;
$XVIII_3$	$A_{XVIII-3}$ from TST loss of one rotor, Ea_{XVIII3} from estimation;
XIX_1	Estimate from CHCl2 + Cl; [175]
XIX_{-1}	Via XIX_1 and <MR>;
XIX_2	Via XIX_{-2} and <MR>, A_{XIX-2} = 2E13 (taken as O + CH_3O) [223], Ea_{XIX-2}= 3 by estimation;
XIX_3	A_{XIX-3} from TST loss of one rotor, Ea_{XIX3} by estimation;
XX_1	Estimate from CCl_3 + Cl; [175]
XX_{-1}	Via XX_1 and <MR>;
XX_2	Via XX_{-2} and <MR>, A_{XX-2} = 3.66E13 (taken as CCl_3 + Cl combination), [175] Ea_{XX-2}= 0;
XX_3	Via XX_{-3} and <MR>, A_{XX-3} from TST and loss of one rotor, degeneracy=3, Ea_{XX3} by estimation;
XXI_1	Estimate from CCl_3 + Cl; [175]
XXI_{-1}	Via XXI_1 and <MR>;
XXI_2	Via XXI_{-2} and <MR>, A_{XXI-2} = 2E13 (taken as CH_3O + O), [223] Ea_{XXI-2}= 3;

APPENDIX B

MECHANISM FOR THE PYROLYSIS AND OXIDATION OF $CHCL_3$

This appendix lists the full mechanism for the pyrolysis and oxidation of $CHCl_3$, as discussed in Chapter 6.

```
ELEMENTS
C  H  O  CL  AR
END
SPECIES
CHCL3    C2CL4     CO       CCL4      HCL
CO2      C2CL2     C2HCL5    C2CL3     C2HCL3
CHCL2CCL2  C2CL6     H        O        OH
O2       HO2       H2O       H2O2      H2
CL       CL2       CH2CL     CH2CL2    CHCL2
CCL3     CCL2      HOCL      CLO
CLOCL    CHCL2CHCL2 CHCL2CHCL  C2CL5     C2HCL
CHCCL2   CH2CLCCL2O CHCLCCL   CHO      CHCLO
CCLO     CCL2OO    CHCL2OCL  CHCLOCCL2  CCL2CCL2O
CCL2O    CHCL2O    CCL3O     CHCL2OH   CHCLOH
CHCL2OO   CHCL2OOH  CCL2OH    CCL2OOH   CCL3OH
CCL3OO    CCL3OOH   CHCLCCL2OH CHCLCCLOH  CHCLCHCL
CCL2CCL2OH C2CL3OH   CCL2CCLO  CCL2CO    CHCL2CCL2O
CHCL2CCLO  AR       CL2C*CCLOO CL2C*CCLO. CCL3OCL
CHCLCCL3  CL2C.COOCL CL2CCOCLO. O*CC*O    CL2C.OCCLO
CO.CL2CCLO CH2O     CJHCLOOCL  CCL3CCLOH  CCL3CCLO
CCL2CHCLOH CCL2CHCLO. CCL2C.OHCL CCL3C.HOH  CHCL2CHO
CCL3CHO   CCL2CHOH   CHCL2CCLOH CH2CLCCLO  CHCL
CLOCO
CCL2*C:  C4CL6DE13  C4CL4    C2CL     C4CL2
CLC.*C*O  CCL      CLOO     CCL2T
END
REACTIONS
 ! INITIAL STEPS  /
 ! huy-ijck paper
 CHCL3     <=> CCL2 + HCL        1.93E+37  -7.42    63230.    !  1.00E+00 atm,  300-2000 K,  20% err  ::CM  :
 CHCL3     <=> CHCL2 + CL        8.85E+50  -12.94   76497.    !  1.00E+00 atm,  300-2000 K,  2% err  ::CM  :
 CHCL3     <=> CCL3 + H        2.66E+34  -11.86   95343.   !  1.00E+00 atm,  300-2000 K,  3% err  ::CM  :
 CHCL3     <=> CHCL + CL2        3.51E+23  -10.59   109234.   !  1.00E+00 atm,  300-2000 K,  3% err  ::CM  :

 CHCL3 + CL = CCL3 + HCL              2.00E13    0.0     2743.    !nist faster, 73CLY/WAL
!CHCL3 + CL = CCL3 + HCL              4.94E12    0.0     2623.    !nist '96DEM
 CHCL3 + CL = CHCL2 + CL2             1.33E14    0.0     20160.    ! trend=jongwoo
 CHCL3 + H = CHCL2 + HCL              9.00E13    0.0     6560.    !lizhu trend deg=3
 CHCL3 + CHCL2 = CCL3 + CH2CL2           1.81E09    0.0     6399.
!CHCL3 + CCL2 = CCL3 + CHCL2            2.00E12    0.0    29700.    !EST/JWB

!  huy-ijck paper
 CCL2 + CHCL3      <=> C2HCL5          1.52E+55  -14.68    22722.    !  1.00E+00 atm,  300-2000 K,  33% err  ::CM  :
 CCL2 + CHCL3      <=> HCL + C2CL4       1.01E+12  -0.77    15396.    !  1.00E+00 atm,  300-2000 K,  7% err  ::CM  :
 CCL2 + CHCL3      <=> CHCL2CCL2 + CL     1.32E+15  -1.19    15349.    !  1.00E+00 atm,  300-2000 K,  7% err  ::CM  :
 CCL2 + CHCL3      <=> CHCL2 + CCL3      8.24E+10   0.00    15576.    !  1.00E+00 atm,  300-2000 K,  5% err  ::CM  :
 C2HCL5    <=> HCL + C2CL4       8.74E+38  -7.83    70779.    !  1.00E+00 atm,  300-2000 K,  48% err  ::CM  :
 C2HCL5    <=> CHCL2CCL2 + CL     5.40E+47  -9.98    74497.    !  1.00E+00 atm,  300-2000 K,  47% err  ::CM  :
 C2HCL5    <=> CHCL2 + CCL3      1.10E+55  -12.37    81721.    !  1.00E+00 atm,  300-2000 K,  39% err  ::CM  :
!c2hcl5->cl + chcl2c.cl2 Ea =  impt

! FIRST ORDER ADDUCT + FIRST ORDER ADDUCT
! huy-ijck paper
 CCL2 + CCL2       <=> C2CL4          4.46E+48  -11.78    9105.    !  1.00E+00 atm,  300-2000 K,  25% err  ::CM  :
 CCL2 + CCL2       <=> C2CL3 + CL       1.41E+23  -3.11    4705.    !  1.00E+00 atm,  300-2000 K,  9% err  ::CM  :
 C2CL4    <=> C2CL3 + CL       1.56E+26  -3.70    90803.    !  1.00E+00 atm,  300-2000 K,  27% err  ::CM  :

 !c2cl5.inp    trend
 CCL2 + CCL3       <=> C2CL5          3.23E-05  -0.71    -945.    !  1.00E+00 atm,  300-2000 K,  7% err  ::CM  :
 CCL2 + CCL3       <=> C2CL4 + CL       7.41E+12  -0.04     44.    !  1.00E+00 atm,  300-2000 K,  0% err  ::CM  :
 CCL2 + CCL3       <=> C2CL3 + CL2      1.10E+01   2.81    32589.    !  1.00E+00 atm,  300-2000 K,  6% err  ::CM  :
 C2CL5    <=> C2CL4 + CL       2.24E+26  -4.98    12905.    !  1.00E+00 atm,  300-2000 K,  17% err  ::CM  :
 C2CL5    <=> C2CL3 + CL2      3.69E-14  -4.51    88652.    !  1.00E+00 atm,  300-2000 K,  18% err  ::CM  :

!c2cl6.inp      trend
 C2CL5 + CL        <=> C2CL6          1.87E+52  -12.48    11181.    !  1.00E+00 atm,  300-2000 K,  61% err  ::CM  :
 C2CL5 + CL        <=> CCL3 + CCL3      9.41E+30  -4.91    14228.    !  1.00E+00 atm,  300-2000 K,  9% err  ::CM  :
 C2CL5 + CL        <=> C2CL4 + CL2      3.73E+11  -0.46    29202.    !  1.00E+00 atm,  300-2000 K,  3% err  ::CM  :

 C2CL6 + H         <=> C2CL5 + HCL       1.80E+14   0.      5440.    ! lizhu  trend deg=6
```

```
C2CL6 + CL        <=> C2CL5 + CL2        2.66E+14   0.     15640.   ! jongwoo

!C2HCL5 + CL = C2CL5 + HCL              5.78E12    0.00   4137.    !nist 92sen
 C2HCL5 + CL = C2CL5 + HCL              6.30E12    0.00   3300.    !YSW
 C2HCL5 + CL = CHCL2CCL2 + CL2            1.33E14    0.00   15230.   !lizhu add
 C2HCL5 + CL = CHCLCCL3 + CL2             8.88E13    0.00   20640.   !lizhu add
 C2HCL5 + H = CHCL2CCL2 + HCL             9.00E13    0.0    5090.    !lizhu trend  deg=3

 CCL4 + H = CCL3 + HCL                 1.20E14    0.0    5230.    !lizhu trend  deg=4

 C2HCL3 + CL = C2CL3 + HCL              4.00E13    0.     5270.    ! A=est Ea=trend   A=lizhu
 C2CL4 + H = C2CL3 + HCL               1.20E14    0.0    8690.    !lizhu trend
 C2CL4 + CL = C2CL3 + CL2              1.78E14    0.0    28840.   ! jongwoo  trend

!chcl2ccl2b.inp  trend
 CCL2 + CHCL2      <=> CHCL2CCL2        3.08E-02  -1.52   -389.    ! 1.00E+00 atm, 300-2000 K, 21% err ::CM ::
 CCL2 + CHCL2      <=> C2HCL3 + CL      9.62E+12  -0.01    7.      ! 1.00E+00 atm, 300-2000 K,  0% err ::CM ::
 CCL2 + CHCL2      <=> C2CL4 + H        1.36E-02   2.43   -929.    ! 1.00E+00 atm, 300-2000 K,  3% err ::CM ::
 CHCL2CCL2  <=> C2HCL3 + CL         6.46E+39  -8.77   27203.   ! 1.00E+00 atm, 300-2000 K, 13% err ::CM ::
 CHCL2CCL2  <=> C2CL4 + H          1.89E+30 -10.82   45723.   ! 1.00E+00 atm, 300-2000 K, 24% err ::CM ::

 C2HCL3 = CHCLCCL + CL                6.630E13   0.     83720.  ! trend
 C2HCL3 = CHCCL2 + CL                 3.910E14   0.     89610.  ! trend
 C2HCL3 = C2CL2 + HCL                 1.000E14   0.     69314.  ! nist c2h3cl eli hcl

!chcl2chcl2a.inp  trend
 CHCL2 + CHCL2      <=> CHCL2CHCL2        1.66E+83  -23.45   17082.   ! 1.00E+00 atm, 300-2000 K, 38% err ::CM ::
 CHCL2 + CHCL2      <=> CHCL2CHCL + CL    8.92E+10   0.74    5403.    ! 1.00E+00 atm, 300-2000 K, 17% err ::CM ::
 CHCL2 + CHCL2      <=> C2HCL3 + HCL      1.29E+21  -2.50    3375.    ! 1.00E+00 atm, 300-2000 K,  2% err ::CM ::
 CHCL2CHCL2 <=> CHCL2CHCL + CL      2.86E+77  -20.20   86154.   ! 1.00E+00 atm, 300-2000 K, 22% err ::CM ::
 CHCL2CHCL2 <=> C2HCL3 + HCL        1.17E+36  -7.02    50792.   ! 1.00E+00 atm, 300-2000 K, 44% err ::CM ::

  ! FINAL PRODUCT CHANELS
 CCL4 = CCL3 + CL                    2.70E16    0.     66850.  !trend
!CL + CL + M = CL2 + M                 2.23E14    0.00   -1800.  !nist 81BAU
 H + H + M = H2 + M                  5.44E18   -1.30    0.     !nist tsang
 HCL + M = H + CL + M                  4.40E13    0.0    103090. !A=nist 81BAU/DUX, Ear=0 by est
 HCL + H = CL + H2                   2.30E13    0.0    3499.   !nist 68WES/DEH
 CL2 + H = HCL + CL                   1.91E13    0.0    0.      !nist 93SEE/JAY

 CCL4 = CCL2 + CL2                   1.80E+15   0.384  128510. ! Li Zhu Calc=tccl3 at cbsQ//b3

 CL + CCL2 = CCL3                    5.70E13    0.0    0.      !trend  not impt

 CCL2T + M = CCL2 + M                  1.00E+13   0.0    0.     ! est boz
 CCL2T + CL2 = CCL3 + CL                6.89E+11   0.0    0.     ! jongwoo  Ea=0.40*dHrxn+10.32 for C1 clc

!H + CCL2 = CHCL2                    1.00E14    0.0    0.      ! est won

 CL + CL + M = CL2 + M                 2.00E15    0.00   0.     !nist 81BAU

!chcl2.inp
 CCL2 + H          <=> CHCL2           5.82E+24  -4.65    2025.    ! 1.00E+00  atm, 300-2500 K,  8% err, 1.00
 CCL2 + H          <=> CHCL + CL        1.40E+14  -.07     30.      ! 1.00E+00  atm, 300-2500 K,  0% err, 1.00
 CHCL2            <=> CHCL + CL        6.22E+28  -5.28    86555.   ! 1.00E+00  atm, 300-2500 K,  8% err, 1.00

  ! MINOR CHANNEL
 CCL4 + CL = CCL3 + CL2                1.78E14    0.0    16670.  !trend
 C2CL3 = C2CL2 + CL                  1.00E14    0.0    27050.  !BETA-CIS  est from chcl*chcl+cl
!C2CL4 + H = CHCL2CCL2                  2.00E13    0.0    1500.   !lizhu see kerr and moss p121
 CHCLCCL = C2HCL + CL                  3.42E14    0.0    29350.  ! lizhu est from c2h3cl+cl
!CHCLCCL = C2CL2 + H                  2.35E14    0.0    48050.  ! EST LIZHU
 CHCCL2 = C2HCL + CL                  1.39E15    0.0    22030.  ! lizhu est from cl+c2h3cl, Hrxn=20.03
 C2HCL3 + H = CHCLCHCL + CL              3.70E13    0.0    7841.   !nist tsang
!C2HCL3 + H = CHCLCCL + HCL              3.80E14    0.0    13286.  !nist tsang
!C2HCL3 + H = CHCCL2  + HCL              1.00E13    0.0    5500.   !YSW
 C2HCL3 + H = CHCCL2  + HCL              3.00E13    0.0    10350.  !lizhu trend  Ea=12.55+0.23*Hrxn

!CH2CLCCL2 = CH2CCL2 + CL               4.655E41   -9.23   29650.  !LAY
  ! SUBMAJOR
```

```
!CH2CCL2 = CH2CCL + CL              1.88E41  -8.39   93580. !HANK94
!CH2CCL2 = C2HCL + HCL              6.33E32  -5.89   73390. !(")
 !CH2CCL2 + H = CH2CCL + HCL         1.20E13    0.0    5500. !JWB88
 !CH2CCL2 + H = CHCCL2 + H2          1.58E13    0.0    6000. !YSW
 !CH2CCL2 + H = CHCL2CH2            7.21E24   -4.89   7920. !GYW
 !CH2CCL2 + H = C2H3CL + CL          1.00E13    0.00   5800. !GYW
 !CH2CCL2 + CL = CHCCL2 + HCL         2.50E13    0.0    8500. !JWB93
 !C2HCL3 + H = CH2CLCCL2            1.51E23   -4.18   7520. !HO-CM)
 !C2HCL3 + H = CH2CCL2 + CL          1.45E13   -0.01   5830. !(")
 !C2HCL3 + H = CHCL2CHCL            4.03E17   -2.94   2240. !YSW
 !CHCL2CHCL = CHCLCHCL + CL            6.18E13    0.00  14870. !lizhu trend
  !CHCL2CHCL2 + H =CHCL2CHCL+HCL      3.60E12  0.0    4200.
  !CH2CL2 + CL = CH2CL + CL2     1.00E14  0.0   21400.  (K-M)
  !CH2CL2 + CL = CHCL2 + HCL     5.00E13  0.0    2900.  (K-M)
  !CH2CCL = C2HCL + H          6.00E13  0.0   40600.  (")
 !!!

!C2CL3 + CCL3 = C3CL6E              5.37E12  0.   0.
!C2CL3 + CHCL2 = C2CL3CHCL2              9.12E12  0.   0.
!C2CL3 + CCL2 = C2CL3CCL2              9.12E12  0.   0.

 !!OXIDATION PART
 !!!
 CHCL3 + OH = CCL3 + H2O      1.02E04  2.80     199.  !91COH/WES
 CHCL3 + HO2 = CCL3 + H2O2    4.50E10  0.0    12950.  ! Won thesis p181 from 1/4*(ch4+ho2), Ea=Hr+7
 CHCL3 + O = CCL3 + OH        3.00E12  0.0     4968.  !88HER
 CHCL3 + CLO = CCL3 + HOCL    5.00E11  0.0     7600.  !LAY/ADJUSTED
 !CHCL3 + CCLO = CCL3 + CHCLO  3.43E04  2.5    13513.  !lay ?
 CCL4 + OH = CCL3 + HOCL      6.03E11  0.0     4491.  !nist 97ATK/BAU
 CCL4 + O = CCL3 + CLO        3.00E11  0.0     4372.  !(HERRON)
 C2HCL5 + OH = C2CL5 + H2O    9.72E6   2.0     1200.  ! A, Ea=lizhu trend in vcl+oh paper
 !C2HCL5 + O = C2CL5 + OH      1.20E12  0.0     2500.  ! won
 C2HCL5 + O = C2CL5 + OH      3.00E12  0.0     5000.  ! lizhu est from trend
 !C2HCL5 + O2 = C2CL5 + HO2    1.00E12  0.0    45500.  ! won
 !C2HCL5 + HO2 = C2CL5 + H2O2  7.40E09  0.0    10500.
 C2HCL3 + OH = C2CL3 + H2O    9.72E6   2.0     3000.  ! A,Ea=lizhu trend in vcl+oh paper
 !C2HCL3 + O2 = C2CL3 + HO2    2.30E12  0.0    61900.
 !C2HCL3 + O = CHCLO + CCL2    5.900E10 0.        0.  ! lizhu      not impt
 CHCLO = CHO + CL             5.39E29 -5.08   92830.  !HO'92
 CHCLO = CO + HCL             1.10E30 -5.19   92960.  !HO ?
 !CHCLO = CCLO+H               5.40E09  0.0    84700.  !YSW ?
 CHCLO + OH = CCLO + H2O      2.21E13  0.0     2820.  ! nist 92FRA2
 !CHCLO + OH = CCLO + H2O      7.50E12  0.0     1200.  ! ho'92,
 CHCLO + O = CCLO + OH        8.80E12  0.0     3500.  ! HO'92
 !CHCLO + O2 = CCLO + HO2      4.50E12  0.0    41800.  ! won
 CHCLO + CL = CCLO + HCL      7.23E12  0.0     1620.  ! nist 97ATK/BAU
 !CHCLO + CL = CCLO + HCL      2.40E13  0.0      500.  ! ho'92
 CHCLO + H = CHO + HCL        1.20E12  0.0    15000.  ! HO'92
 CHCLO + H = CH2O + CL        6.99E14 -0.58    6360.  ! HO'92
 CHCLO + CLO = CCLO + HOCL    3.00E11  0.0     7000.  ! DEMORE JPL'87, hank p160
 CCL2O + OH = CCLO + HOCL     1.00E13  0.0    15000.  ! boz/est hank 159
 !CCL2O + O = CCLO + CLO       6.00E09  0.0        0.  ! nist 88HER
 CCL2O + O = CCLO + CLO       2.00E13  0.0    17000.  ! boz/est hank 159 dHrxn=7.46
 CCL2O + H = CCLO + HCL       1.20E14  0.0    10400.  ! boz/est hank 159
 CCLO + CL2 = CCL2O + CL      2.52E12  0.0     2960.  !LAY  52BUR/DAI
 !ADJUSTED FROM REFERENCE  2.52E12  0.0     2960.  !52BUR/DAI
 !REFERENCE 3.16E14  0.0   23500.  !(K-M)
 !CHO
 !CHO = CO + H              1.57E14  0.0    15760.  ! 94BAU/COB    not hi-p limit
 CHO = CO + H              5.00E13  0.0    15545.  ! Krasnoperov in He   CHO.inp   *110%   = same
 CHO + OH = CO + H2O          5.00E13  0.0        0.  !  84WAR
 CHO + O = CO + OH           3.00E13  0.0        0.  ! 84WAR
 CHO + O2 = CO + HO2          3.00E12  0.0        0.  ! 84WAR
 CHO + HO2= CO + H2O2          3.00E13  0.         0.  ! 86TSA/HAM
 CHO + H = CO + H2           2.16E14  0.0        0.  !(COMB.CHEM.) nist 93HID/TAN2
 CHO + CL = CO + HCL          1.69E14  0.0        0.  ! nist,+Br,84POU/LAV
 !!CCLO
 CCLO = CO + CL              2.47E14  0.       5882.  ! nist  97ATK/BAU
!CCLO + OH = CO + HOCL        3.30E12  0.0        0.  !(WDC) won hank p159
!CCLO + OH = CO + HOCL        1.30E15  0.0     3319.  !from cclo+cl/ 81BAU/DUX
```

```
!CCLO + O = CO2 + CL         4.00E13  0.0      0.  !(JWB'94)
!CCLO + O2 = CO2 + CLO        1.00E13  0.0      0.  !(JWB EST)
!CCLO + H = CO + HCL         3.50E16 -0.79   5000.  !(BARAT PHD DISS)
!CCLO + CL = CO + CL2         1.30E15  0.     3319.  ! 81BAU/DUX
!CCLO + CLOO = CCL2O + O2     4.79E13  0.0    1139.  !EST FROM CCLO+CLNO, 52BUR/DAI
!!CO
 CO + OH = CO2 + H          1.00E11  0.0      0.  !98BOH/ZETD
 CO + O + M = CO2 + M         6.17E14  0.0   3001.  !86TSA/HAM
 CO + HO2 = CO2 + OH          1.50E14  0.0  23648.  !86TSA/HAM
 CO + O2 =CO2 + O           2.53E12  0.0  47693.  !86TSA/HAM
!CO + CLO = CO2 + CL          6.03E11  0.0  17400.  !KEE,SANDIA/HO'92
! cloco.inp   Florent LOUIS
 CO + CLO          <=> CLOCO            3.87E+24  -6.24   14300.    !  1.00E+00 atm,  300-2000 K,   2% err  ::CM  :
 CO + CLO          <=> CO2 + CL          2.67E+15  -1.18   12294.   .!  1.00E+00 atm,  300-2000 K,   1% err  ::CM  :
 CLOCO     <=> CO2 + CL          1.22E+15  -1.86    5853.    !  1.00E+00 atm,  300-2000 K,   4% err  ::CM  :


!!CHEMISTRY OF CCL2   ! ccl2oo.inp Ea=14 by lay
!ccl2ooa A=est Ea=5.12 calc
 CCL2 + O2         <=> CCL2OO            8.53E+23  -8.59    7426.    !  1.00E+00 atm,  300-2000 K,   2% err  ::CM  ::
 CCL2 + O2         <=> CCL2O + O          1.06E+12  -0.01    5128.    !  1.00E+00 atm,  300-2000 K,   0% err  ::CM  ::
 CCL2 + O2         <=> CCLO + CLO          3.80E+04   1.75   14866.    !  1.00E+00 atm,  300-2000 K,   2% err  ::CM  ::
 CCL2OO    <=> CCL2O + O         5.30E+12  -0.86    2325.    !  1.00E+00 atm,  300-2000 K,  24% err  ::CM  ::
 CCL2OO    <=> CCLO + CLO         3.88E-03  -0.04   27883.    !  1.00E+00 atm,  300-2000 K,  27% err  ::CM  ::
!ccl2oob A,Ea= calc assume no ir, co lower

! ccl2oh.inp   trend chcl2+cl
CCL2 + OH          <=> CCL2OH            2.00E+00  -1.47     427.    !  1.00E+00 atm,  300-2000 K,  19% err  ::CM  ::
 CCL2 + OH          <=> CCL2O + H          3.31E+15  -0.60     534.    !  1.00E+00 atm,  300-2000 K,   3% err  ::CM  ::
 CCL2 + OH          <=> CCLO + HCL          8.46E+13  -0.27     343.    !  1.00E+00 atm,  300-2000 K,   3% err  ::CM  ::
 CCL2 + OH          <=> CHCL2O           6.20E-07  -0.27      16.    !  1.00E+00 atm,  300-2000 K,  29% err  ::CM  ::
 CCL2 + OH          <=> CHCLO + CL          1.10E+12   0.14     131.    !  1.00E+00 atm,  300-2000 K,   3% err  ::CM  ::
 CCL2 + OH          <=> CHCL2 + O          6.66E+00   3.01   12699.    !  1.00E+00 atm,  300-2000 K,   3% err  ::CM  ::
 CCL2OH    <=> CCL2O + H         5.60E+31  -6.36   30828.    !  1.00E+00 atm,  300-2000 K,   7% err  ::CM  ::
 CCL2OH    <=> CCLO + HCL         4.80E+36  -9.15   41057.    !  1.00E+00 atm,  300-2000 K,   9% err  ::CM  ::
 CCL2OH    <=> CHCL2O          1.47E+32  -9.35   49309.    !  1.00E+00 atm,  300-2000 K,  11% err  ::CM  ::
 CHCL2O    <=> CHCLO + CL         4.92E+28  -5.54   18545.    !  1.00E+00 atm,  300-2000 K,   9% err  ::CM  ::
 CHCL2O    <=> CHCL2 + O         1.02E-04  -5.13   86428.    !  1.00E+00 atm,  300-2000 K,   9% err  ::CM  ::
 CHCL2O    <=> CCL2OH          1.45E+16  -5.16   36511.    !  1.00E+00 atm,  300-2000 K,   9% err  ::CM  ::

! ccl2o.inp  use cf2+o = 1.23e13   spin
 CCL2 + O          <=> CCL2O            1.18E-09   0.27   -1572.    !  1.00E+00 atm,  300-2000 K,  21% err  ::CM  ::
 CCL2 + O          <=> CCLO + CL          1.21E+13   0.00       1.    !  1.00E+00 atm,  300-2000 K,   0% err  ::CM  ::
 CCL2 + O          <=> CO + CL2          8.19E+10   0.10     -69.    !  1.00E+00 atm,  300-2000 K,   0% err  ::CM  ::
 CCL2O    <=> CCLO + CL         6.45E+33  -6.49   75447.    !  1.00E+00 atm,  300-2000 K,   4% err  ::CM  ::
 CCL2O    <=> CO + CL2         1.31E+26  -6.55   84061.    !  1.00E+00 atm,  300-2000 K,   4% err  ::CM  ::

!chemistry of chcl2
!chcl2oh.inp   trend  oh=cl
 CHCL2 + OH         <=> CHCL2OH           5.23E-14   2.24   -9820.    !  1.00E+00 atm,  300-2000 K,  34% err  ::CM  ::
 CHCL2 + OH         <=> CHCLOH + CL         4.17E+05   2.35    -886.    !  1.00E+00 atm,  300-2000 K,   9% err  ::CM  ::
 CHCL2 + OH         <=> CHCLO + HCL         9.44E+16  -1.04     927.    !  1.00E+00 atm,  300-2000 K,   5% err  ::CM  ::
 CHCL2OH   <=> CHCLOH + CL        1.12E+43 -13.81   80480.    !  1.00E+00 atm,  300-2000 K,   6% err  ::CM  ::
 CHCL2OH   <=> CHCLO + HCL        1.58E+36  -7.37   43589.    !  1.00E+00 atm,  300-2000 K,  22% err  ::CM  ::

!chcl2oo.inp     97DEM/SAN
 CHCL2 + O2         <=> CHCL2OO           4.47E+40  -9.49    6859.    !  1.00E+00 atm,  300-2000 K,  27% err  ::CM  ::
 CHCL2 + O2         <=> CHCL2O + O         1.95E+17  -1.37   34218.    !  1.00E+00 atm,  300-2000 K,   6% err  ::CM  ::
 CHCL2 + O2         <=> CHCLO + CLO         1.47E+17  -1.67    7742.    !  1.00E+00 atm,  300-2000 K,   9% err  ::CM  ::
 duplicate
 CHCL2 + O2         <=> CCL2OOH           1.03E-05  -0.58   17160.    !  1.00E+00 atm,  300-2000 K,  11% err  ::CM  ::
 CHCL2 + O2         <=> CCL2O + OH         4.22E+15  -1.29   17196.    !  1.00E+00 atm,  300-2000 K,   5% err  ::CM  ::
 CHCL2 + O2         <=> CCL2 + HO2         1.07E+05   2.15   40239.    !  1.00E+00 atm,  300-2000 K,  16% err  ::CM  ::
 CHCL2 + O2         <=> CJHCLOOCL          1.38E+03  -3.46   27226.    !  1.00E+00 atm,  300-2000 K,  28% err  ::CM  ::
 CHCL2 + O2         <=> CHCLO + CLO         6.75E+15  -1.29   28172.    !  1.00E+00 atm,  300-2000 K,   5% err  ::CM  ::
 duplicate
 CHCL2OO   <=> CHCL2O + O        2.63E+28  -7.79   63695.    !  1.00E+00 atm,  300-2000 K,   5% err  ::CM  ::
 CHCL2OO   <=> CHCLO + CLO        6.79E+29  -5.84   34740.    !  1.00E+00 atm,  300-2000 K,   6% err  ::CM  ::
 CHCL2OO   <=> CCL2OOH         6.36E+31  -7.26   46243.    !  1.00E+00 atm,  300-2000 K,   6% err  ::CM  ::
 CHCL2OO   <=> CJHCLOOCL        1.86E+29  -7.65   57544.    !  1.00E+00 atm,  300-2000 K,   6% err  ::CM  ::
```

```
 CCL2OOH   <=> CCL2O + OH       6.28E+15  -1.92    4688.   ! 1.00E+00 atm, 300-2000 K,  8% err ::CM ::
 CCL2OOH   <=> CCL2 + HO2       1.51E-13  -0.01   57599.   ! 1.00E+00 atm, 300-2000 K,  6% err ::CM ::
 CCL2OOH   <=> CHCL2OO          1.92E-06  -0.03   34641.   ! 1.00E+00 atm, 300-2000 K,  6% err ::CM ::
 CJHCLOOCL <=> CHCLO + CLO      1.57E+37  -7.93   25986.   ! 1.00E+00 atm, 300-2000 K, 14% err ::CM ::
 CJHCLOOCL <=> CHCL2OO          5.25E+20  -6.10   32980.   ! 1.00E+00 atm, 300-2000 K, 13% err ::CM ::

!chcl2ooh  use trend ho2=cl
 CHCL2 + HO2       <=> CHCL2OOH       2.19E+52 -15.27    5982.   ! 1.00E+00 atm, 300-2000 K,  9% err ::CM ::
 CHCL2 + HO2       <=> CHCL2O + OH    9.64E+13  -0.07      69.   ! 1.00E+00 atm, 300-2000 K,  0% err ::CM ::
 CHCL2 + HO2       <=> CCL2O + H2O    4.51E+07   0.94    -288.   ! 1.00E+00 atm, 300-2000 K,  2% err ::CM ::
 CHCL2OOH  <=> CHCL2O + OH       2.06E+44  -9.54   51401.   ! 1.00E+00 atm, 300-2000 K, 19% err ::CM ::
 CHCL2OOH  <=> CCL2O + H2O       3.24E+47 -11.76   57979.   ! 1.00E+00 atm, 300-2000 K, 11% err ::CM ::

! chcl2ocl.inp  use trend ocl=cl
 CHCL2 + CLO       <=> CHCL2OCL       1.01E+45 -13.78    4368.   ! 1.00E+00 atm, 300-2000 K,  7% err ::CM ::
 CHCL2 + CLO       <=> CHCL2O + CL    2.20E+15  -0.50     478.   ! 1.00E+00 atm, 300-2000 K,  3% err ::CM ::
 CHCL2 + CLO       <=> CCL2O + HCL    5.94E+11  -0.02     283.   ! 1.00E+00 atm, 300-2000 K,  4% err ::CM ::
 CHCL2OCL  <=> CHCL2O + CL       2.32E+40  -8.54   47160.   ! 1.00E+00 atm, 300-2000 K, 16% err ::CM ::
 CHCL2OCL  <=> CCL2O + HCL       1.14E+43 -10.18   52117.   ! 1.00E+00 atm, 300-2000 K, 10% err ::CM ::

!ccl3oh.inp
 CCL3 + OH        <=> CCL3OH         7.85E+50 -15.95    4524.   ! 1.00E+00 atm, 300-2000 K,  7% err ::CM ::
 CCL3 + OH        <=> CCL2OH + CL    3.07E+13   0.02     247.   ! 1.00E+00 atm, 300-2000 K,  1% err ::CM ::
 CCL3 + OH        <=> CCL2O + HCL    4.87E+19  -2.25    1350.   ! 1.00E+00 atm, 300-2000 K,  3% err ::CM ::
 CCL3OH    <=> CCL2OH + CL       3.10E+54 -13.47   77793.   ! 1.00E+00 atm, 300-2000 K,  8% err ::CM ::
 CCL3OH    <=> CCL2O + HCL       2.81E+30  -5.56   49985.   ! 1.00E+00 atm, 300-2000 K, 29% err ::CM ::

! ccl3oo.inp   calc'd  old=nist
 CCL3 + O2        <=> CCL3OO         2.92E+46 -12.17    6115.   ! 1.00E+00 atm, 300-2000 K,  8% err ::CM ::
 CCL3 + O2        <=> CCL3O + O      2.17E+15  -0.79   35838.   ! 1.00E+00 atm, 300-2000 K,  7% err ::CM ::
 CCL3 + O2        <=> CCL2O + CLO    6.51E+09   0.23   15627.   ! 1.00E+00 atm, 300-2000 K,  2% err ::CM ::
 CCL3OO    <=> CCL3O + O         3.22E+00  -1.23   52891.   ! 1.00E+00 atm, 300-2000 K, 26% err ::CM ::
 CCL3OO    <=> CCL2O + CLO       3.64E+07  -1.20   33447.   ! 1.00E+00 atm, 300-2000 K, 26% err ::CM ::

!ccl3o.inp    (ch3)3C. + o
CCL3 + O         <=> CCL3O          4.49E-05  -0.64     229.   ! 1.00E+00 atm, 300-2000 K, 27% err ::CM ::
 CCL3 + O        <=> CCL2O + CL     2.08E+13  -0.01       6.   ! 1.00E+00 atm, 300-2000 K,  0% err ::CM ::
 CCL3O     <=> CCL2O + CL        1.02E+18  -2.61    7410.   ! 1.00E+00 atm, 300-2000 K, 11% err ::CM ::

!ccl3ooh   trend ccl3+cl
 CCL3 + HO2       <=> CCL3OOH        9.03E+27  -6.09    1543.   ! 1.00E+00  atm, 300-2500 K, 18% err, 1.00
 CCL3 + HO2       <=> CCL3O + OH     1.35E+14   -.18     194.   ! 1.00E+00  atm, 300-2500 K,  1% err, 1.00
 CCL3OOH          <=> CCL3O + OH     7.59E+49 -11.33   51108.   ! 1.00E+00  atm, 300-2500 K, 18% err, 1.00

!c2hcl3oha from tak
 C2HCL3 + OH      <=> CCL2CHCLOH      1.58E+60 -18.65    7650.   ! 1.00E+00 atm, 300-2000 K,  6% err ::CM ::
 C2HCL3 + OH      <=> C2CL3OH + H     4.46E-11   6.31    3006.   ! 1.00E+00 atm, 300-2000 K, 13% err ::CM ::
 C2HCL3 + OH      <=> CCL2CHOH + CL   3.28E+05   2.10   -1553.   ! 1.00E+00 atm, 300-2000 K,  0% err ::CM ::
 duplicate
 C2HCL3 + OH      <=> CCL2CHCLO.      4.09E-21   2.56     -68.   ! 1.00E+00 atm, 300-2000 K, 96% err ::CM ::
 C2HCL3 + OH      <=> CHCL2CCLO + H   1.32E-22   9.01    8379.   ! 1.00E+00 atm, 300-2000 K, 24% err ::CM ::
 C2HCL3 + OH      <=> CHCL2CHO + CL   1.41E-14   6.50    7451.   ! 1.00E+00 atm, 300-2000 K, 15% err ::CM ::
 C2HCL3 + OH      <=> CHCL2 + CHCLO   1.98E-12   6.61    7615.   ! 1.00E+00 atm, 300-2000 K, 10% err ::CM ::
 C2HCL3 + OH      <=> CCL2C.OHCL      7.49E+61 -17.95   19999.   ! 1.00E+00 atm, 300-2000 K, 45% err ::CM ::
 C2HCL3 + OH      <=> C2CL3OH + H     1.57E-18   8.51    8321.   ! 1.00E+00 atm, 300-2000 K, 20% err ::CM ::
 C2HCL3 + OH      <=> CHCL2CCLO + H   5.73E-17   7.78    8663.   ! 1.00E+00 atm, 300-2000 K, 21% err ::CM ::
 C2HCL3 + OH      <=> CHCLCCLOH + CL  5.00E-07   5.12    5163.   ! 1.00E+00 atm, 300-2000 K,  8% err ::CM ::
 C2HCL3 + OH      <=> CCL3C.HOH       3.86E+59 -18.74    8002.   ! 1.00E+00 atm, 300-2000 K,  5% err ::CM ::
 C2HCL3 + OH      <=> CCL3CHO + H     1.11E-11   6.61   18203.   ! 1.00E+00 atm, 300-2000 K, 15% err ::CM ::
 C2HCL3 + OH      <=> CCL2CHOH + CL   6.29E+04   2.39   -1197.   ! 1.00E+00 atm, 300-2000 K,  0% err ::CM ::
 duplicate
 CCL2CHCLOH <=> C2CL3OH + H       6.83E+34 -11.31   42102.   ! 1.00E+00 atm, 300-2000 K, 27% err ::CM ::
 CCL2CHCLOH <=> CCL2CHOH + CL     1.07E+39  -8.87   23834.   ! 1.00E+00 atm, 300-2000 K, 14% err ::CM ::
 CCL2CHCLOH <=> CCL2CHCLO.        1.54E+29 -10.48   46612.   ! 1.00E+00 atm, 300-2000 K, 26% err ::CM ::
 CCL2CHCLOH <=> CCL2C.OHCL        6.81E+34 -11.31   42102.   ! 1.00E+00 atm, 300-2000 K, 27% err ::CM ::
 CCL2CHCLOH <=> CCL3C.HOH         2.75E+34  -7.26   22397.   ! 1.00E+00 atm, 300-2000 K, 11% err ::CM ::
 CCL2CHCLO. <=> CHCL2CCLO + H     7.74E+19  -6.03   30956.   ! 1.00E+00 atm, 300-2000 K, 20% err ::CM ::
 CCL2CHCLO. <=> CHCL2CHO + CL     1.84E+28  -7.28   20779.   ! 1.00E+00 atm, 300-2000 K, 22% err ::CM ::
 CCL2CHCLO. <=> CHCL2 + CHCLO     1.00E+31  -6.23   17175.   ! 1.00E+00 atm, 300-2000 K, 23% err ::CM ::
 CCL2C.OHCL <=> C2CL3OH + H       1.06E+50 -12.63   48530.   ! 1.00E+00 atm, 300-2000 K, 16% err ::CM ::
```

```
CCL2C.OHCL <=> CHCL2CCLO + H       1.81E+52  -13.64   49223.   ! 1.00E+00 atm, 300-2000 K, 17% err ::CM ::
CCL2C.OHCL <=> CHCLCCLOH + CL      3.01E+38  -8.24    31885.   ! 1.00E+00 atm, 300-2000 K, 12% err ::CM ::
CCL3C.HOH  <=> CCL3CHO + H         1.13E+08  -5.56    49887.   ! 1.00E+00 atm, 300-2000 K, 26% err ::CM ::
CCL3C.HOH  <=> CCL2CHOH + CL       1.55E+27  -5.25    14090.   ! 1.00E+00 atm, 300-2000 K, 21% err ::CM ::

!c2hcl3ohb tak
C2HCL3 + OH        <=> CHCLCCL2OH        1.51E+24  -9.24    450.    ! 1.00E+00 atm, 300-2000 K, 130% err ::CM ::
C2HCL3 + OH        <=> CHCLCCLOH + CL    6.60E+05   2.30    1550.   ! 1.00E+00 atm, 300-2000 K,   1% err ::CM ::
duplicate
C2HCL3 + OH        <=> CHCL2CCLOH        5.71E+39  -14.03   5090.   ! 1.00E+00 atm, 300-2000 K, 54% err ::CM ::
C2HCL3 + OH        <=> C2CL3OH + H       7.99E-14   7.28    4221.   ! 1.00E+00 atm, 300-2000 K, 17% err ::CM ::
C2HCL3 + OH        <=> CHCL2CCLO + H     4.18E-12   6.50    4594.   ! 1.00E+00 atm, 300-2000 K, 18% err ::CM ::
C2HCL3 + OH        <=> CHCLCCLOH + CL    4.25E+02   2.85    1500.   ! 1.00E+00 atm, 300-2000 K,   3% err ::CM ::
duplicate
C2HCL3 + OH        <=> CH2CLCCL2O        5.98E-25   3.98    9652.   ! 1.00E+00 atm, 300-2000 K, 29% err ::CM ::
C2HCL3 + OH        <=> CCL2O + CH2CL     1.83E-11   6.48    10085.  ! 1.00E+00 atm, 300-2000 K, 18% err ::CM ::
C2HCL3 + OH        <=> CH2CLCCLO + CL    1.01E-08   5.12    10086.  ! 1.00E+00 atm, 300-2000 K, 18% err ::CM ::
CHCLCCL2OH <=> CHCLCCLOH + CL    8.06E+20  -3.38    9127.   ! 1.00E+00 atm, 300-2000 K, 18% err ::CM ::
CHCLCCL2OH <=> CHCL2CCLOH        4.30E+19  -4.08    12107.  ! 1.00E+00 atm, 300-2000 K, 22% err ::CM ::
CHCLCCL2OH <=> CH2CLCCL2O        4.37E+00  -2.30    35969.  ! 1.00E+00 atm, 300-2000 K, 21% err ::CM ::

CHCL2CCLOH <=> C2CL3OH + H       3.84E+20  -6.58    38930.  ! 1.00E+00 atm, 300-2000 K, 19% err ::CM ::
CHCL2CCLOH <=> CHCL2CCLO + H     1.08E+22  -7.38    39736.  ! 1.00E+00 atm, 300-2000 K, 19% err ::CM ::
CHCL2CCLOH <=> CHCLCCLOH + CL    4.39E+30  -6.19    18070.  ! 1.00E+00 atm, 300-2000 K, 14% err ::CM ::

CH2CLCCL2O <=> CCL2O + CH2CL     2.05E+26  -4.91    13006.  ! 1.00E+00 atm, 300-2000 K, 22% err ::CM ::
CH2CLCCL2O <=> CH2CLCCLO + CL    1.15E+29  -6.30    13001.  ! 1.00E+00 atm, 300-2000 K, 22% err ::CM ::


C2HCL3 + O = C2CL3 + OH      3.12E12  0.0   7000. !FONTIJN'93? won thesis p143
!C2HCL3 + O = CHCLCCL2O      1.941E0  2.55  2020. !(LAY'94)
!C2HCL3 + O = CHCL + CCL2O   2.015E11 -0.1  4500. !(LAY'94)
!C2HCL3 + O = CHCLOCCL2      2.559E0  2.48  0.
!C2HCL3 + O = CCL2+CHCLO     6.15E11  -0.1  2000.

!C2HCL3 + H = CHCL2CHCL      5.49E08  0.0   1000. !(YSW)
!C2HCL3 + H = CHCLCHCL + CL  7.04E12  0.0   7500. !(")

!C2CL4 + CLO = CCL3 + CCL2O   4.00E13  0.0  23000. !(LAY)
C2CL4 + CLO = CCL2CCLO + CL2  4.00E13  0.0  21000. !LAY bozzelli
!SENSITIVE RXN, ADJUSTED BY LAY

!C2CL4 + O2 = C2CL3 + CLOO   4.22E13  0.0  96350. !LAY
!A FROM C2H4+O2=C2H3+HO2, Ea=del Hr + 2
!CLOO = CL + O2              1.69E14  0.   3617. ! nist 92ATK/BAU
!LAY/DISSOC BASED ON 92ATK/BAU H.P.

! ccl2ccl2oh.inp   from tak
C2CL4 + OH        <=> CCL2CCL2OH        3.63E+89  -26.28   18605.  ! 1.00E+00 atm, 300-2000 K, 57% err ::CM ::
C2CL4 + OH        <=> CHCL2CCLO + CL    2.07E+06   1.87    197.    ! 1.00E+00 atm, 300-2000 K,  1% err ::CM ::
C2CL4 + OH        <=> CCL2CCLOH + CL    2.26E-07   5.11    5694.   ! 1.00E+00 atm, 300-2000 K, 14% err ::CM ::
duplicate
C2CL4 + OH        <=> CCL3CCLOH         1.03E+88  -26.59   17354.  ! 1.00E+00 atm, 300-2000 K, 47% err ::CM ::
C2CL4 + OH        <=> CCL2CCLOH+CL      1.18E+10   0.63    674.    ! 1.00E+00 atm, 300-2000 K,  4% err ::CM ::
duplicate
C2CL4 + OH        <=> CCL3CCLO + H      1.03E-01   4.18    2956.   ! 1.00E+00 atm, 300-2000 K, 13% err ::CM ::
CCL2CCL2OH <=> CHCL2CCLO + CL    2.16E+41  -10.34   27049.  ! 1.00E+00 atm, 300-2000 K, 27% err ::CM ::
CCL2CCL2OH <=> CCL2CCLOH + CL    3.22E+30  -10.26   40103.  ! 1.00E+00 atm, 300-2000 K, 38% err ::CM ::
CCL2CCL2OH <=> CCL3CCLOH         6.88E+32  -6.87    18608.  ! 1.00E+00 atm, 300-2000 K, 13% err ::CM ::
CCL3CCLOH  <=> CCL2CCLOH+CL      7.64E+24  -5.99    16039.  ! 1.00E+00 atm, 300-2000 K, 27% err ::CM ::
CCL3CCLOH  <=> CCL3CCLO + H      5.09E+09  -3.10    25581.  ! 1.00E+00 atm, 300-2000 K, 24% err ::CM ::

C2CL4 + OH = C2CL3 + HOCL    3.00E11  0.0   6400. ! WON P143 dHrxn=33.46
!C2CL4 + OH = C2CL3 + HOCL   1.78E14  0.0  29970. ! JONGWOO  OH=CL
C2CL4 + O = C2CL3 + CLO      3.00E07  0.0   7190. !LAY'94/FONT  dHrxn=24.93

!c2cl4o.inp
C2CL4 + O         <=> CCL2CCL2O         4.07E-07  -0.99    3772.   ! 1.00E+00 atm, 300-2000 K,  9% err ::CM ::
C2CL4 + O         <=> CCL2O + CCL2      4.73E+07   0.78    4252.   ! 1.00E+00 atm, 300-2000 K,  1% err ::CM ::
C2CL4 + O         <=> CCL2CCLO + CL     6.76E+11  -0.02    4514.   ! 1.00E+00 atm, 300-2000 K,  0% err ::CM ::
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 CCL2CCL2O  <=> CCL2O + CCL2        3.38E+03   0.17    10073.    !  1.00E+00 atm,  300-2000 K,  16% err  ::CM  ::
 CCL2CCL2O  <=> CCL2CCLO + CL        7.22E+12   -0.97    3475.    !  1.00E+00 atm,  300-2000 K,  19% err  ::CM  ::

!C2CL3OH + OH = CCL2CCLO+H2O 4.00E05   2.1    2500.  !(MDF WARTZ)
 C2CL3OH + OH = CCL2CCLO+H2O 1.55E6   2.2    1000.  !ch3cho+oh=ch2cho+h2o 96TAY/RAH
 C2CL3OH + CL = CCL2CCLO+HCL 2.00E13   0.0    3199.  !91DOB/BEN c2h4+cl A=6.92e13, Ea=3199
 CCL2CCLO = CCL2CO + CL       3.30E14   0.0    15780.  ! Ar=6.92e13(ch2ccl2+cl trend) (nist has ch2co+cl)

 CCL2CO + OH = CCL2O + CHO    6.00E12   0.0    2300.  !(LIKE CH2CO+OH) EST LAY
 CCL2CO + O = CCLO + CCLO     3.00E11   0.0       0.  !(LIKE CH2CO+O)  EST LAY

! CCl2CO.inp
 CCL2CO           <=> CCL2 + CO          6.58E+40   -9.04    38339.    !  1.00E+00  atm,  250-2000 K,   7% err, 1.00

 CHCCL2 + O2 = CCL2O + CHO    3.01E12   0.0    -330.  ! 89RUS/SEE CH2=CCl + O2 = CH2O + ClCO
 CHCLCCL + O2 = CHCLO + CCLO   3.01E12   0.0    -330.  ! 89RUS/SEE CH2=CCl + O2 = CH2O + ClCO

 O2 + M = O + O + M          1.81E18  -1.0   118097.  !  86tsang
!O2 + M = O + O + M          1.20E14   0.0   107794.  ! 84WAR
 H + O2 + M = HO2 + M         6.42E18  -1.0       0.  !(86TSA/HAM)
 H + O2 = OH + O            1.69E17  -0.9   17388.  !(86TSA/HAM)
 O + H2O = OH + OH           4.58E09  1.30  17100.  !(86TSA/HAM)
 H + H2O = H2 + OH           4.59E08  1.6   18570.  ! 84WAR
 H + OH + M = H2O + M         2.22E22  -2.0      0.  !tsang
!H + OH + M = H2O + M         7.50E26  -2.6      0.  !(MILLER 19TH SYMP)??
 O + HO2 = OH + O2           1.75E13   0.0    -397.  !(86TSA/HAM)
 OH + HO2 = H2O +O2           1.45E16  -1.0      0.  !(86TSA/HAM)
 H + HO2 = OH + OH           1.50E14   0.0    1004.  !84WAR
 H + HO2 = H2 + O2           2.50E13   0.0     694.  !84WAR
 H + O + M = OH + M          4.71E18  -1.0      0.  !(86TSA/HAM)
 H2O2 = OH + OH             1.20E17   0.0   45411.  !84WAR
 H2O2 + OH = H2O + HO2        7.83E12   0.0    1331.  !92BAU/COB
 H2O2 + O = OH + HO2          2.80E13   0.0    6405.  !84WAR
 H2O2 + H = OH + H2O          2.41E13   0.0    3974.  ! 86TSA/HAM
 H2O2 + H = HO2 + H2          4.82E13   0.0    7949.  ! 86TSA/HAM
 HCL + O = OH + CL           6.03E12   0.0    6558.  !97DEM/SAN
 OH + HCL = H2O + CL          1.45E12   0.      656.  !97ATK
 HOCL + O = OH + CLO          6.03E12   0.0    2583.  ! 97DEM/SAN
 CL2 + OH = CL + HOCL         8.43E11   0.0    1788.  ! 97DEM/SAN
 CL + HO2 = HCL + O2          1.08E13   0.0    -338.  ! 97DEM/SAN
 CL + HO2 = OH + CLO          2.47E13   0.0     894.  !97ATK
 CL + O2 = CLO + O           8.77E14   0.0   55045.  !81BAU/DUX
!CL + O2 = CLOO             5.04E18  -1.5      0.  ! 97DEM/SAN

!CLOO + CLOO = 2CLO + O2       9.64E12   0.       0.  !  91BAE/HIP

 CLO + CL = O + CL2          1.05E12   0.0    9121.  !81BAU
 CLOCL + CL = CL2 + CLO        3.73E13   0.0    -258.  !97ATK
 OH + HOCL = H2O + CLO        1.81E12   0.0     994.  ! 97DEM/SAN
 CLO + M = CL + O + M         1.07E16   0.0   63580.  !LAY
 HOCL + M = OH + CL + M       2.85E14   0.0   55330.  !Ho/boz, Ar=3.61e13 from ch3+ch3 , Ear=0

!CCL3OCL = CCL3O + CL         5.20E+12  0.      500.  ! ?

 CHCL3 + O2 = CCL3 + HO2      1.00E13   0.0   47200.  ! see rxn below same
!  5.00E03   2.80    199.  !LAY
!ESTIMATED FROM CHCL3 + OH
!ESTIMATED FROM HCO+C3CH=CH2O+C3C., 90TSA Ar=3.25e9, Ear=3.553
!CCL3 + HO2 = CHCL3 + O2      3.01E11   0.0       0.  ! 86TSA/HAM  úC2H5 + HO2 = C2H6 + O2

 CCL2 + CLO = CCL2O + CL      1.00E+12  0.     8000.

! lizhu c4cl6   t17a.inp
 C2CL3+O2         <=> CL2C*CCLOO         1.22E+20   -3.78   -5360.    !  1.00E+00  atm,  700-1400 K,   2% err, 1.00
 C2CL3+O2         <=> CCL2CO+CLO         5.83E+14   -1.14    2899.    !  1.00E+00  atm,  700-1400 K,   0% err, 1.00
 C2CL3+O2         <=> CL2C*CCLO.+O        5.13E+16   -1.30    3560.    !  1.00E+00  atm,  700-1400 K,   0% err, 1.00
 C2CL3+O2         <=> CL2C.COOCL        6.08E+22   -4.50    2767.    !  1.00E+00  atm,  700-1400 K,   0% err, 1.00
 C2CL3+O2         <=> CL2CCOCLO.        6.86E+24   -4.72    4254.    !  1.00E+00  atm,  700-1400 K,   0% err, 1.00
 C2CL3+O2         <=> CO.CL2CCLO        1.64E+15   -2.88    1222.    !  1.00E+00  atm,  700-1400 K,   1% err, 1.00
 C2CL3+O2         <=> O*CC*O+CL         1.59E+23   -3.83    2977.    !  1.00E+00  atm,  700-1400 K,   0% err, 1.00
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C2CL3+O2        <=> CCL2O+CCLO       2.17E+22  -3.67   2826.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
duplicate
C2CL3+O2        <=> CL2C.OCCLO       3.26E+20  -4.59  -2014.   ! 1.00E+00 atm, 700-1400 K,  3% err, 1.00
C2CL3+O2        <=> CCL2O+CCLO       6.27E+23  -3.85   2985.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
duplicate
CL2C*CCLOO      <=> CCL2CO+CLO       7.05E+25  -4.93  30699.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
CL2C*CCLOO      <=> CL2C*CCLO.+O     3.22E+25  -4.50  31726.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
CL2C*CCLOO      <=> CL2C.COOCL       1.73E+39  -9.67  30927.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
CL2C*CCLOO      <=> CL2CCOCLO.       1.04E+41  -9.79  32345.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
CL2C*CCLOO      <=> CO.CL2CCLO       1.46E+31  -7.88  29232.   ! 1.00E+00 atm, 700-1400 K,  1% err, 1.00
CL2C*CCLOO      <=> O*CC*O+CL        3.26E+39  -8.96  31115.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
CL2C*CCLOO      <=> CCL2O+CCLO       6.58E+38  -8.86  31023.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
duplicate
CL2C*CCLOO      <=> CL2C.OCCLO       5.70E+35  -9.32  25739.   ! 1.00E+00 atm, 700-1400 K,  4% err, 1.00
CL2C*CCLOO      <=> CCL2O+CCLO       1.35E+40  -8.98  31131.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
duplicate
CL2C.COOCL      <=> CCL2CO+CLO       1.71E+29  -6.57  26145.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
CL2C.COOCL      <=> CL2C*CCLO.+O     4.23E+36  -8.27  31792.   ! 1.00E+00 atm, 700-1400 K,  3% err, 1.00
CL2C.COOCL      <=> CL2CCOCLO.       7.54E+11  -1.44    625.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
CL2C.COOCL      <=> CO.CL2CCLO       2.41E+02    .37  -2331.   ! 1.00E+00 atm, 700-1400 K,  1% err, 1.00
CL2C.COOCL      <=> O*CC*O+CL        7.77E+09   -.44   -567.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
CL2C.COOCL      <=> CCL2O+CCLO       6.18E+08   -.21   -704.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
duplicate
CL2C.COOCL      <=> CL2C.OCCLO       3.48E+08  -1.58  -5540.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
CL2C.COOCL      <=> CCL2O+CCLO       3.32E+10   -.47   -584.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
duplicate
CL2CCOCLO.      <=> CCL2CO+CLO       1.42E+25  -5.41  66403.   ! 1.00E+00 atm, 700-1400 K,  1% err, 1.00
CL2CCOCLO.      <=> CL2C*CCLO.+O     1.23E+26  -5.29  67507.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
CL2CCOCLO.      <=> CO.CL2CCLO       5.47E+06   -.84   1095.   ! 1.00E+00 atm, 700-1400 K,  1% err, 1.00
CL2CCOCLO.      <=> O*CC*O+CL        9.70E+11  -1.03   2666.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
CL2CCOCLO.      <=> CCL2O+CCLO       6.26E+09   -.49   2546.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
duplicate
CL2CCOCLO.      <=> CL2C.OCCLO       1.60E+15  -3.40  -2890.   ! 1.00E+00 atm, 700-1400 K,  3% err, 1.00
CL2CCOCLO.      <=> CCL2O+CCLO       4.39E+11   -.80   1178.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
duplicate
CO.CL2CCLO      <=> CCL2CO+CLO       1.30E+15  -3.00 100107.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
CO.CL2CCLO      <=> CL2C*CCLO.+O     1.29E+16  -2.90 101231.   ! 1.00E+00 atm, 700-1400 K,  1% err, 1.00
CO.CL2CCLO      <=> O*CC*O+CL        6.81E+11   -.96   2975.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00
CO.CL2CCLO      <=> CCL2O+CCLO       1.81E+11   -.77   9350.   ! 1.00E+00 atm, 700-1400 K,  1% err, 1.00
duplicate
CO.CL2CCLO      <=> CL2C.OCCLO       8.40E+06  -2.18   -557.   ! 1.00E+00 atm, 700-1400 K,  1% err, 1.00
CO.CL2CCLO      <=> CCL2O+CCLO       1.53E+12  -2.31  14142.   ! 1.00E+00 atm, 700-1400 K,  4% err, 1.00
duplicate
CL2C.OCCLO      <=> CCL2CO+CLO       2.23E+19  -4.75 128708.   ! 1.00E+00 atm, 700-1400 K,  3% err, 1.00
CL2C.OCCLO      <=> CL2C*CCLO.+O     2.37E+20  -4.67 129844.   ! 1.00E+00 atm, 700-1400 K,  3% err, 1.00
CL2C.OCCLO      <=> O*CC*O+CL        6.82E+28  -5.87  37774.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
CL2C.OCCLO      <=> CCL2O+CCLO       1.60E+30  -6.37  43822.   ! 1.00E+00 atm, 700-1400 K,  1% err, 1.00
duplicate
CL2C.OCCLO      <=> CCL2O+CCLO       3.20E+52 -12.29  46058.   ! 1.00E+00 atm, 700-1400 K,  2% err, 1.00
duplicate

!CHCL2 + CLO = CHCL3 + O     5.00E+11  0.    1000. ! est
 CHCL2 + CLO = CHCL3 + O     4.64E+11  0.    5660. !from chcl2+cl2 jongwoo

!FOLLOWING ARE NOT IN PRINT VERSION
!CHCL2 + O2 = CHCL2OO       4.54E29 -6.25  2450. !(LARRY)
!CHCL2 + O2 = CHCL2O + O    5.82E00  1.84  31800. !(LAY)
!CHCL2 + O2 = CCL2O + OH    7.07E02  2.65  16260. !(LAY)
!CCL3 + O2 = CCL2OOCL       4.26E04  0.0   3000. !(")

!lizhu add  can't reduce c2cl2
!C2CL2          <=> C2CL+CL         6.37E+15   0.0   108950.   ! trend cl+chcl=ch.
!C2CL2+CL          <=> C2CL+CL2        8.88E+13   0.0    43600.   ! al hfrxn=52.93
!2C2CL          = C4CL2         2.63E+13   0.      0.     ! lgA=13.88-0.23*2
 C2CL2+M          = CCL2*C:+M        2.50E+15  -.64   49700.   ! chad
 CCL2*C:+O2         = CCL2+CO2        1.00E+13   0.0      0.    ! chad
!C2CL+O2        <=> CLC.*C*O+O       2.50E+12   0.0      0.    ! al4
!C2CL+O2        <=> CCL+CO2          2.50E+12   0.0      0.    ! al4
!C2CL+O2        <=> CCLO+CO          5.00E+12   0.0      0.    ! nist c2cl3+o2, no effect
!CCL2*C:+C2CL2       = C4CL4           1.00E+13   0.     20000.
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!CCL2*C:+C2CL4        = C4CL6DE13         1.00E+13   0.    20000.

! LIZHU ADD 8/11/2000 BENZENE   NO CHANGE
!C4CL6DE13           <=> C4CL5.N+CL        1.69E+58  -12.71   101483.   ! 1.00E+00 atm, 700-1400 K,  6% err, 1.00 x N2
!C4CL6DE13+CL        <=> C4CL5.N+CL2        1.78E+14   0.0    26100.   ! al hfrxn=25.62
!C4CL4               <=> C4CL3NV.+CL       2.27E+43  -8.29   107621.   ! 1.00E+00 atm, 700-1400 K,  4% err, 1.00 x N2

!C4CL6DE13+C2CL3      = C6CL9V            2.00E+12   0.0     4500.
!C6CL9V               = C6CL8TE+CL        3.06e+15   0.0    13440.   ! logAr=14.14-0.15*(3) Ear=0
!C6CL8TE              = C6CL7N+CL         1.34e+14   0.0    80840.   ! logAr=13.24-1.38*(1) Ear=0
!C6CL8TE              = C6CL7S+CL         4.42e+15   0.0    88630.   ! logAr=13.24-1.38*(0) Ear=0
!C6CL8TE              = C6CL7V+CL         8.08e+15   0.0    88520.   ! logAr=13.24-1.38*(0) Ear=0
!C6CL8TE+CL           = C6CL7N+CL2         1.33e+14   0.0    25690.   ! al
!C6CL8TE+CL           = C6CL7S+CL2         8.88e+13   0.0    30380.   ! al
!C6CL8TE+CL           = C6CL7V+CL2         8.88e+13   0.0    30380.   ! al
!C4CL6DE13+C2CL       = C6CL7A             2.00E+12   0.0     4500.   !
!C6CL7A               = C6CL6N+CL         6.05E+15   0.0     9250.   ! lgAr=14.14-0.15*2, Ear=0

!C4CL4+C2CL3         <=> C6CL7S            2.00E+12   0.0     4500.   ! Estimated from C2Cl4+C2Cl3 Table 2
!C6CL7S              <=> C6CL6S+CL         3.99E+14   0.0     7320.   ! <MR> Ar=3e13, Ear=0
!C6CL7S              <=> C6CL7N           2.59E+13   0.0     6200.   ! Ar=3.56e13 Eaf=6.2 Table 3
!C6CL7N              <=> CYC6CL7          6.00E+11   0.0     4500.   ! Ar=TST LOSS TWO ROTOR, Ear=4.5 (R.+C=C)
!C4CL4+C2CL          <=> C6CL5A            2.00E+12   0.0     4500.   !
!C6CL5A+CL2           = C6CL6N+CL          2.35E+12   0.0        0.   ! al rev

!C4CL5.N+C2CL2        = C6CL7N            2.00E+12   0.     4500.
!C4CL5.N+C2CL2        = CYC6CL7            2.00E+12   0.     4500.   ! 2+4

!C4CL4+C2CL2          = CYC6CL6           4.47E+11   0.    30100.   ! nist HC's, NOT REAL
!C4CL4+CCL2*C:        = C6CL6N            1.00E+13   0.    20000.   ! insertion, bozzelli

!CYC6CL7             <=> CYC6CL6+CL        6.27E+13   0.0    37270.   ! Ar=3e13, Ear=1 (TST of C6H6+Cl)
!CYC6CL7+CL           = CYC6CL6+CL2        4.44E+13   0.    10700.   ! al dHrxn=1

!C6CL6N               = C6CL5N+CL         5.52E+12   0.    82600.   ! Ar=13.24-1.38*2 trend  deg=2
!C6CL6N+CL            = C6CL5N+CL2         8.88E+13   0.    26970.   ! al
!C6CL6N               = C6CL5S+CL         2.97E+15   0.    91010.   ! Ar=13.24-1.38*(zero) trend
!C6CL6N+CL            = C6CL5S+CL2         4.44E+13   0.    32000.   ! al
!C6CL6N               = C6CL5A+CL         1.50E+15   0.    87910.   ! ar=13.24-1.38*(zero) trend
!C6CL6N+CL            = C6CL5A+CL2         4.44E+13   0.    30380.   ! al
!C6CL6N               = C6CL5T+CL         1.02E+13   0.    79840.   ! ar=13.24-1.38*(zero) trend
!C6CL6N+CL            = C6CL5T+CL2         4.44E+13   0.    26650.   ! al

!C6CL6S               = C6CL5B+CL         5.66E+14   0.    82690.   ! ar=13.24-1.38*1 trend  deg=4
!C6CL6S+CL            = C6CL5B+CL2         1.78E+14   0.    26970.   ! al

!C4CL2+C2CL3         <=> C6CL5S            2.00E+12   0.0     4500.   ! Estimated from C2Cl4+C2Cl3 Table 2
!C6CL5S+CCL4         <=> C6CL6N+CCL3        2.50E+12   0.0    10000.   ! al5
!C6CL5S              <=> C6CL5N           1.91E+13   0.0     6200.   ! Ar=3.56e13 Eaf=6.2  Table 3
!C6CL5S              <=> C6CL4S+CL         1.19E+14   0.0    11320.   ! <MR> Ar=3e13, Ear=0 TABLE 2
!C4CL3NV.+C2CL2       = C6CL5N             2.00E+12   0.0     4500.   ! est
!C6CL5N              <=> C6CL4N+CL         3.63E+14   0.0    26520.   ! <MR> Ar=3e13, Ear=0 TABLE 2
!C6CL5N              <=> CYC6CL5          6.00E+11   0.0     4500.   ! Ar=TST LOSS of TWO ROTOR, Ea =4.5 (R.+C=C)
!CYC6CL5+CCL4        <=> CYC6CL6+CCL3       2.50E+12   0.0    10000.   ! al5T
!CYC6CL5+CL2         <=> CYC6CL6+CL         2.50E+12   0.0    10000.   ! al5T
!CYC6CL5+CL          <=> CYC6CL6           1.00E+14   0.0        0.   ! lizhu

!C4CL5.N+C2CL4        = NC6CL9DE           2.00E+12   0.     4500.
!NC6CL9DE             = C6CL8TE+CL         3.65E+14   0.    14450.   ! logAr=14.14-0.15*(4) Ear=0

! 2CJ*C*C             = CYC6CL6          3.00E+11   0.        0.   ! nist  2 c.=c=ch2
! CJC#C+CJC*C          = C#CCCC*C          3.20E+12   0.        0.   ! trend
! C#CCCC*C+CL          = C6CL7A+CL2         8.88E+13   0.    16110.

END
```

APPENDIX C

INPUT PARAMETERS FOR THE QRRK-MASTER EQUATION CALCULATIONS OF 1,3-C_4CL_6 PROLYSIS AND OXIDATION

This appendix lists the input rate constants for the QRRK - master equation analysis for 1,3-C_4Cl_6 pyrolysis and oxidation, as discussed in Chapter 7.

Set 1 Input parameters of 1,3-C_4Cl_6 dissociation for the QRRK calculation

Reaction		A	n	Ea
k_1	C=C-C=C → C=C-C.=C + Cl	1.47E+15	0	72.14
k_2	C=C-C=C → C=C-C=C. + Cl	6.90E+15	0	81.26
k_3	C=C-C=C → 2 C_2Cl_3	8.92E+16	0	112.24

k_1 from k_{-1} and <MR>. A_{-1} = 1.58E+13 (from secondary R. + CH_3 association [94]); Ea_{-1} = 0.

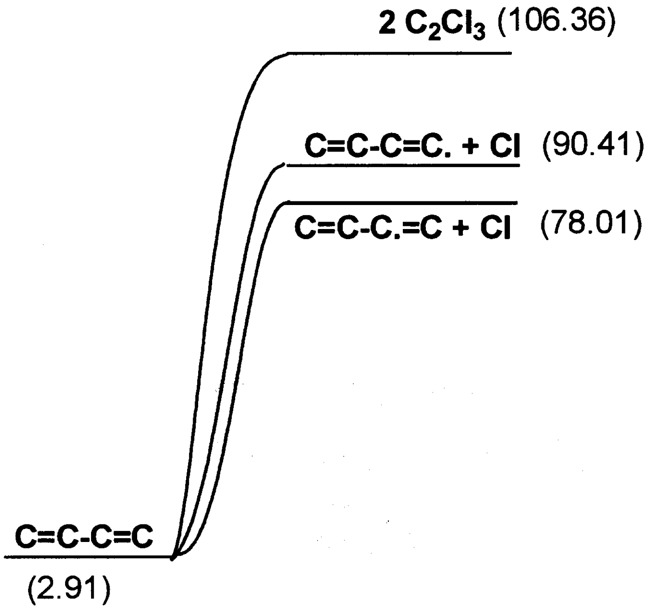
k_2 from k_{-2} and <MR>. A_{-2} = 1.99E+13 (from primary R. + CH_3 association [94]); Ea_{-2} = 0.

k_3 from k_{-3} and <MR>. A_{-3} = 3.16E+12 (from secondary R. + secondary R. association [94]); Ea_{-3} = 0.

Lennard-Jones parameters: σ = 5.40Å; ε/k = 516 K. [22,205]

Reduced frequency sets (from CPFIT [19]) are:

1,3-C_4Cl_6	Vibration	Modes	Freq. (cm^{-1})
	1	11.018	158.3
	2	4.895	401.5
	3	7.587	1035.1
	mean	23.5	352.4



Set 2 Input parameters of Cl addition to C_4Cl_6 for the QRRK calculation

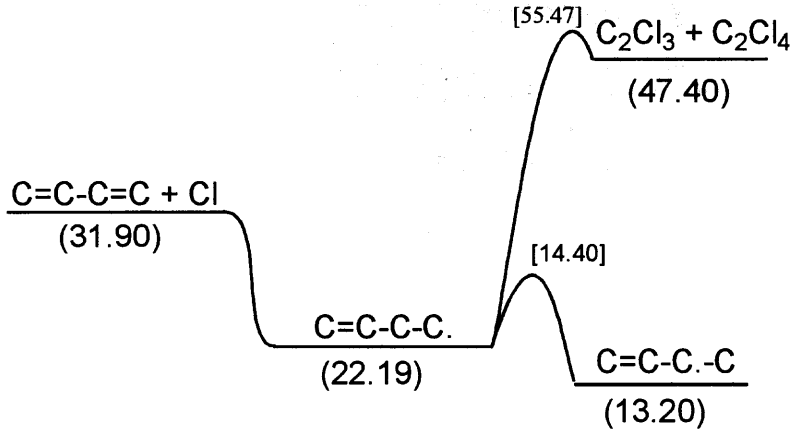
Reaction		A	n	Ea
k_1	C=C-C=C + Cl → C=C-C-C.	3.47E+13	0	0
k_{-1}	C=C-C-C. → C=C-C=C + Cl	1.96E+14	0	12.11
k_2	C=C-C-C. → C_2Cl_4 + C_2Cl_3	3.51E+13	0	44.42
k_3	C=C-C-C. → C=C-C.-C	1.06E+12	0	6.2
k_{-3}	C=C-C.-C → C=C-C-C.	1.64E+13	0	10.61

k_1 $A_1 = 2\times10^{(14.14-0.15\times4)}$ (from trend plot of Cl addition to vinyl chloride [176]). $Ea_1 = 0$
k_{-1} from k_1 and <MR>.
k_2 from k_{-2} and <MR>. $A_{-2} = 0.8E+11$, $Ea_{-2} = 4.5$ (estimated from ref. [230]).
k_3 A_3 from TST estimation. $Ea_3 = 6.2$ [231]
k_{-3} from k_3 and <MR>.

Lennard-Jones parameters: $\sigma = 5.40$Å; $\varepsilon/k = 516$ K. [22,205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C_4Cl_7P	1	13.928	403.6
	2	10.381	402.9
	3	1.691	1880.5
	mean	26.0	445.8
C_4Cl_7S	1	12.467	177.6
	2	5.653	403.9
	3	7.880	1180.3
	mean	26.0	377.0



Set 3 Input parameters of C_4Cl_5. dissociation for the QRRK calculation

Reaction		A	n	Ea
k_1	C=C-C=C. → C=C-C≡C + Cl	2.73E+14	0	17.65
k_2	C=C-C=C. → C_2Cl_2 + C_2Cl_3	2.89E+13	0	58.93
k_3	C=C-C=C. → C=C-C.=C	1.06E+12	0	6.2
k_{-3}	C=C-C.=C → C=C-C=C.	3.94E+12	0	15.32
k_4	C=C-C.=C → C=C-C≡C + Cl	1.02E+15	0	26.78
k_5	C=C-C.=C → C=C=C=C + Cl	3.39E+14	0	46.13

k_1 from k_{-1} and <MR>. A_{-1} = 2.13E+13 (taken as one half of Cl + CH≡CH [232]). Ea_{-1} = 0.

k_2 from k_{-2} and <MR>. A_{-2} = 0.8E+11, Ea_{-2} = 4.5 (estimated from ref. [230]).

k_3 A_3 from estimation. = 6.2 [231].

k_{-3} from k_3 and <MR>.

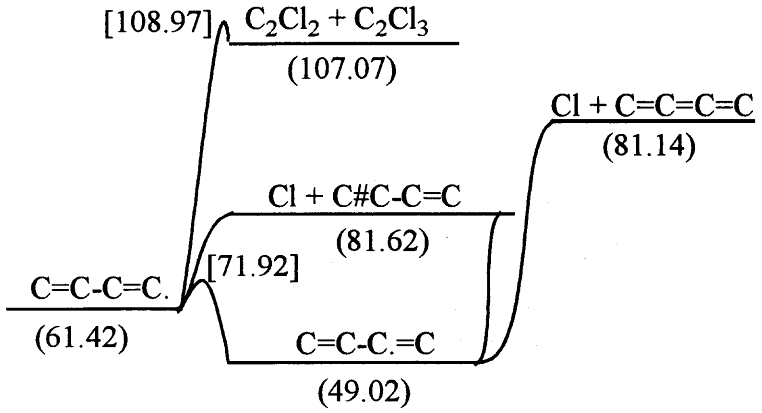
k_4 from k_{-4} and <MR>. A_{-4} = 2.13E+13, same as A_{-1}. Ea_{-4} = 0.

k_5 from k_{-5} and <MR>. A_{-5} = $10^{(14.14-0.15x3)}$ (from trend plot of Cl addition to vinyl chloride [176]), deg. = 2; Ea_{-5} = 0

Lennard-Jones parameters: σ = 5.40Å; ε/k = 516 K. [22,205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C_4Cl_5N	1	9.950	212.3
	2	4.672	401.6
	3	5.878	1304.6
	Mean	20.500	413.2
C_4Cl_5S	1	10.322	410.6
	2	6.147	404.7
	3	4.031	1085.4
	Mean	20.500	494.9



Set 4 Input parameters of C_4Cl_4 dissociation for the QRRK calculation

Reaction		A	n	Ea
k_2	C=C-C≡C → C=C.-C≡C + Cl	8.69E+14	0	86.72
k_1	C=C-C≡C → C.=C-C≡C + Cl	5.31E+15	0	94.47
k_3	C=C-C≡C → C=C-C≡C. + Cl	2.25E+15	0	111.20

k_1 from k_{-1} and <MR>. A_{-1} = 1.58E+13 (from secondary R. + CH_3 association) [94]. Ea_{-1} = 0.

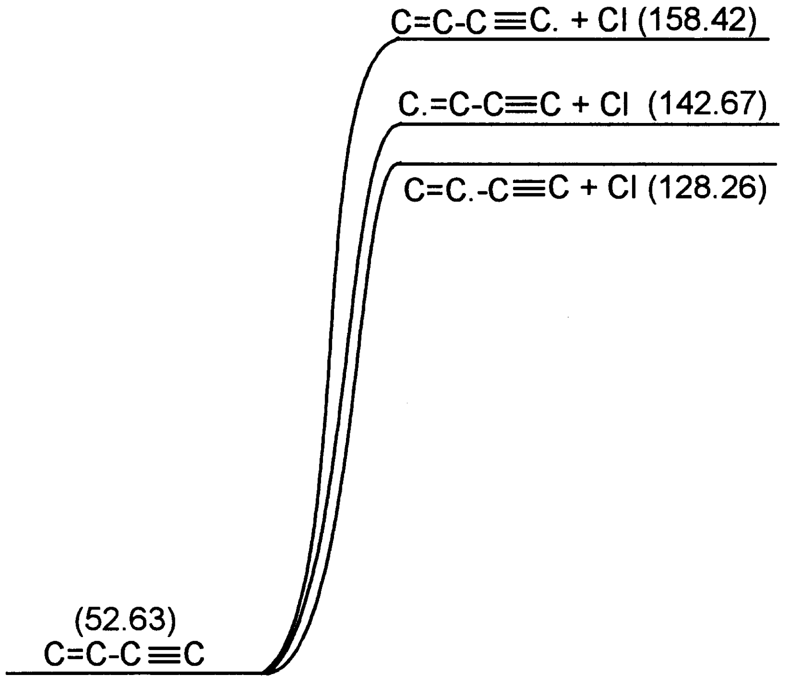
k_2 from k_{-2} and <MR>. A_{-2} = 1.99E+13 (from primary R. + CH_3 association) [94] x 2 (deg). Ea_{-2} = 0.

k_3 from k_{-3} and <MR>. A_{-3} = 1.99E+13 (from primary R. + CH_3 association) [94]. Ea_{-3} = 0.

Lennard-Jones parameters: σ = 5.40Å; ε/k = 516 K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C_4Cl_4	1	7.244	132.4
	2	1.750	744.0
	3	8.506	870.0
	Mean	17.500	392.9



Set 5 Input parameters of C_4Cl_3. dissociation for the QRRK calculation

Reaction		A	n	Ea
k_1	C.=C-C≡C → C≡C-C≡C + Cl	1.16E+14	0	21.59
k_2	C.=C-C≡C → C=C.-C≡C	1.06E+12	0	6.2
k_{-2}	C=C.-C≡C → C.=C-C≡C	2.57E+12	0	13.95
k_3	C=C.-C≡C → C≡C-C≡C + Cl	2.81E+14	0	29.34

k_1 from k_{-1} and <MR>. A_{-1} = 2.13E+13 (taken as one half of Cl + CH≡CH [232]), deg. = 2. Ea_{-1} = 0.

k_2 A_2 from estimation, see above tables, Ea_2 from ref. [231].

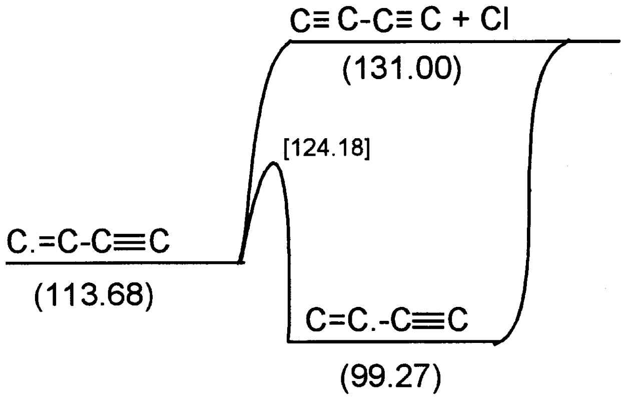
k_{-2} from k_2 and <MR>.

k_3 from k_{-3} and <MR>. A_{-3} = 2.13E+13 same as A_{-1}. Ea_{-3} = 0.

Lennard-Jones parameters: σ = 5.50Å; ε/k = 530 K. [22,205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C.=C-C≡C	1	10.548	310.1
	2	14.477	1643.4
	3	-11.963	1679.3
	Mean	14.500	480.9
C=C.-C≡C	1	5.476	100.0
	2	2.395	679.0
	3	6.629	668.4
	Mean	14.500	327.1



Set 6 Input parameters of C_2Cl_4 dissociation for the QRRK calculation

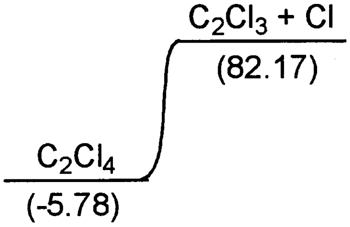
Reaction		A	n	Ea
k_1	$C_2Cl_4 \rightarrow C_2Cl_3 + Cl$	1.05E+15	0	84.43

k_1 from k_{-1} and <MR>. $\log A_{-1} = 13.24 - 1.38*(1)$, [175]. $Ea_{-1} = 0$.

Lennard-Jones parameters: $\sigma = 5.50$Å; $\varepsilon/k = 530$ K. [22,205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C_2Cl_4	1	7.264	250.0
	2	5.726	1101.8
	3	-0.991	3511.9
	Mean	12.000	407.9



Set 7 Input parameters of Cl addition to C_2Cl_4 for the QRRK calculation

Reaction		A	n	Ea
k_1	$C_2Cl_4 + Cl \rightarrow C_2Cl_5$	2.24E+16	-1.2	0
k_{-1}	$C_2Cl_5 \rightarrow C_2Cl_4 + Cl$	4.69E+16	-1.2	15.80

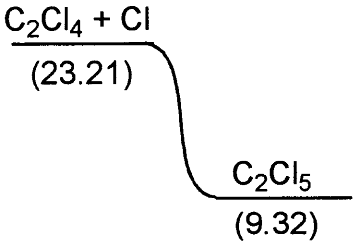
k_1 97DEM/SAN.

k_{-1} from k_1 and <MR>.

Lennard-Jones parameters: $\sigma = 5.80Å$; $\varepsilon/k = 580$ K. [22,205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C_2Cl_5	1	4.510	100.7
	2	9.400	568.9
	3	0.590	1912.6
	Mean	14.500	348.8



Set 8 Input parameters of Cl combination with C_2Cl_5 for the QRRK calculation

Reaction		A	n	Ea
k_1	$C_2Cl_5 + Cl \rightarrow C_2Cl_6$	2.45E+13	0	0
k_{-1}	$C_2Cl_6 \rightarrow C_2Cl_5 + Cl$	4.36E+16	0	68.35
k_2	$C_2Cl_6 \rightarrow 2\ CCl_3$	3.98E+17	0	67.60

k_1 96HUY/NAR.

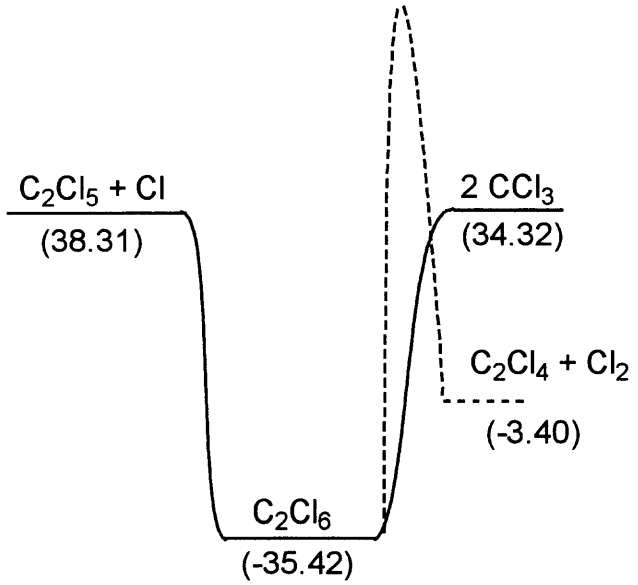
k_{-1} from k_1 and <MR>.

k_2 A_2 from 96HUY/THE, $Ea_{-2} = 0$

Lennard-Jones parameters: $\sigma = 6.0$Å; $\varepsilon/k = 600$ K. [22,205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C_2Cl_6	1	8.608	293.1
	2	6.799	518.5
	3	2.093	602.1
	Mean	17.5	398.7



Set 9 Input parameters of C_2Cl_3 dissociation for the QRRK calculation

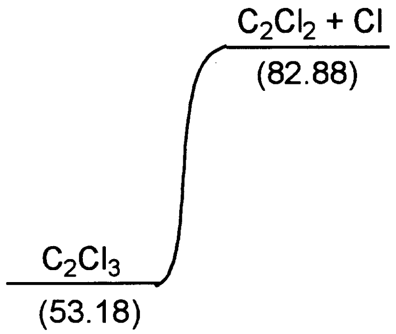
Reaction		A	n	Ea
k_1	$C_2Cl_3 \rightarrow C_2Cl_2 + Cl$	8.83E+13	0	26.53

k_1 from k_{-1} and <MR>. A_{-1} = 3.78E+13 (C_2H_2 + Cl by Atkinson and Aschmann, Int. J. Chem. Kinet., 1985,17,33). Ea_{-1}=0

Lennard-Jones parameters: σ = 5.26Å; ε/k = 560 K. [22,205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C_2Cl_3	1	3.985	118.3
	2	0.900	428.9
	3	4.115	1197.2
	Mean	9.0	387.8



Set 10 Input parameters of CCl_3 dissociation for the QRRK calculation

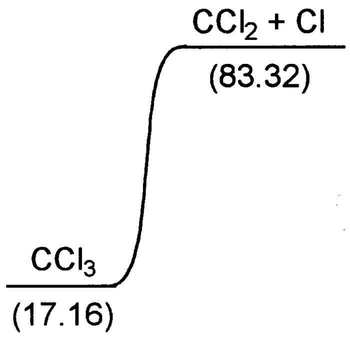
Reaction		A	n	Ea
k_1	$CCl_3 \rightarrow CCl_2 + Cl$	5.9475E+14	0.18824	68.42

k_1 A_1 = TST by MOPAC6/PM3, Ea_{-1}= 0.

Lennard-Jones parameters: σ = 5.26Å; ε/k = 560 K. [22,205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
CCl_3	1	2.411	100.3
	2	0.905	756.7
	3	2.684	699.9
	Mean	6.000	324.5



Set 11 Input parameters of Cl association with CCl_3 for the QRRK calculation

Reaction		A	n	Ea
k_1	$CCl_3 + Cl \rightarrow CCl_4$	3.92E+13	0	0
k_{-1}	$CCl_4 \rightarrow CCl_3 + Cl$	6.40E+16	0	67.46
k_2	$CCl_4 \rightarrow CCl_2 + Cl_2$	1.00E+14	0	101.54

k_1 92ELL.

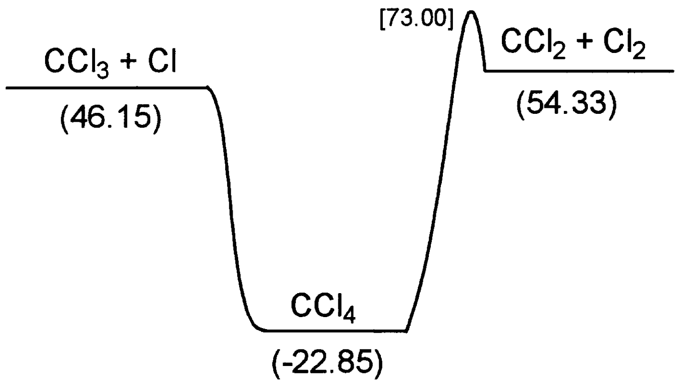
k_{-1} from k_1 and <MR>.

k_2 A_2 from estimation, Ea_{-2} = 16 is estimated in this study.

Lennard-Jones parameters: σ = 5.26Å; ε/k = 520 K. [22,205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
CCl_4	1	4.378	290.5
	2	3.407	525.9
	3	1.215	605.2
	Mean	9.000	401.6



Set 12 Input parameters of $C_4Cl_5N + O_2$ for QRRK calculation

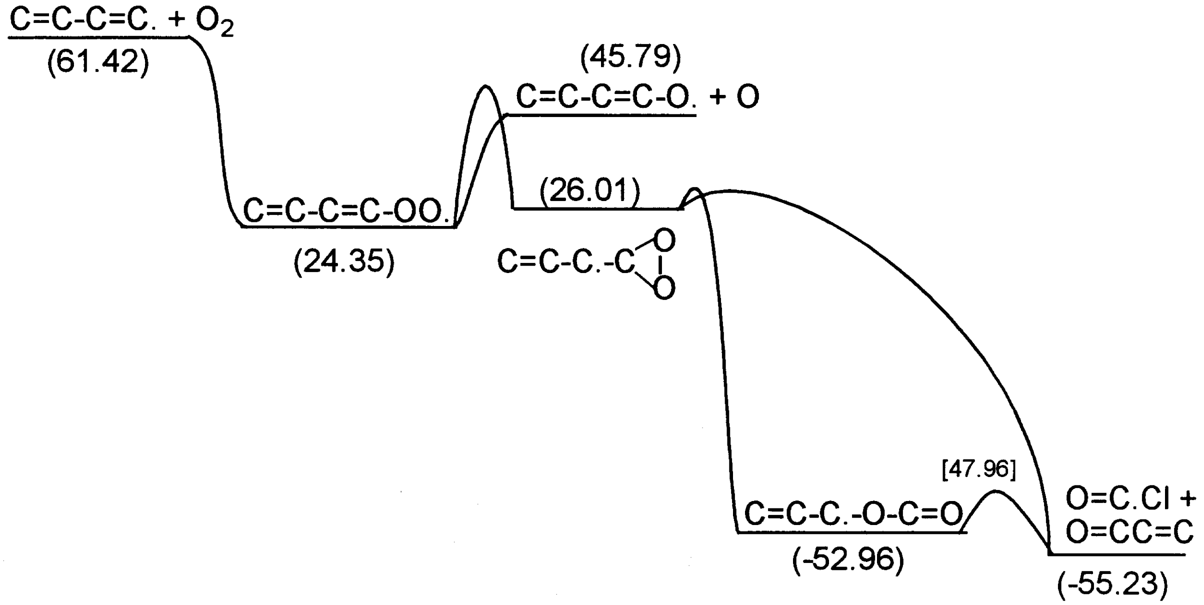
Reaction		A	n	Ea
k_1	C=C-C=C. + O_2 → C=C-C=COO.	5.00E+12	0	0
k_{-1}	C=C-C=COO. → C=C-C=C. + O_2	2.78E+13	0	36.38
k_2	C=C-C=COO. → C=C-C=C-O. + O	2.40E+14	0	27.14
k_3	C=C-C=COO. → C=C-C.Y(COO)	1.00E+13	0	19.32
k_{-3}	C=C-C.Y(COO) → C=C-C=COO.	7.65E+12	0	0
k_4	C=C-C.Y(COO) → C=C-C=O + CClO	1.00E+13	0	0

k_1	89RUS/SEE. Assume Ea_1 =0
k_{-1}	from k_1 and <MR>.
k_2	from k_{-2} and <MR>. A_{-2} = 4.5e13 from estimation, Ea_{-2} = 0.
k_3	A_3 from estimation.
k_{-3}	from k_3 and <MR>. Ea_{-3} = 0 from estimation.
k_4	A_4 from estimation. Ea_4 = 0 from estimation.

Lennard-Jones parameters: σ = 6.57Å; ε/k = 696.3 K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C=C-C=COO.	1	13.521	278.3
	2	7.628	401.0
	3	4.851	1853.8
	Mean	26.000	441.3
C=C-C.Y(COO)	1	12.084	100.3
	2	4.622	544.1
	3	9.294	892.7
	Mean	26.000	295.9



Set 13 Input parameters of $C_4Cl_5S + O_2$ for QRRK calculation

Reaction		A	n	Ea
k_1	C=C-C.=C + O_2 → C=C-C(OO.)=C	5.00E+12	0	0
k_{-1}	C=C-C(OO.)=C → C=C-C.=C + O_2	2.45E+13	0	15.62
k_2	C=C-C(OO.)=C → C=C(O.)-C=C + O	2.85E+14	0	33.51
k_3	C=C-C(OO.)=C → C=C-Y(COO)-C.	1.00E+13	0	8.94
k_{-3}	C=C-Y(COO)-C. → C=C-C(OO.)=C	7.78E+13	0	0
k_4	C=C-Y(COO)-C. → CCl_2O + C=C-C.=O	1.00E+13	0	0

k_1 89RUS/SEE. Assume $Ea_1 = 0$

k_{-1} from k_1 and <MR>.

k_2 from k_{-2} and <MR>. $A_{-2} = 4.5e13$ from estimation, $Ea_{-2} = 0$.

k_3 A_3 from estimation.

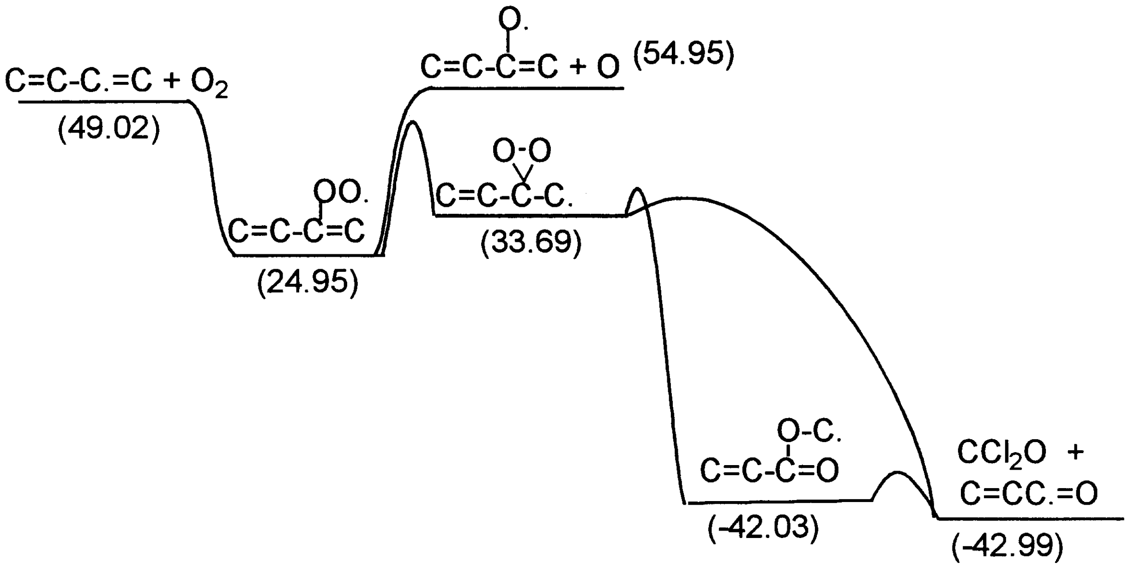
k_{-3} from k_3 and <MR>. $Ea_{-3} = 0$ from estimation.

k_4 A_4 from estimation. $Ea_4 = 0$ from estimation.

Lennard-Jones parameters: $\sigma = 5.40$Å; $\varepsilon/k = 516$ K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C=C-C(OO.)=C	1	15.356	183.2
	2	7.730	935.0
	3	2.914	1999.4
	Mean	26.000	388.7
C=C-Y(COO)-C.	1	14.666	354.6
	2	10.960	786.5
	3	0.373	1991.6
	Mean	26.000	508.6



Set 14 Input parameters of C=CC=C-O. dissociation for the QRRK calculation

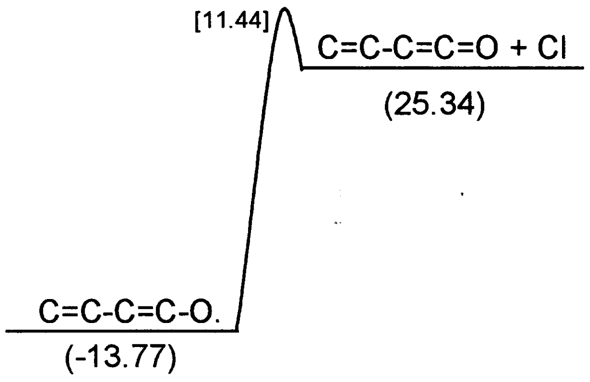
	Reaction	A	n	Ea
k_1	C=C-C=C-O. → C=C-C=C=O + Cl	5.00E+13	0	32.97

k_1 A_1 is estimated. Ea_{-1} = 5 (C_2H_3 + CO -> C=C-C=O by 86TSA/HAM)

Lennard-Jones parameters: σ = 5.15Å; ε/k = 498.3 K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C=C-C=C-O.	1	11.573	243.8
	2	6.350	402.2
	3	5.577	1382.7
	Mean	23.500	421.4



Set 15 Input parameters of C_2Cl_3CClO dissociation for the QRRK calculation

Reaction		A	n	Ea
k_1	C=C-C=O → C=C-C.=O + Cl	4.63E+14	0	73.86
k_2	C=C-C=O → C=C. + CClO	1.13E+17	0	95.42

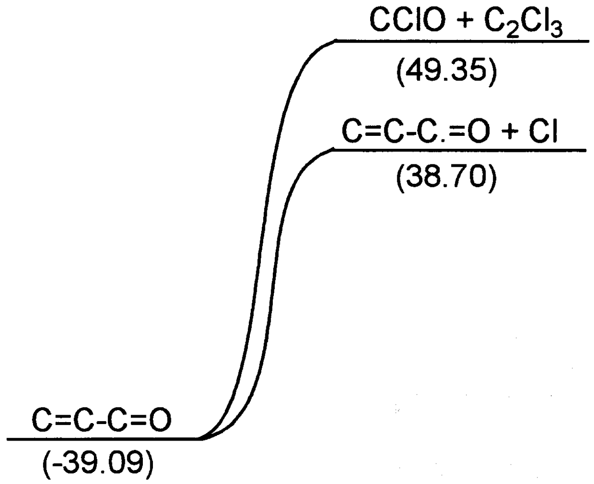
k_1 from k_{-1} and <MR>, A_{-1} = 1.58E+13 (from secondary R. + CH_3 by Allra and Shaw), Ea_{-1} = 0.

k_2 from k_{-2} and <MR>, A_{-2} = 3.16E+12 (from secondary R. + secondary R. by Allra and Shaw), Ea_{-2} = 0.

Lennard-Jones parameters: σ = 5.15Å; ε/k = 498.3 K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C=C-C=O	1	13.486	324.7
	2	3.867	1306.6
	3	0.146	3991.3
	Mean	17.500	451.1



Set 16 Input parameters of $C_2Cl_3C.O$ dissociation for the QRRK calculation

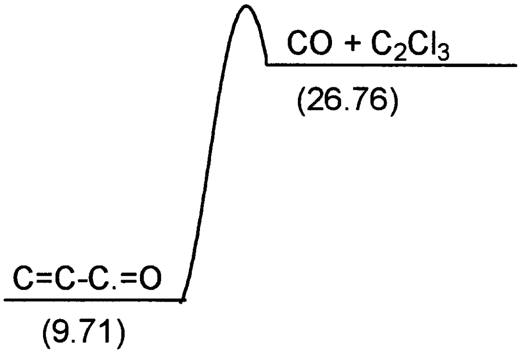
Reaction		A	n	Ea
k_1	C=C-C.=O → C_2Cl_3 + CO	1.53E+14	0	31.42

k_1 from k_{-1} and <MR>. A_{-1} = 1.51E+11, Ea_{-1} = 4.81 (taken as C_2H_3 + CO → CH_2=CHCO, Tsang, W.; Hampson, R. F., J. Phys. Chem. Ref. Data, 1986,15,1087).

Lennard-Jones parameters: σ = 5.15Å; ε/k = 498.3 K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
C=C-C.=O	1	11.797	381.8
	2	2.273	1117.4
	3	0.430	3991.4
	Mean	14.500	484.4



Set 17 Input parameters of $C_2Cl_3 + O_2$ for QRRK calculation

Reaction		A	n	Ea
k_1	$C_2Cl_3 + O_2 \rightarrow CCl_2{=}CClOO.$	1.21E+12	0	0
k_{-1}	$CCl_2{=}CClOO. \rightarrow C_2Cl_3 + O_2$	6.82E+13	0	37.14
k_2	$CCl_2{=}CClOO. \rightarrow CCl_2{=}CClO. + O$	1.09E+14	0	34.64
k_3	$CCl_2{=}CClOO. \rightarrow CCl_2CO + ClO$	6.41E+9	1	23.5
k_4	$CCl_2{=}CClOO. \rightarrow C.Cl_2Y(COO)Cl$	6.41E+9	1	23.5
k_{-4}	$C.Cl_2Y(COO)Cl \rightarrow CCl_2{=}CClOO.$	5.85E+8	1	8.02
k_5	$C.Cl_2Y(COO)Cl \rightarrow Cl_2Y(COC)ClO.$	6.41E+9	1	5
k_{-5}	$Cl_2Y(COC)ClO. \rightarrow C.Cl_2Y(COO)Cl$	4.57E+10	1	41.15
k_6	$Cl_2Y(COC)ClO. \rightarrow CCl_2O.CClO$	5.36E+7	1	4
k_{-6}	$CCl_2O.CClO \rightarrow Cl_2Y(COC)ClO.$	7.31E+8	1	43.60
k_7	$CCl_2O.CClO \rightarrow CCl_2O + CClO$	4.73E+14	0	0
k_{10}	$CCl_2O.CClO \rightarrow O{=}C{-}C{=}O + Cl$	4.00E+13	0	9
k_8	$Cl_2Y(COC)ClO. \rightarrow C.Cl_2OCClO$	3.24E+9	1	4
k_{-8}	$C.Cl_2OCClO \rightarrow Cl_2Y(COC)ClO.$	6.41E+9	1	76.79
k_9	$C.Cl_2OCClO \rightarrow CCl_2O + CClO$	6.82E+13	0	30.73

k_1 A_1 from Russell, J. J. et al., J. Phys. Chem., 1989,93,1934.

k_{-1} from k_1 and <MR>.

k_2 from k_{-2} and <MR>, A_{-2} = 2.00E+13 (taken as O + CH_3O, Herron, J. T., Phys, Chem. Ref. Data, 1988,17,967). Ea_{-2} = 0 by estimation.

k_3 A_3, n from estimation. Ea_3 = 23.5 (Carpenter, B. K., J. Am. Chem. Soc., 1993,115,9806). **Not find.**

k_4 same as k_3.

k_{-4} from k_4 and <MR>.

k_5 A_5 from A_3, Ea_3 = 5 by estimation.

k_{-5} from k_5 and <MR>.

k_6 A_6 from A_{-6} and <MR>. Ea_6 = 4. (Carpenter, B. K., J. Am. Chem. Soc., 1993,115,9806). **Not find.**

k_{-6} A_{-6} from estimation. Ea_{-6} from Ea_6 and <MR>.

k_7 from k_{-7} and <MR>. A_{-7} = 5.2E+11, Ea_{-7} = 6.5 (CO + CH_3, Anastasi and Maw, J. Chem. Soc. Faraday Trans. 1, 1982,78,2423).

k_8 A_8 from A_{-8} and <MR>. Ea_8 = 4 by estimation.

k_{-8} A_{-8} from estimation.

k_9 from k_{-9} and <MR>. A_{-9} = 5.2E+11, Ea_{-7} = 6.5 (CO + CH_3, Anastasi and Maw, J. Chem. Soc. Faraday Trans. 1, 1982,78,2423).

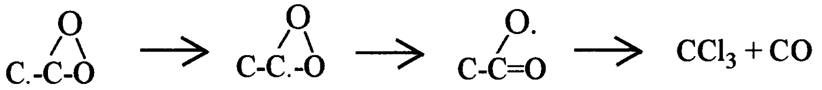
k_{10} from CCl_3O -> CCl_2O +Cl.(97ATK/BAU)

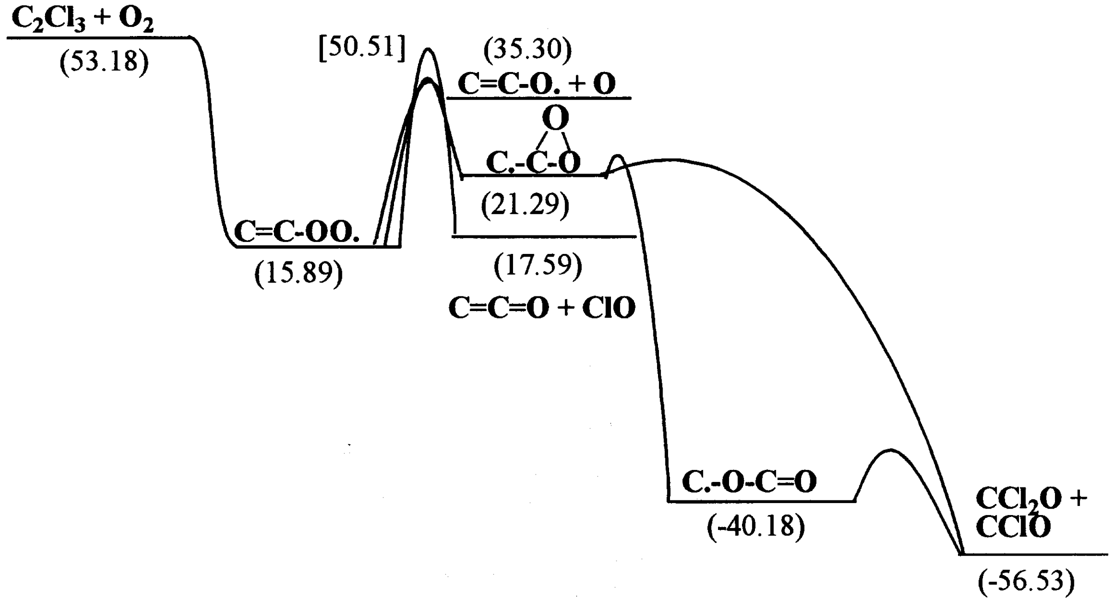
Lennard-Jones parameters: σ = 4.63Å; ε/k = 380 K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
$CCl_2{=}CClOO.$	1	10.093	307.9
	2	3.329	1580.3
	3	1.078	3980.8
	Mean	14.500	542.2
$C.Cl_2(COO)Cl$	1	7.112	305.9
	2	5.776	516.0
	3	1.611	602.1
	Mean	14.500	406.2
$Cl_2(COC)ClO.$	1	8.831	362.2
	2	4.729	637.8
	3	1.440	601.1
	Mean	15.000	454.5
$CCl_2O.CClO$	1	7.551	358.7
	2	4.836	401.1
	3	2.113	1684.8

	Mean	14.500	466.5
C.Cl$_2$OCClO	1	6.554	195.9
	2	2.849	401.7
	3	4.597	1186.2
	Mean	14.000	409.6





Set 18 Input parameters of CCl_2O dissociation for the QRRK calculation

Reaction		A	n	Ea
k_1	$CCl_2O \rightarrow CClO + Cl$	5.71E+15	0	72.41
k_2	$CCl_2O \rightarrow CO + Cl_2$	1.45E+14	0	82.46

k_1 Lim, K. P.; Michael, J. V., J. Phys. Chem., 1994,98,211.

k_2 Lim, K. P.; Michael, J. V., J. Phys. Chem., 1994,98,211.

Lennard-Jones parameters: σ = 4.3Å; ε/k = 280.3 K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
CCl_2O	1	2.289	316.2
	2	2.500	800.0
	3	1.211	2152.6
	Mean	6.000	685.6

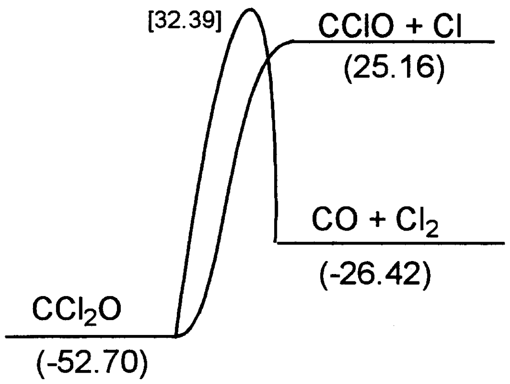


Table 19 Input parameters of CClO + O_2 QRRK calculation

Reaction		A	n	Ea
k_1	CClO + O_2 → O=CClOO.	2.59E+11	0	0
k_{-1}	O=CClOO. → C.ClO + O_2	7.19E+12	0	42.36
k_2	O=CClOO. → CO_2 + ClO	6.00E+12	0	4

k_1 96HEW/BRA

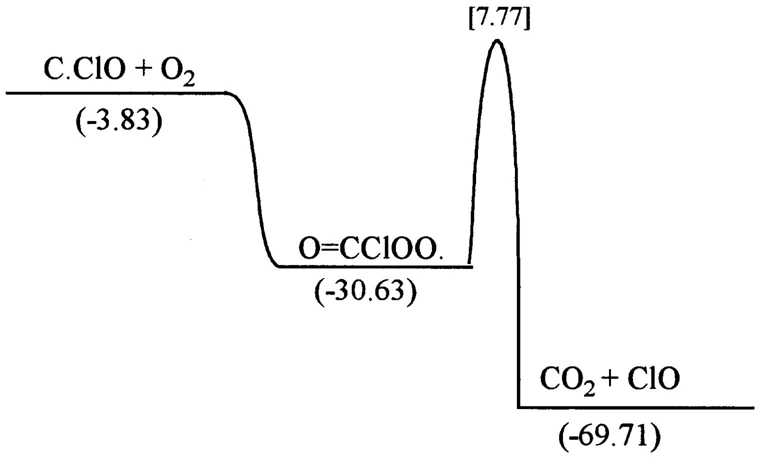
k_{-1} from k_1 and <MR>.

k_2 from personal communication with J Bozzelli, and Tsan Lay, unpublished work in this laboratory on $CCl_3 + O_2 \Rightarrow CCl_3OO. \Rightarrow [C.Cl_2OOCl]^\# \Rightarrow CCl_2O + ClO$, modeling of experimental data. A_2 from estimation. $Ea_2 = 4$.

Lennard-Jones parameters: $\sigma = 5.15$Å; $\varepsilon/k = 550$ K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
O=CClOO.	1	5.648	417.9
	2	1.105	1212.5
	3	1.747	2270.1
	Mean	8.500	679.6



Set 20 Input parameters of CClO dissociation for the QRRK calculation

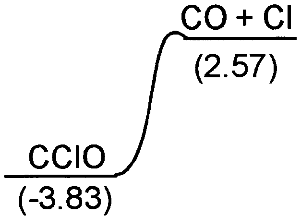
Reaction		A	n	Ea
k_1	CClO → CO + Cl	1.69E+10	0	5.05

k_1 from k_{-1} and <MR>. A_{-1} = 2.05E+10, Ea_{-1} = 0. (96HEW/BRA)

Lennard-Jones parameters: σ = 4.0Å; ε/k = 270 K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

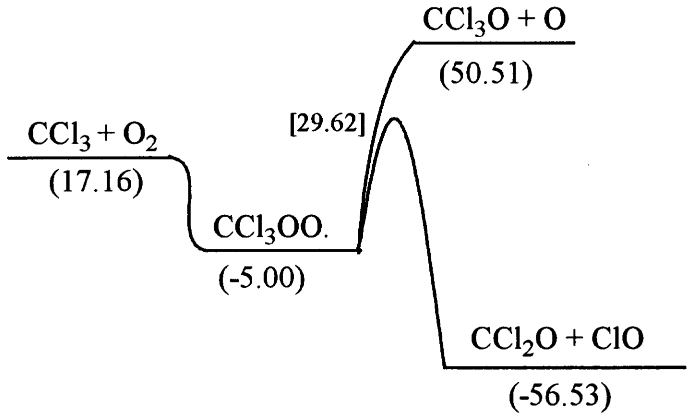
	Vibration	Modes	Freq. (cm^{-1})
CClO	1	1.181	278.9
	2	0.780	802.2
	3	1.039	2017.7
	Mean	3.000	728.3



Set 21 Input parameters of CCl_3 + O_2 QRRK calculation

Reaction		A	n	Ea
k_1	$CCl_3 + O_2 \rightarrow CCl_3OO$	2.27E17	-2.1	0
k_{-1}	$CCl_3OO \rightarrow CCl_3 + O_2$	7.65E19	-2.1	19.5
k_2	$CCl_3OO \rightarrow CCl_3O + O$	4.33E15	0	54.18
k_3	$CCl_3OO \rightarrow CCl_2O + ClO$	6.85E11	0.47	34.85

See Chloroform mechanism (Appendix A and B) for same reactions.



Set 22 Input parameters of $ClCO_2$ dissociation for the QRRK calculation

Reaction		A	n	Ea
k_{-1}	$ClCO_2 \rightarrow CO_2 + Cl$	1.47E+13	0	0

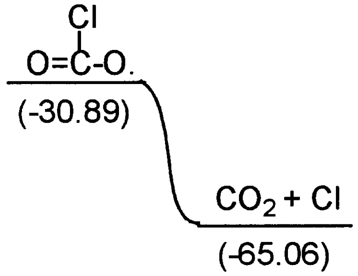
k_1 from k_{-1} and <MR>.

k_{-1} A_{-1} = 1.87E+13, Ea_1 = 0 (Cl + FC(O)O. -> adduct, 97COB/CRO)

Lennard-Jones parameters: σ = 4.3Å; ε/k = 350.3 K. [22], [205]

Reduced frequency sets (from CPFIT [19]) are:

	Vibration	Modes	Freq. (cm^{-1})
O=CClO.	1	3.733	525.7
	2	1.980	1465.2
	3	0.287	3997.0
	Mean	6.000	812.4



APPENDIX D

MECHANISM FOR THE PYROLYSIS AND OXIDATION OF 1,3-C_4CL_6

This appendix lists the full mechanism for the pyrolysis and oxidation of 1,3-C_4Cl_6, as discussed in Chapter 7.

```
ELEMENTS
C CL N O
END
SPECIES
 O        O2       N2       CO       CO2      CL
 CL2      LC3CL6    CYC6CL6   C*C*C     C2CL3CCLO  CYC4CL4O
 C4CL4     C2CL2     CYOC      CYC3CL4E   C*CYC5DE   STYRENE
 CCL       CLO       CCLO      CCL2O      CLCO2.     CLC*OQ.
 CCL2T     CCL2      C2CL3     C2CL4      C2CL5      C2CL6
 CCL3      CCL4      C2CL      C4CL2      C4CL3.S    C4CL3NV.
 C4CL5.N   C4CL5.S   C4CL4A    C4CL6DE13  C4CL7.P    C4CL7.S
 NC4CL5Q.  L3VVL2O.  O*COC.L4V  SC4CL5Q.  L2VO.VL3   C2CL3C.*O
 L5VO*COC.  CCL3OO    CLC.*C*O   CCL2CO    CL2C*CCLO.  CL2C*CCLOO
 C.CL2CL*O  C.*OLKT   CCL*OLKT   L2V.LKT   LC.*CLKT   L3VLC*C*O
 CCL3C.*O   L3VK.T    LC#CCCLO   LC#CCJ*O   LC#CCO2.   C.#CC2CL3
 L3VLC.YOO  L3VYOOC.L  SC4L5PXO.  CL2C.COOCL CL2CCOCLO.  CO.CL2CCLO
 CL2C.OCCLO CC*CJ     LC3CL4    CYC6CL7    CYC6CL5    C6CL7N
 C6CL7S    C6CL6N    C6CL6S    C6CL5N     C6CL5S     C6CL4N
 C6CL4S    NC4L5EPO.  CCL3O     C2CL5O     CJ#CCCLO   CJ*CCCLO
 C*CJCCLO   L2C*C*C*O  C#CCCL2O   O*C*C*O    C2CL3CO2.  VL3C*OC.
 V.L2C*OC.  O*CC*O    CYC4CL5O   C*C*CC*O   CJ*C*C     C*CCJC*O
 CJC*CC*O   CJCC*O    CCL3CCLO   CJC*C      C2L3CC*O   O*CC2C*O
 CCJCC*O    CJCCC*O   O*CCC*O    CJCA       CQJCA      CACOJ
 CAC*O      CYOOCVJ   COJCYOV    CJYOC*C    C*CQC*O    C*COJC*O
 CYOOCJCO   COCOCOJ   CCLOCJ*O   O2S       L2C4JJ     C*CC*C:
 C*CC:      C*C:      C6CL9V    C6CL8TE    C6CL7V     C6CL7A
 C6CL5A     NC6CL9DE   C3CL7N    C4CL3A     C*CYC5RA   C*CYC5RB
 IC4L4C*C.  CJ*CCC*O   YCCJCC*O   C2CL5OO    C2CL5OJ    CYC3CL5J
 CYC3CL6    CJC#C     CYCJ*C    CCJ*C      C#CCCC*C   C6CL10E24
 LC8CL10    LC8CL9N   PRESTYR1   CJCC*C*O   C*CCCJ*O   LC8CL10A
 IC8CL9A    IC8CL9B   PRESTYR3   PRESTYR5   C#CCC*O    C*CJCC*O
 CYC6CL9    CYC6CL8   CJC*CC    C6CL10E14  C6CL9DE14  CYC6CL9A
 CJCOJ     LC8CL12   LC8CL11   CYC8CL11   CYC8CL10   C6CL9E14N
 C5CL8DE13  C5CL7DE13  LC8CL9T   PRESTYR2   LC8CL11B   C7CL11
 C7CL10TE   C8CL13    C8CL12B   C8CL11N    CCJYDE13   LC8CL11A
 CYC8CL11A  CYC8CL10A  PRESTYR4   LC8CL8N    LC8CL8A    C6CL5T
 C6CL5B    PRESTYR6   CJCYDE13   CYC6C*CJ   C6CL11E4   C6CL11E5
 CYC8CL11B  C6CL6A    C6CL7B    CCL2OO     CLOCO
END
REACTIONS
! try c4 + c2 => (single direction) c6 !!!  c6 just littile higher
! c2cl4 + c2cl3 addition use A=2e12, Ea=4.5 (no diff if use 3.1)
! use c2cl4= -2.63 from chlorovinyl alcohol , no big change
! Table t1 diff LJ  deg=1  when slow = c4cl6 up, ccl2o down/ ccl4, c2cl4 down    ccl2T/ccl2 no diff
! t1 trend + calc Hf by b3
 C4CL6DE13        <=> C4CL5.S+CL        5.89E+32  -5.22   81479.   ! 1.00E+00  atm,  700-1200 K,   2% err, 1.00 x N2
 C4CL6DE13        <=> C4CL5.N+CL        1.75E+52  -11.34  101941.   ! 1.00E+00  atm,  700-1200 K,   3% err, 1.00 x N2
 C4CL6DE13        <=> 2C2CL3           1.72E+79  -18.89  126211.   ! 1.00E+00  atm,  700-1200 K,   2% err, 1.00 x N2

 C4CL6DE13+CL      <=> C4CL5.S+CL2       8.88E+13   0.0    20660.   ! a1,dhfrxn  *.64 +9.7 = Ea
 C4CL6DE13+CL      <=> C4CL5.N+CL2       1.78E+14   0.0    28590.   ! a1

! Table t2   delete c4cl7.s->c4cl6+cl, no change
 C4CL6DE13+CL      <=> C4CL7.P          2.60E+20  -3.36   -1696.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 C4CL6DE13+CL      <=> C2CL4+C2CL3        2.30E+14  -.08   24346.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 C4CL6DE13+CL      <=> C4CL7.S          5.64E+30  -6.60   -153.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2
 C4CL7.P         <=> C2CL4+C2CL3       4.37E+21  -3.28   34817.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 C4CL7.P         <=> C4CL7.S        3.69E+56  -15.22   14175.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2
 C4CL7.S         <=> C2CL4+C2CL3       3.11E+23  -3.75   43145.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2

! not consider c4cl7s can go to c.-c=c-c

! Table t3 --chemmaster not work
 C4CL5.N         <=> CL+C4CL4         3.81E+37  -7.97   23431.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 duplicate
 C4CL5.N         <=> C2CL2+C2CL3       4.17E+20  -3.24   53075.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 C4CL5.N         <=> C4CL5.S        5.34E+62  -16.18   26781.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 C4CL5.N         <=> CL+C4CL4         6.03E+58  -14.50   33248.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 duplicate
 C4CL5.N         <=> CL+C4CL4A        4.11E+57  -14.67   33347.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
```

```
C4CL5.S        <=> CL+C4CL4         3.28E+52  -12.45   38097.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
duplicate
C4CL5.S        <=> C2CL2+C2CL3       7.74E+11  -1.32   56548.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2
C4CL5.S        <=> CL+C4CL4         2.30E+39  -8.32   32944.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 duplicate
C4CL5.S        <=> CL+C4CL4A         1.80E+38  -8.51   33036.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2

! Table 4
C4CL4   <=> C4CL3.S+CL        7.24E+16  -1.12   75800.   ! 1.00E+00 atm,  700-1400 K,   1% err  ::CM  :
C4CL4   <=> C4CL3NV.+CL        5.96E+27  -3.91   94524.   ! 1.00E+00 atm,  700-1400 K,   3% err  ::CM  :
C4CL4   <=> C.#CC2CL3+CL       1.75E+47  -9.85  119121.   ! 1.00E+00 atm,  700-1400 K,   3% err  ::CM  :

C4CL4+CL        <=> C4CL3.S+CL2       4.44E+13   0.0    21000.   ! a1 hfrxn=18.76
C4CL4+CL        <=> C4CL3NV.+CL2       8.88E+13   0.0    30220.   ! a1 hfrxn=33.18
C4CL4+CL        <=> C.#CC2CL3+CL2      4.44E+13   0.0    40300.   ! a1 hfrxn=
C4CL4A+CL        <=> C4CL3A+CL2        1.78E+14   0.0    39770.   ! a1,hfrxn=
!C4CL4A+CL       <=> C4CL3.S+CL2       1.78E+14   0.0    16700.   ! a1, NO BIG CHANGE HFRXN=10.92

! T5
C4CL3NV.        <=> C4CL2+CL          4.07E+25  -4.63   15948.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
duplicate
C4CL3NV.        <=> C4CL3.S         3.10E+48 -12.01   20121.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
C4CL3NV.        <=> C4CL2+CL          5.20E+44 -10.36   26882.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
duplicate
C4CL3.S        <=> C4CL2+CL         1.79E+43  -9.86   35168.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2
duplicate
C4CL3.S        <=> C4CL2+CL         5.84E+37  -8.06   32799.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2
duplicate

C4CL2          = 2C2CL          1.22E+16   0.     166280.   ! lgAr=13.88-0.23*(2)
!C.#CC2CL3       <=> C4CL3.S          1.00E+11   0.0    15000.   ! exothermo, CO2 LIT'L HIGH
!C4CL3.S          = C*C:+C2CL

! t6 slow has no effect, since c2cl3will effect ccl4, new c2cl4 thermo
C2CL4         <=> C2CL3+CL         1.31E+36  -6.50   96206.   ! 1.00E+00  atm,  700-1400 K,   3% err, 1.00 x N2

C2CL4+CL        <=> C2CL3+CL2         1.78E+14   0.0    28880.   ! Hrxn = 31.16, jongwoo   *.64+9.7

! T7
C2CL4+CL        <=> C2CL5           4.16E+16  -2.27   -4907.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2

! T8
C2CL5+CL        <=> C2CL6           9.03E+75 -19.65   22567.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
C2CL5+CL        <=> 2CCL3           4.36E+24  -3.21    7631.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2
C2CL6         <=> 2CCL3          4.54E+79 -19.25   90921.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2

C2CL6+CL        <=> C2CL5+CL2         2.66E+14   0.0    19780.   ! hfrxn= 8.96

! Table t9
C2CL3         <=> C2CL2+CL         8.00E+42  -9.79   33438.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2

C2CL2         <=> C2CL+CL         5.36E+14   0.0   108970.   ! trend cl+chcl=ch. Ar=1.74e13
C2CL2+CL        <=> C2CL+CL2          8.88E+13   0.0    43500.   ! a1 hfrxn=52.78

! T10  use PM3 calc. tst
!CCL3          <=> CCL2+CL          9.45E+40  -8.63   75186.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2

! T11 eliminated
CCL4 = CCL3 + CL                 2.61E16     0.     67020.  !trend
CCL4 + CL = CCL3 + CL2              1.78E14    0.0    16750.  !trend

!CCL2+M         <=> CCL2T+M          5.00E+13   0.0    12000.   ! Ea=dH A=0.25*collision rate, estimated this study
!CCL2T+CL2        <=> CCL3+CL          8.00E+11   0.0     2100.   ! from CCl2 + HCl ???  CL2, CO2 DOWN, LOW TEMP
!CCL3+CL          =  CCL2T+CL2         1.33E+14   0.0    24700.   ! HFRXN=23.41

!lower this rxn = all up but c4cl6, co/co2 better
!CL + CL + M = CL2 + M              2.23E14    0.00   -1800.  !nist 81BAU
CL + CL + M = CL2 + M              2.00E15    0.00      0.  !nist  96SON/SU
```

```
! Table 12   need to speed it up
C4CL5.N+O2         <=> NC4CL5Q.         1.72E+20  -3.47   -1916.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
C4CL5.N+O2         <=> L3VVL2O.+O         7.26E+12   -.23    -363.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
C4CL5.N+O2         <=> L3VLC.YOO        1.19E+12  -1.30     127.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
C4CL5.N+O2         <=> CCLO+C2CL3CCLO      4.52E+10    .06     772.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
duplicate
C4CL5.N+O2         <=> O*COC.L4V         3.20E+08   -.96    2975.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
C4CL5.N+O2         <=> CCLO+C2CL3CCLO      4.52E+10    .06     772.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
duplicate
NC4CL5Q.          <=> L3VVL2O.+O        1.32E+39  -8.41   26805.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
NC4CL5Q.          <=> L3VLC.YOO        2.86E+38  -9.47   28011.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
NC4CL5Q.          <=> CCLO+C2CL3CCLO      8.31E+32  -6.96   27034.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
duplicate
NC4CL5Q.          <=> O*COC.L4V         2.19E+32  -8.38   30119.   ! 1.00E+00 atm,  700-1400 K,   2% err, 1.00 x N2
NC4CL5Q.          <=> CCLO+C2CL3CCLO      8.31E+32  -6.96   27034.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
duplicate
L3VLC.YOO          <=> L3VVL2O.+O        1.18E+19  -2.68   23018.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
L3VLC.YOO          <=> CCLO+C2CL3CCLO      1.55E+11   -.65     -39.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
duplicate
L3VLC.YOO          <=> O*COC.L4V         3.34E+10  -2.08    2237.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
L3VLC.YOO          <=> CCLO+C2CL3CCLO      1.55E+11   -.65     -39.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
duplicate
O*COC.L4V          <=> L3VVL2O.+O        5.51E+26  -6.52   84843.   ! 1.00E+00 atm,  700-1400 K,  24% err, 1.00 x N2
O*COC.L4V          <=> CCLO+C2CL3CCLO      4.59E+13  -1.44   88519.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
duplicate
O*COC.L4V          <=> CCLO+C2CL3CCLO      6.69E+17  -2.54    7539.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
duplicate

!C4CL4+O xxx

! Table 13 diff LJ lit'l change   reduce A of ->ccl2o+c2cl3c.*o = lower cocl2 and c4cl6
C4CL5.S+O2         <=> SC4CL5Q.         2.90E+44 -10.27    9985.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
C4CL5.S+O2         <=> L2VO.VL3+O        3.00E+26  -3.97   12971.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
C4CL5.S+O2         <=> L3VYOOC.L         3.94E+42 -10.16   17224.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
C4CL5.S+O2         <=> CCL2O+C2CL3C.*O     3.64E+36  -7.48   13931.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
duplicate
C4CL5.S+O2         <=> L5VO*COC.         2.15E+35  -8.24   13836.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
C4CL5.S+O2         <=> CCL2O+C2CL3C.*O     3.64E+36  -7.48   13932.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
duplicate
SC4CL5Q.          <=> L2VO.VL3+O        3.71E+36  -7.44   33865.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
SC4CL5Q.          <=> L3VYOOC.L         3.75E+51 -13.17   36999.   ! 1.00E+00 atm,  700-1400 K,   2% err, 1.00 x N2
SC4CL5Q.          <=> CCL2O+C2CL3C.*O     1.66E+46 -10.73   34206.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
duplicate
SC4CL5Q.          <=> L5VO*COC.         7.23E+44 -11.44   34058.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
SC4CL5Q.          <=> CCL2O+C2CL3C.*O     1.66E+46 -10.73   34206.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
duplicate
L3VYOOC.L          <=> L2VO.VL3+O        9.89E+38  -8.12   33205.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
L3VYOOC.L          <=> CCL2O+C2CL3C.*O     3.47E+18  -2.88    4860.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
duplicate
L3VYOOC.L          <=> L5VO*COC.         2.21E+17  -3.64    4666.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
L3VYOOC.L          <=> CCL2O+C2CL3C.*O     3.47E+18  -2.88    4860.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
duplicate
L5VO*COC.          <=> L2VO.VL3+O        2.59E+88 -28.37  112513.   ! 1.00E+00 atm,  700-1400 K,   2% err, 1.00 x N2
L5VO*COC.          <=> CCL2O+C2CL3C.*O     3.70E+85 -24.73  104990.   ! 1.00E+00 atm,  700-1400 K,   1% err, 1.00 x N2
duplicate
L5VO*COC.          <=> CCL2O+C2CL3C.*O     8.20E+10   -.49    -524.   ! 1.00E+00 atm,  700-1400 K,   0% err, 1.00 x N2
duplicate

!C.#CC2CL3+O2       <=> 2CO+C2CL3          5.00E+12   0.0      0.   ! 4/28/99  not impt
C.#CC2CL3+O2        <=> O*C*C*O+C2CL3      2.50E+12   0.0      0.   ! 4/28/99, no change

L2VO.VL3          <=> C2CL3+CCL2CO       2.69E+13   0.0   52420.   ! rev=1.51e11, 4.809 (co+c2h3) 86TSA/HAM

! make CY/C(=O)C=CC
!make ring ?
!L3VVL2O.          = C*CCJC*O          1.00E+13   0.       0.   ! resonance, lizhu
!C*CCJC*O          = CJC*CC*O          1.00E+13   0.       0.   ! resonance, lizhu
!CJC*CC*O          = C*C*CC*O+CL       6.31E+13   0.69  44700.   ! lizhu, see H + CH2=C=CH2 92TSA/WAL
!CYC4CL5O           = CYC4CL4O+CL       2.01E+14   0.       0.   ! krev=1e13,1, lizhu
!YCCJCC*O           = CYC4CL4O+CL       2.16E+13   0.   14080.   ! krev=1e13,1, lizhu
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!C*C*CC*O          = CJ*C*C+CCLO       6.58E+17   0.    78090.   ! Ar=13.88-0.23*2  trend
!CJC*CC*O          = CYC4CL5O         8.00E+11   0.    55420.   ! LIZHU  Ear=2?
!CJ*CCC*O          = CYC4CL5O         8.00E+11   0.    29950.   ! LIZHU
!C*CCCJ*O          = YCCJCC*O         8.00E+11   0.    6700.   ! LIZHU
!L2VO.VL3          = VL3C*OC.        1.00E+13   0.       0.   ! RESONANCE, lizhu
!VL3C*OC.+CL         = V.L2C*OC.+CL2     8.88E+13   0.    27200.   ! hFRXN=27.41, lizhu
!V.L2C*OC.          = CYC4CL4O         1.00E+13   0.       0.   ! guess, lizhu
!VL3C*OC.           = CYC4CL4O+CL        5.18E+11   0.    18800.   ! krev=1e13*2,1, lizhu

! Table 14b
 L3VVL2O.        <=> L3VLC*C*O+CL       2.18E+44  -9.30   55821.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2

 L3VLC*C*O+CL       <=> CL2+LC.*CLKT       8.88E+13   0.0    29760.   ! a1 Ea=DelH+1   HFRXN=26.99
 L3VLC*C*O+CL       <=> CL2+L2V.LKT       4.44E+13   0.0    24720.   ! a1 Ea=DelH+2   HFRXN=6.22
 L3VLC*C*O+CL       <=> CL2+L3VK.T       4.44E+13   0.0    12860.   ! a1 Ea=DelH+2   HFRXN=21
!L3VLC*C*O+CL       <=> C2CL4+CLC.*C*O      3.47E+13   0.    24000.   !    Hf=24.01 see c2cl3cclo+cl//cocl2, ccl4, c2cl4
lit'l low

 L3VLC*C*O        <=> C2CL3+CLC.*C*O     2.72E+17   0.0   107440.   ! Ar=13.88-0.23*2, 0.0
 L3VLC*C*O+CL       <=> CJCC*C*O          4.90E+13   0.       0.   ! Af=14.14-0.15*3  trend
 L3VLC*C*O+CL       <=> C*CCCJ*O          6.92E+13   0.       0.   ! Af=14.14-0.15*2
 CJCC*C*O         = C2CL4+CLC.*C*O     6.21E+14   0.    47740.   ! Ar=0.8e12, 4.5  deg=2
 C*CCCJ*O         = C2CL3+CCL2CO     1.01E+14   0.    45160.   ! Ar=0.8e12  4.5

 LC.*CLKT+O2       <=> CCLO+CCL*OLKT      2.50E+12   0.0       0.   ! a5 A was 8e11
 CCL*OLKT+CL       <=> C.*OLKT+CL2       4.44E+13   0.0    20900.   ! a1 HFRXN=17.57
!C.*OLKT         <=> CO+CLC.*C*O       5.00E+13   0.0    24000.   ! high pressure limit, Ea=dH+???
!C.*OLKT         <=> CO+CLC.*C*O       3.86E+13   0.0    32730.   ! lizhu, rev=t3-k2, 1000K Af/r=482.9, dU=28.23
 C.*OLKT         <=> CO+CLC.*C*O       7.29E+13   0.0    33000.   ! Af/r=482.9, dU=28.23 rev=1.51e11, 4.809 (co+c2h3)

 L2V.LKT+O2       <=> CCL2O+C.*OLKT      2.50E+12   0.0       0.   ! a5  A was 8e11
 L3VK.T+O2       <=> CO2+C2CL3C.*O      2.50E+12   0.0       0.   ! a5  A was 8e11

! Table t15
 C2CL3CCLO       <=> C2CL3C.*O+CL       7.81E+43  -8.77   90224.   ! 1.00E+00  atm,  700-1400 K,   4% err, 1.00 x N2
 C2CL3CCLO       <=> CCLO+C2CL3        1.11E+62 -13.70  105744.   ! 1.00E+00  atm,  700-1400 K,   4% err, 1.00 x N2

!C2CL3CCLO+CL       <=> C2CL4+CCLO        1.25E+13   0.0    15000.   ! a6, ccl4 up, c2cl4 down
!C2CL3CCLO+CL       <=> C2CL3+CCL2O        1.25E+13   0.0    12000.   ! a6

 C2CL3CCLO+CL       <=> C2CL3+CCL2O       3.47E+13   0.0    10580.   ! lizhu cl addi trend Hfrxn=        14.14-0.15*Hrxn
 C2CL3CCLO+CL       <=> C2CL4+CCLO        3.47E+13   0.0       0.   ! lz,add trend lgA=14.14-.15*4, Hfrxn=

!C2CL3CCLO+CL       <=> CJCC*O          3.47E+13   0.0       0.   ! A=14.14-0.15*(4)
!CJCC*O         <=> C2CL4+CCLO       4.63E+14   0.0    35700.   ! rv=0.8e12,4.5(tab2)Af/r=579,dU=31.21

 C2CL3CCLO+CL       = CJ*CCCLO+CL2       8.88E+13   0.    27000.   ! Hfrxn=27.08
 C2CL3CCLO+CL       = C*CJCCLO+CL2       4.44E+13   0.    18800.   ! Hfrxn=14.17
 C2CL3CCLO+CL       = C2CL3C.*O+CL2      4.44E+13   0.    20900.   ! Hfrxn=17.57
!see end   not impt
!C2CL3C.*O+O        = C2CL3CO2.        2.50E+13   0.       0.   ! LIZHU  ccl3+o /88HER    no effect
!C2CL3CO2.         = C2CL3+CO2        8.01E+13   0.     680.   ! LIZHU REV 1E12,0  no effect

! Table t16
 C2CL3C.*O       <=> C2CL3+CO         6.69E+22  -4.02   14317.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2

! T17, lower the Ea of c2cl3+o2->cclco+clo      reduce A of ->ccl2o+cclo no change
 C2CL3+O2        <=> CL2C*CCLOO       6.11E+02   1.25   -9755.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 C2CL3+O2        <=> CCL2CO+CLO       3.05E+03   2.18    3320.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 C2CL3+O2        <=> CL2C*CCLO.+O      3.86E+12   -.16    -620.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 C2CL3+O2        <=> CL2C.COOCL       2.09E+10   -.85    1379.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 C2CL3+O2        <=> CCLO+CCL2O       1.27E+06   1.48    -140.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 CL2C*CCLOO        <=> CCL2CO+CLO       1.39E+02   1.82   25149.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 CL2C*CCLOO        <=> CL2C*CCLO.+O      4.12E+23  -4.25   14990.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2
 CL2C*CCLOO        <=> CL2C.COOCL       3.91E+15  -3.20   17169.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 CL2C*CCLOO        <=> CCLO+CCL2O       3.86E+06    .47   14051.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 CL2C.COOCL        <=> CCL2CO+CLO       2.33E+08   -.15   27921.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 CL2C.COOCL        <=> CL2C*CCLO.+O      1.21E+12  -1.04   15402.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 CL2C.COOCL        <=> CCLO+CCL2O       2.31E+12   -.94    2139.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
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!C2CL3+O        <=> CO+CCL3         2.50E+13   0.0    6200.   ! a10, Awas 1.3e13, Ea was 0, lizhu change
!C2CL3+O        <=> CL2C*CCLO.       5.00E+12   0.0      0.   !
 CL2C*CCLO.      <=> C.CL2CL*O         1.00E+13   0.0      0.   ! resonance structure
 C.CL2CL*O       <=> CCL2CO+CL         5.00E+13   0.0   30800.   ! a8 dHrxn=26.28,plus 4.5, A see tab14b, ccl4\ if Ea\
!C.CL2CL*O       <=> CCL2CO+CL         4.06E+14   0.0   25050.   ! Ar=14.14, 0.0 trend
 C.CL2CL*O       <=> CO+CCL3          4.00E+12   0.0   15700.   ! a11 dHrxn=11.23  plus 4.5?
 CCL2CO+CL        <=> CL2+CLC.*C*O       8.88E+13   0.0   28000.   ! a FROM JONGWOO HFRXN=28.67
 CLC.*C*O+O2      <=> CCLO+CO2          1.00E+12   0.0      0.   ! a5, Ea=0 no change

! Table 18
 CCL2O          <=> CCLO+CL          2.29E+38  -7.90   77769.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 CCL2O          <=> CL2+CO          2.73E+28  -5.82   85983.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2

!CCLO+CL          =  CO+CL2          1.50E+19  -2.17    1500.   ! BAULCH '81 should have been in rxn set below
 CCLO+CL          =  CO+CL2          1.30E+15   0.0     3319.   ! nist 81bau/dux, necessary? lit'l change

 CCL2O+CL        <=> CCLO+CL2          8.88E+13   0.0   22420.   ! a1 HFRXN=19.88, new cclo thermo
!CCLO+CL2          =  CCL2O+CL         1.68E+10   0.       0.   ! (96HEW/BRA + 83OHT2) = 0.065*(cocl+o2)  not good

! Table 19    co/co2 ratio
 CCLO+O2        <=> CLC*OQ.          2.52E+38  -8.92    7105.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 CCLO+O2         <=> CO2+CLO          2.54E+11   -.10   14191.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 CLC*OQ.        <=> CO2+CLO          1.35E+23  -4.43   38699.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2


! Table 20
 CCLO           <=> CL+CO           5.19E+12  -1.32    4565.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2

! Table 21 impt for ccl4
!ccl3oo = chloroform mec    Ea lower = ccl4 c2cl4 low / cocl2 up
 CCL3 + O2       <=> CCL3OO           3.90E+25  -5.54    -200.   ! 1.00E+00  atm,  300-2500 K,  31% err, 1.00 x N2
 CCL3 + O2       <=> CCL3O + O          2.75E+17  -1.43   36360.   ! 1.00E+00  atm,  300-2500 K,  15% err, 1.00 x N2
 CCL3 + O2       <=> CCL2O + CLO         7.63E+10   -.10   15755.   ! 1.00E+00  atm,  300-2500 K,   8% err, 1.00 x N2
 CCL3OO         <=> CCL3O + O          1.65E+11   -.03   53257.   ! 1.00E+00  atm,  300-2500 K,  12% err, 1.00 x N2
 CCL3OO         <=> CCL2O + CLO         2.69E+08    .27   32951.   ! 1.00E+00  atm,  300-2500 K,  19% err, 1.00 x N2

! from chloroform mec
!CCL2 + O2       <=> CCL2OO           1.36E+08   -.28    4448.   ! 1.00E+00  atm,  300-2500 K,   6% err, 1.00 x AR
!CCL2 + O2       <=> CCL2O + O          1.09E+12   -.01    5132.   ! 1.00E+00  atm,  300-2500 K,   0% err, 1.00 x AR
!CCL2 + O2       <=> CCLO + CLO          1.42E+05   1.58   14895.   ! 1.00E+00  atm,  300-2500 K,   3% err, 1.00 x AR
!CCL2OO         <=> CCL2O + O          1.13E+12   -.86    1898.   ! 1.00E+00  atm,  300-2500 K,   1% err, 1.00 x AR
!CCL2OO         <=> CCLO + CLO          6.69E+08   -.10   27925.   ! 1.00E+00  atm,  300-2500 K,   7% err, 1.00 x AR

!CCL+O2         <=> CO2+CL          1.75E+12   0.0       0.   ! O2 assciation, Cl elimination / 80TIE/WAM
 C2CL+O2        <=> CLC.*C*O+O         2.50E+12   0.0       0.   ! a14
!C2CL+O2        <=> CCL+CO2           2.50E+12   0.0       0.   ! a14
 C2CL+O2        <=> CCLO+CO           2.41E+12   0.0       0.   ! nist c2cl3+o2, no effect  / c2h+o2

! Table 22       use cl+fcoo.  same
 CLCO2.          <=> CL+CO2          2.35E+11   -.64    -105.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2

 CO+O2           <=> CO2+O          2.53E+12   0.0    47693.   ! Tsang and Hampson, J Phy Chem Ref Data 1986,15,1087
 CO+O+M           <=> CO2+M          6.17E+14   0.0     3001.   ! Tsang and Hampson, J Phy Chem Ref Data 1986,15,1087

 O2 + M          <=> O + O + M         1.81E18   -1.0   118097. ! 86tsang

! cloco.inp   Florent LOUIS
 CO + CLO        <=> CLOCO           1.22E+13  -2.00   10909.   ! 1.00E+00  atm,  300-2500 K,   6% err, 1.00 x AR
 CO + CLO        <=> CO2 + CL          2.79E+14   -.89   12150.   ! 1.00E+00  atm,  300-2500 K,   1% err, 1.00 x AR
 CLOCO          <=> CO2 + CL          1.51E+20  -3.59    8245.   ! 1.00E+00  atm,  300-2500 K,   1% err, 1.00 x AR

 CL + O2         <=> CLO + O          8.77E+14   0.0    55045.  !81BAU/DUX
!CL2+O          <=> CLO+CL          4.46E+12   0.0     3279.   ! Wine et al., J Phy Chem  1985,89,3914
 CLO+CL          <=> CL2+O          1.05E+12   0.0     9121.   ! NIST 81BAU/DUX

 C4CL3.S+O2      <=> LC#CCJ*O+CCL2O      2.50E+12   0.0       0.   ! jwb 597 need ca. A was 3e12, need low
 C4CL3NV.+O2      <=> LC#CCCLO+CCLO      5.00E+12   0.0       0.   ! jwb 597 need ca. A was 4e12  need hi

!2 CL abstr
 LC#CCCLO+CL      <=> LC#CCJ*O+CL2       4.44E+13   0.     26400.   ! a1 HFRXN=26.11
```

```
 LC#CCJ*O         <=> C2CL+CO          8.05E+12   0.     49300.   ! LIZHU from c2h3+co,nist Af/r=53.3, dU=44.5
 LC#CCJ*O+CL        <=> C2CL+CCLO          1.00E+14   0.0    28300.   ! 4/28/99  worse
 LC#CCJ*O+O2        <=> CLC.*C*O+CO2        8.00E+11   0.       0.   ! NEED CA
 LC#CCCLO+CL         <=> CJ#CCCLO+CL2         4.44E+13   0.     44700.   ! a1 Hfrxn=54.75

!3 CL add
 LC#CCCLO+CL         <=> CJ*CCCLO            3.00E+13   0.      3000.   ! Ea was 6.52 kcal
 CJ*CCCLO          <=> C2CL2+CCLO          6.77E+14   0.     47300.   ! lizhu, from c2h2+ch3=cc*c.,92Bau/cob /1123,39.57
 LC#CCCLO+CL           =  C*CJCCLO          3.00E+13   0.      3000.   ! lizhu
 C*CJCCLO           =  L2C*C*C*O+CL        1.05E+16   0.      4640.   ! lizhu C=C=C+CL, 88WAL/SKE, /39.76,46.4
 LC#CCCLO+CL           =  C#CCCL2O          3.00E+13   0.      3000.   ! lizhu
 C#CCCL2O           =  C2CL+CCL2O        2.36E+13   0.     35600.   ! lizhu rev=7.9e10,6.7  nist for ch2o

!+O
 LC#CCCLO+O         <=> CLC.*C*O+CCLO       5.00E+12   0.      3000.   !        no eff
 LC#CCCLO+O         <=> LC#CCO2.+CL         1.50E+13   0.      4000.   ! jwb 597 need added loss rxn here
 LC#CCO2.          =  C2CL+CO2          2.81E+13   0.     21450.   ! lizhu   rev 1e12,0
 LC#CCO2.+CL        <=> LC#CCJ*O+CLO        2.50E+13   0.     23000.   ! jwb 597

! BENZENE and LINEAR C6
! ADD 1/20/2000
 C4CL6DE13+C2CL3      =  C6CL9V            2.00E+12   0.0     4500.
 C6CL9V            =  C6CL8TE+CL        3.06e+15   0.0    13440.   ! logAr=14.14-0.15*(3) Ear=0
 C6CL8TE            =  C6CL7N+CL         1.34e+14   0.0    80840.   ! logAr=13.24-1.38*(1) Ear=0
 C6CL8TE            =  C6CL7S+CL        4.42e+15   0.0    88630.   ! logAr=13.24-1.38*(0) Ear=0
 C6CL8TE            =  C6CL7V+CL         8.08e+15   0.0    88520.   ! logAr=13.24-1.38*(0) Ear=0
 C6CL8TE+CL           =  C6CL7N+CL2          1.33e+14   0.0    25690.   ! a1
 C6CL8TE+CL           =  C6CL7S+CL2          8.88e+13   0.0    30380.   ! a1
 C6CL8TE+CL           =  C6CL7V+CL2          8.88e+13   0.0    30380.   ! a1
 C4CL6DE13+C2CL      =  C6CL7A            2.00E+12   0.0     4500.   !
 C6CL7A            =  C6CL6N+CL        6.05E+15   0.0     9250.   ! lgAr=14.14-0.15*2, Ear=0

 C4CL4+C2CL3        <=> C6CL7S            2.00E+12   0.0     4500.   ! Estimated from C2Cl4+C2Cl3 Table 2
 C6CL7S         <=> C6CL6S+CL        3.99E+14   0.0     7320.   ! <MR> Ar=3e13, Ear=0
 C6CL7S         <=> C6CL7N          2.59E+13   0.0     6200.   ! Ar=3.56e13 Eaf=6.2  Table 3
 C6CL7N          <=> CYC6CL7          6.00E+11   0.0     4500.   ! Ar=TST LOSS TWO ROTOR, Ear=4.5 (R.+C=C)
 C4CL4+C2CL        <=> C6CL5A           2.00E+12   0.0     4500.   !
!C6CL5A+CL2          =  C6CL6N+CL          2.35E+12   0.0        0.   ! a1 rev

 C4CL5.N+C2CL2        =  C6CL7N           2.00E+12   0.      4500.
 C4CL5.N+C2CL2        =  CYC6CL7           2.00E+12   0.      4500.   ! 2+4

!lizhu
!C4CL4+C2CL2          =  CYC6CL6          4.47E+11   0.     30100.   ! nist HC's, NOT REAL
 C4CL4+C*C:          =  C6CL6N          1.00E+13   0.     20000.   ! insertion, bozzelli

 CYC6CL7         <=> CYC6CL6+CL         6.27E+13   0.0    37270.   ! Ar=3e13, Ear=1 (TST of C6H6+Cl)
!CYC6CL7+CL          =  CYC6CL6+CL2         4.44E+13   0.     10700.   ! a1 dHrxn=1

 C6CL6N           =  C6CL5N+CL        5.52E+12   0.     82600.   ! Ar=13.24-1.38*2 trend  deg=2
 C6CL6N+CL          =  C6CL5N+CL2          8.88E+13   0.     26970.   ! a1
 C6CL6N           =  C6CL5S+CL       2.97E+15   0.     91010.   ! Ar=13.24-1.38*(zero) trend
 C6CL6N+CL          =  C6CL5S+CL2         4.44E+13   0.     32000.   ! a1
 C6CL6N           =  C6CL5A+CL        1.50E+15   0.     87910.   ! ar=13.24-1.38*(zero) trend
 C6CL6N+CL          =  C6CL5A+CL2         4.44E+13   0.     30380.   ! a1
 C6CL6N           =  C6CL5T+CL       1.02E+13   0.     79840.   ! ar=13.24-1.38*(zero) trend
 C6CL6N+CL          =  C6CL5T+CL2         4.44E+13   0.     26650.   ! a1

 C6CL6S          =  C6CL5B+CL        5.66E+14   0.     82690.   ! ar=13.24-1.38*1 trend  deg=4
 C6CL6S+CL          =  C6CL5B+CL2         1.78E+14   0.     26970.   ! a1

 C4CL2+C2CL3        <=> C6CL5S           2.00E+12   0.0     4500.   ! Estimated from C2Cl4+C2Cl3 Table 2
 C6CL5S+CCL4        <=> C6CL6N+CCL3         2.50E+12   0.0    10000.   ! a15
 C6CL5S         <=> C6CL5N          1.91E+13   0.0     6200.   ! Ar=3.56e13 Eaf=6.2  Table 3
 C6CL5S         <=> C6CL4S+CL          1.19E+14   0.0    11320.   ! <MR> Ar=3e13, Ear=0 TABLE 2
 C4CL3NV.+C2CL2       =  C6CL5N           2.00E+12   0.0     4500.   ! est
 C6CL5N          <=> C6CL4N+CL          3.63E+14   0.0    26520.   ! <MR> Ar=3e13, Ear=0 TABLE 2
 C6CL5N          <=> CYC6CL5          6.00E+11   0.0     4500.   ! Ar=TST LOSS of TWO ROTOR, Ea =4.5 (R.+C=C)
 CYC6CL5+CCL4       <=> CYC6CL6+CCL3        2.50E+12   0.0    10000.   ! a15T
 CYC6CL5+CL2        <=> CYC6CL6+CL         2.50E+12   0.0    10000.   ! a15T
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CYC6CL5+CL        <=> CYC6CL6          1.00E+14   0.0      0.   ! lizhu

C4CL5.N+C2CL4       = NC6CL9DE         2.00E+12   0.    4500.
NC6CL9DE          = C6CL8TE+CL       3.65E+14   0.    14450.   ! logAr=14.14-0.15*(4) Ear=0

2CJ*C*C           = CYC6CL6        3.00E+11   0.       0.   ! nist 2 c.=c=ch2
CJC#C+CJC*C         = C#CCCC*C         3.20E+12   0.      0.   ! trend
C#CCCC*C+CL          = C6CL7A+CL2        8.88E+13   0.    16110.

!C8
2C4CL5.N          = LC8CL10         9.12E+12   0.       0.   ! k=13.88-0.23*4=3.16e12
LC8CL10           = LC8CL9N+CL        1.37E+14   0.    80860.   ! krev=13.24-1.38*1=7.24e11
LC8CL10+CL          = LC8CL9N+CL2       1.78E+14   0.    29230.   ! a1
LC8CL9N           = PRESTYR1         8.00E+11   0.    4500.
PRESTYR1           = STYRENE+CL        8.81E+14   0.    23620.   ! krev=14.14-0.15*2 trend  *****
C4CL5.N+C4CL3NV.    = LC8CL8N          2.63E+13   0.       0.   ! k=13.88-0.23*2  trend
LC8CL8N+CL          = LC8CL9N          4.90E+13   0.       0.   ! a1 a=14.14-0.15*3  trend

! styrene will be lower
!C4CL5.N+C4CL5.S     = LC8CL10A          9.12E+12   0.       0.   ! Af=13.88-0.23*4  trend
!LC8CL10A            = IC8CL9A+CL       1.91E+14   0.    81920.   ! Ar=13.24-1.38*1 trend
!LC8CL10A            = IC8CL9B+CL       8.37E+13   0.    79940.   ! Ar=13.24-1.38*1 trend
!LC8CL10A+CL          = IC8CL9A+CL2       8.88E+13   0.    26260.   ! a1
!LC8CL10A+CL          = IC8CL9B+CL2       8.88E+13   0.    24990.   ! a1
!IC8CL9A           = PRESTYR3         8.00E+11   0.    4500.
!IC8CL9B           = PRESTYR5         8.00E+11   0.    4500.
!PRESTYR3           = STYRENE+CL        6.92E+14   0.    27360.   ! Ar=14.14-0.15*2 trend
!PRESTYR5           = STYRENE+CL        2.38E+14   0.    24390.   ! Ar=14.14-0.15*2 trend

CYC6CL5+C2CL3      <=> STYRENE          2.20E+12   0.0      0.   ! CCL3+CCL3 a16
CYC6CL5+C2CL4      <=> PRESTYR6         8.00E+11   0.0    4500.   ! EST
PRESTYR6         <=> STYRENE+CL       3.45E+14   0.0    12260.   ! REV=CL+C2CL4
CYC6CL6+C*C:       <=> STYRENE         1.00E+13   0.0      0.   ! bozzelli
CYC6CL6+C2CL3      <=> PRESTYR1         8.00E+11   0.0    4500.   ! EST
CYC6CL7+C2CL3      <=> CYC8CL10         2.20E+12   0.0      0.   ! CCL3+CCL3 a16
CYC6CL7+C2CL4      <=> CJCYDE13         2.20E+12   0.0      0.   ! CCL3+CCL3 a16 *****
CJCYDE13          = CYC8CL10+CL      6.17E+14   0.    18020.   ! REV=CL+C2CL4 *****
!CYC6CL5+C2CL       <=>               2.20E+12   0.0      0.   ! CCL3+CCL3 a16
!CYC6CL6+C2CL       <=>               8.00E+11   0.0    4500.   ! CCL3+CCL3 a16
!CYC6CL7+C2CL       <=> C#CYDE13         2.20E+12   0.0      0.   ! CCL3+CCL3 a16
CYC6CL5+C2CL2      <=> CYC6C*CJ         2.20E+12   0.0      0.   ! CCL3+CCL3 a16
CYC6C*CJ+CL         = STYRENE         7.24E+11   0.       0.   ! C2CL3+CL
!CYC6CL7+C2CL2      <=> C*CJDE13         8.00E+11   0.0    4500.   ! CCL3+CCL3 a16

!LINEAR C3
CCL3+C2CL3        <=> LC3CL6          2.20E+12   0.0      0.   ! CCL3+CCL3 a16

LC3CL6          <=> CJC*C+CL        9.52E+14   0.0    67230.   ! <MR> Ar=2.45e13, Ear=0   see c2cl5+cl=96HUY/NAR
LC3CL6          <=> CCJ*C+CL        1.28E+14   0.0    79270.   ! <MR> Ar=7.24e11, Ear=0  deg=1  trend
LC3CL6          <=> CC*CJ+CL        1.48E+14   0.0    85970.   ! <MR> Ar=7.24e11, Ear=0  deg=2  trend
LC3CL6+CL         <=> CJC*C+CL2        1.33E+14   0.0    16610.   ! a1
LC3CL6+CL         <=> CCJ*C+CL2        4.44E+13   0.0    24340.   ! a1
LC3CL6+CL         <=> CC*CJ+CL2        8.88E+13   0.0    28890.   ! a1

! Hf lc3cl4 = b3 calc, higher
CC*CJ           <=> LC3CL4+CL        1.62E+15   0.0    28870.   ! #Cl=2
CC*CJ           <=> C*C*C+CL        2.69E+14   0.0    15790.   ! #Cl=2
CC*CJ           <=> CCL3+C2CL2        2.00E+12   0.0    4500.   ! Estimated from C2Cl4+C2Cl3 Table 2

LC3CL4           = CJC#C+CL        3.85E+16   0.    61490.   ! Ar=14.14-0.192*3=3.66e13 deg=3 trend
LC3CL4+CL          = CJC#C+CL2        1.33E+14   0.    13390.   ! a1
LC3CL4           = CCL3+C2CL        1.42E+18   0.    107100.   ! Ar=3.92e13,0 NIST

!CJC#C+O2           = CQJC#C
!COJC#C           = CYOOC*CJ
!CYOOC*CJ           = COJYCO*C
!COJCO*C           = CCL2O+CYC2CL2O
!LC3CL4           = CCL2O+CYC2CL2O     2.50E+12   0.0      0.   !

CJC*C           <=> C*C*C+CL        3.47E+13   0.0    26960.   ! A=14.14-0.15*(CL#), Ear=0 add trend
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CCL3+C2CL4       <=> C3CL7N          5.00E+10   0.0    6600.   ! CCL3+C2F4   nist
 C3CL7N           = LC3CL6+CL        4.20E+14   0.0   14710.   ! A=14.14-0.15*(4 #), Ear=0

 NC4CL5Q.+CL      <=> L3VVL2O.+CLO      5.00E+12   0.0      0.   ! a4 was 5.05e12
 SC4CL5Q.+CL      <=> L2VO.VL3+CLO      5.00E+12   0.0      0.   ! a4
 CL2C*CCLOO+CL     = CL2C*CCLO.+CLO   5.00E+12   0.0      0.   ! no change
 CLC*OQ.+CL        = CLCO2.+CLO       5.00E+12   0.0      0.   ! LIZHU
 CCL3OO+CL         = CCL3O+CLO        5.00E+12   0.0      0.   ! lizhu add, no change

 CCLO+O           = CO+CLO         1.00E+13   0.00      0.   !jwb 95 est need chemact
!CCL2O+O          <=> CCLO+CLO        2.00E+13   0.0   17000.   ! a12
 CCL2O+O          <=> CCLO+CLO        6.00E+09   0.0       0.   ! nist  , no big change

 C4CL5.N+CLO      <=> L3VVL2O.+CL     1.00E+13   0.0       0.   ! a2
 C4CL5.N+CLO      <=> C4CL6DE13+O     1.00E+12   0.0    2000.   ! a3
 C4CL5.S+CLO      <=> L2VO.VL3+CL     1.00E+13   0.0       0.   ! a2 Ea was 2000       no change
 C4CL5.S+CLO      <=> C4CL6DE13+O     1.00E+12   0.0    2000.   ! a3 Ea was 10kcal, lit'l change

!CCL3+CLO         <=> CCL3O+CL        1.00E+13   0.0       0.   ! a3, lit'l change
!CCL3+CLO         <=> CCL4+O          1.00E+12   0.0    2000.   ! a2
 CCL3+CLO         <=> CCL3O+CL        5.00E+12   0.0       0.   ! 8/18/99, try/co down/cocl2 down, ccl4 c2cl4 up
 CCL3+CLO         <=> CCL4+O          5.00E+12   0.0    2000.   ! 8/18/99, try

 C2CL3+CLO        <=> CL2C*CCLO.+CL    1.00E+13   0.0       0.   ! a2  A was 5.1e12
 C2CL3+CLO        <=> C2CL4+O          1.00E+12   0.0    2000.   ! a3 A was 9.1e11, Ea was 0
 C2CL5+CLO        <=> C2CL5O+CL        1.00E+13   0.0       0.   ! a3, jwb est, Ea was 1000
 C2CL5+CLO        <=> C2CL6+O          1.00E+12   0.0    2000.   ! a2 Ea was 3000
!CCL2+CLO         <=> CCL2O+CL         1.00E+13   0.0       0.   ! a2  A was 5e13, Ea was 13 kcal
!CCL2+CLO         <=> CCL3+O           1.00E+12   0.0    2000.   ! LIZHU  NO CHANGE
 C2CL+CLO         <=> CLC.*C*O+CL      1.00E+13   0.0       0.   ! LIZHU  NO CHANGE
 C2CL+CLO         <=> C2CL2+O          1.00E+12   0.0    2000.   ! LIZHU  NO CHANGE

!C2CL5O            = CCL3+CCL2O        1.00E+13   0.0    3000.   ! LIZHU ADDED, NO CHANGE
!C2CL5O            = CCL3CCLO+CL       3.00E+13   0.     9660.   ! LIZHU nist 98cza
!CCL3CCLO           = CCL3+CCLO        1.00E+13   0.     3000.   ! LIZHU

!CCL3O             = CCL3+O                                    ! NOT FAVORATE
 CCL3O             = CCL2O+CL          1.00E+13   0.        0.   ! lizhu Hrxn=-6.87, ccl2o/ccl4 lit'l hi

 C4CL6DE13+O       <=> L3VVL2O.+CL         3.52E+12   0.0    2500.   ! Fontijn ???
!C4CL6DE13+O       <=> L3VVL2O.+CL         3.52E+12   0.0       0.   ! LZ, lit'l change
!C4CL6DE13+O       <=> C2CL3CCLO+CCL2T     3.50E+12   0.0    2500.   ! Fontijn ???  ref?
!C4CL6DE13+O       <=> C2CL3CCLO+CCL2T     2.50E+13   0.0       0.   ! o+ccl3 impt c2cl4 hi   /88HER

 C2CL3+O          <=> CCL2CO+CL         2.50E+13   0.0       0.   ! ccl3+o lizhu, A was 1.7e12/C2CL3+O2=5E12,same
 C2CL3+CLO         <=> CO+CCL4          2.50E+13   0.0    6200.   ! a10 /was 1e12,0/ lizhu, same
 CCL2O+O          <=> CLCO2.+CL         2.50E+13   0.0       0.   ! a13,Hrn=-35.9,(Ea/3000),low E=low ccl2o,c2cl4 but hi ccl4
 CCLO+O           <=> CO2+CL          2.50E+13   0.0       0.   ! a9
!CCL3+O           <=> CCL2O+CL          6.19E+13  -0.2     130.   ! a13  ?
 CCL3+O           <=> CCL2O+CL          2.50E+13   0.0       0.   ! 96SEE/SLA/same, 88HER,use/same

 2CCL2             = C2CL4           5.70E+15   0.0    -5948.   ! nist,/97KUM/SU3// c2cl4 up

!CCL3C.*O+M         = CO+CCL3+M         1.19E+14   0.0    1780.   ! NIST, co+ch3=1.52e12,0//Af/r=78.53,dU=1.78
!CCL2CO+CL          = CCL3C.*O        1.50E+13   0.        0.   ! TABLE 7, LIZHU TO REDUCE c=c=o, Hrn=-17.03
!CCL2CO            = CCL2+CO        8.31E+11   0.    51750.   ! rev=6e8, 0.0,  nist

! make cyc-c3cl4o
!CCL2CO+CLO          = COCLCJ*O
!COCLCJ*O           = COJCJ*O
!COJCJ*O           = CYC3CL4O
!COJCJ*O           = CCL2O+CO

!C4CL6N4.MEC STOP HERE// c=c + clo  //comment via addition, cl shift
 C2CL4+CLO         <=> CCL2O+CCL3        1.50E+11   0.0   10500.   ! add Oct, 99
 C2CL4+CLO         <=> CCL3CCLO+CL       4.50E+11   0.0   10500.   ! add oct, 99
 CCL3+CCLO         <=> CCL3CCLO          9.12E+12   0.0       0.
 C4CL6DE13+CLO       <=> CCL2O+CJC*C        1.50E+11   0.0   10500.   ! add Oct, 99
 C4CL6DE13+CLO       <=> C2L3CC*O+CL        4.50E+11   0.0   10500.   ! add oct, 99
 C2L3CC*O+CLO        <=> CCL2O+CJCC*O       1.50E+11   0.0   10500.   ! add Oct, 99
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 C2L3CC*O+CLO      <=> O*CC2C*O+CL       4.50E+11   0.0    10500.   ! add oct, 99
 C2L3CC*O        <=> C2CL3+C.CL2CL*O    5.34E+16   0.0    95240.   ! add oct, 99/REV=10E12.6(allra&shaw, i-c4h9)
 C2L3CC*O        <=> CJC*C+CCLO         5.56E+16   0.0    81040.   ! add Mar,00 /REV=10E12.6(allra&shaw, i-c4h9)
 O*CC2C*O        <=> 2C.CL2CL*O         1.980+17   0.0    81900.   ! add oct, 99/REV=10E12.6(allra&shaw, i-c4h9)
!C2L3CC*O+O        <=> O*CCC*O+CCL2T      2.50E+13   0.0       0.   ! o+ccl3 impt c2cl4 hi   /88HER
 O*CCC*O         =  CCLO+C.CL2CL*O      1.12E+17   0.0    82000.   ! REV=10E12.6
 C2L3CC*O+CL       <=> CCJCC*O           3.46E+13   0.0       0.   ! add oct, 99/SEE TABLE 2
 C2L3CC*O+CL       <=> CJCCC*O           6.93E+13   0.0       0.   ! add oct, 99/SEE TABLE 2
 C2L3CC*O+CL       <=> C*CCJC*O+CL2        8.88E+13   0.0    13500.
 C2L3CC*O+CL       <=> CJ*CCC*O+CL2        8.88E+13   0.0    28960.
 C2L3CC*O+CL       <=> C*CCCJ*O+CL2        4.44E+13   0.0    28450.
 C*CCJC*O         =  C2CL3+CCL2CO       5.08E+14   0.     68500.   ! rev=8e11,4.5
 C*CCJC*O         =  C*C*C+CCLO        2.10E+14   0.     56300.   ! rev=8e11,4.5
 C*CCJC*O         =  L3VLC*C*O+CL       5.40E+15   0.     41550.   ! rev=14.14, 0  trend
 C*CCJC*O         =  C*C*CC*O+CL       9.26E+14   0.     40400.   ! rev=14.14, 0  trend
 CCJCC*O         =  LC3CL6+CCLO       4.06E+12   0.0    27400.
!LC3CL6+CCLO        =  CCJCC*O          2.00E+12   0.0     4500.
 CJCCC*O         =  C2CL4+C.CL2CL*O    3.05E+12   0.0    32800.
!C2CL4+C.CL2CL*O     =  CJCCC*O          2.00E+12   0.0     4500.

 C4CL4+CLO         =  CCL2O+CJC#C       1.50E+11   0.      6200
 C4CL4+CLO         =  C#CCC*O+CL        1.50E+11   0.      6200
 C#CCC*O         =  CCLO+CJC#C        1.06E+17   0.     79930.   ! Ar=13.88-.23*3
 C#CCC*O         =  C2CL+C.CL2CL*O     1.05E+17   0.    122210.   ! Ar=13.88-.23*2 trend
 C#CCC*O+CL         =  CJ*CCC*O         1.38E+14   0.         0.   ! Af=14.14-0.15*0
 C#CCC*O+CL         =  C*CJCC*O         9.77E+13   0.         0.   ! Af=14.14-0.15*1
 CJ*CCC*O         =  C2CL2+C.CL2CL*O    5.36E+14   0.     42760.   ! Ar=8e11, 4.5
 C*CJCC*O         =  C*C*C+CCLO        8.22E+13   0.     31770.   ! Ar=8e11, 4.5

!c4cl4 --> vinylidene + o2

!C4CL4            = C*CC*C:          1.00E+14   0.0    43000.   ! BOZZELLI  OR CHAD-HAI WANG
 C4CL4+M           = C*CC*C:+M          1.00E+14   0.0    62030.   ! BOZZELLI  OR CHAD-HAI WANG
!C4CL4+M           = C*CC*C:+M          4.12E+29  -5.75   46469.   ! chad ch2=c: + o2 (1)
!C*CC*C:+O2          = C*C*C:+CO2          1.00E+13   0.0       0.   ! chad  ch2=c: + o2 -> ch2: + co2
 C*CC*C:+O2          = C*CC:+CO2          1.00E+13   0.0    10000.   !
 C*CC:           = CJ*C*C+CL         1.00E+13   0.0    32330.   ! Ea=dHrxn
!C*CCCl:+O2          = C2CL3+CL+CO2
 CJ*C*C+O2           = C2CL3+CO2          1.00E+13   0.0       0.

!C2CL2+M           = C*C:+M           1.00E+14   0.0    52460.   ! ea=dHrxn
!C*C:+O2           = CCL2T+CO2          1.00E+13   0.0    10000.
!C4CL4+O2 ???
!2C2CL2           = C4CL4            5.50E+12   0.0    37000.   ! insertion   nist 2c2h2->c4h4

!add TABLE 24 10/20/99
 CJCA+O2          <=> CQJCA            8.43E+45  -10.59   10996.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 CJCA+O2          <=> CACOJ+O            1.42E+13   -.03   34328.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 CJCA+O2          <=> CYOOCVJ            1.06E+27   -6.21    5807.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 CJCA+O2          <=> COJCYOV            5.86E+21   -4.63    5525.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 CJCA+O2          <=> CCL2O+CJYOC*C        2.44E+22   -3.96    5728.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 CQJCA          <=> CACOJ+O           2.73E+24   -3.96   60053.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 CQJCA          <=> CYOOCVJ           3.00E+48  -12.93   29141.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 CQJCA          <=> COJCYOV           4.70E+46  -12.40   31442.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 CQJCA          <=> CCL2O+CJYOC*C       2.41E+47  -11.76   31686.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 CYOOCVJ          <=> CACOJ+O            3.90E+17   -2.09   45321.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 CYOOCVJ          <=> COJCYOV            3.52E+24   -6.08   11529.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2
 CYOOCVJ          <=> CCL2O+CJYOC*C        1.29E+25   -5.39   11709.   ! 1.00E+00  atm,  700-1400 K,   2% err, 1.00 x N2
 COJCYOV          <=> CACOJ+O            1.96E+32   -6.91  118669.   ! 1.00E+00  atm,  700-1400 K,   5% err, 1.00 x N2
 COJCYOV          <=> CCL2O+CJYOC*C        6.00E+10    -.42    -691.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2

 CACOJ           = CAC*O+CL          5.00E+13   0.0        0.   ! Af=est., dU=-21.89
 CJYOC*C           = C*CJCCLO          6.22E+11   0.0     4000.   ! Ar=4.61e11, Eaf=4 (Hank)

!add TABLE 25 10/20/99
 C*CJCCLO+O2        <=> C*CQC*O            1.12E+26   -4.96    -597.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 C*CJCCLO+O2        <=> C*COJC*O+O          5.27E+15    -.60   17312.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 C*CJCCLO+O2        <=> CYOOCJCO           6.76E+13   -1.89    4801.   ! 1.00E+00  atm,  700-1400 K,   1% err, 1.00 x N2
 C*CJCCLO+O2        <=> COCOCOJ           4.80E+13   -1.67    9811.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
 C*CJCCLO+O2        <=> CCL2O+CCLOCJ*O       6.21E+12    -.63    8105.   ! 1.00E+00  atm,  700-1400 K,   0% err, 1.00 x N2
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C*CQC*O        <=> C*COJC*O+O        7.78E+06   1.00   26162.   ! 1.00E+00 atm, 700-1400 K,  1% err, 1.00 x N2
C*CQC*O        <=> CYOOCJCO          9.39E+16  -3.77   16290.   ! 1.00E+00 atm, 700-1400 K,  1% err, 1.00 x N2
C*CQC*O        <=> COCOCOJ           1.51E+10  -1.62   18971.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00 x N2
C*CQC*O        <=> CCL2O+CCLOCJ*O    8.42E+08   -.48   17038.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00 x N2
CYOOCJCO        <=> C*COJC*O+O       7.27E+12   -.77   15360.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00 x N2
CYOOCJCO        <=> COCOCOJ          1.81E+10  -1.41    5751.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00 x N2
CYOOCJCO        <=> CCL2O+CCLOCJ*O   2.11E+09   -.36    4042.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00 x N2
COCOCOJ        <=> C*COJC*O+O        1.53E+67 -20.55   95108.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00 x N2
COCOCOJ        <=> CCL2O+CCLOCJ*O    5.08E+11   -.72    1424.   ! 1.00E+00 atm, 700-1400 K,  0% err, 1.00 x N2

CCLOCJ*O        = CCLO+CO          5.00E+13   0.0    1210.  ! A= EST  Ear=5  dU=-3.79
C*COJC*O        = CCL2CO+CCLO      5.00E+13   0.0   26350.  ! dU=21.85 + 4.5, Af/Ar=937.7

! lizhu// make c=cy(c-c=c-c=)  ultraminor product dichloromethylenetetralchloro-1-pentadiene (c6cl6)
 C4CL5.S+C2CL2     = IC4L4C*C.      2.00E+12   0.    4500.
 IC4L4C*C.       = C*CYC5RA       2.00E+12   0.    4500.
 C*CYC5RA         = C*CYC5DE+CL    3.03E+14   0.      0.   ! Ar=14.14-2*.15=6.92E13

 C6CL7S         = C*CYC5RB        2.00E+12   0.    4500.
 C*CYC5RB         = C*CYC5DE+CL    1.38E+14   0.      0.   ! Ar=14.14-2*.15=6.92E13

! make CYOC  tetrachloro oxirane  4/13/2000
 C2CL4+O          = CYOC           7.00E+10   0.      0.   ! c2h4+o 7e11 nist
 C2CL4+CCL3OO       = CYOC+CCL3O     4.60E+06   0.      0.   ! ch3oo+c2h4  4.6e7 nist
 C2CL5+O2          = C2CL5OO       1.00E+11   0.      0.   ! 67HUY/OLB nist
 C2CL5OO          = CYOC+CLO       2.60E+08   0.0     0.   ! c2h5+o2 nist
 C2CL4+C2CL5OO      = CYOC+C2CL5OJ   4.60E+06   0.      0.   ! ch3oo+c2h4  4.6e7 nist

! make CYC*C  cyclopropene  4/13/2000
 CJC*C           = CYC3CL5J       8.00E+10   0.    20000.   ! guess
 CYC3CL5J          = CYC3CL4E+CL    5.90E+15   0.    31510.   ! trend+kr at 300K
 CYC3CL6+CL         = CYC3CL5J+CL2   2.66E+14   0.    32710.   ! al
 CJ*C*C           = CYCJ*C        8.00E+10   0.    40000.   ! guess
 CJC#C           = CYCJ*C        8.00E+10   0.    30000.   ! guess
 CYC3CL4E+CL        = CYCJ*C+CL2    1.78E+14   0.    28200.   ! al
 CYCJ*C+CCL4        = CYC3CL4E+CCL3  2.50E+12   0.    10000.   ! see benzene

!CYOC will be too low
! CYOC           = CJCOJ         1.00E+16   0.    46330.   ! A=est, Ea=dHrxn
! CJCOJ          = CCL2+CCL2O     1.00E+14   0.     5000.   ! est

!make styrene
 C4CL7.S          = CJC*CC         1.00E+13   0.      0.   ! resonance

 C4CL5.N+CJC*CC     = LC8CL12       1.55E+13   0.      0.   ! Af=13.88-.23*3 trend
 LC8CL12          = LC8CL11+CL     7.48E+15   0.    67330.   ! Ar=14.14-0.192*2 deg=3
 LC8CL12+CL         = LC8CL11+CL2    1.33E+14   0.    17070.   ! al
 LC8CL11          = CYC8CL11      8.00E+11   0.     4500.
 CYC8CL11          = CYC8CL10+CL    5.37E+13   0.      0.   ! Ar=14.14-0.15*2  trend  dHrxn(-)
 CYC8CL10          = PRESTYR1+CL    1.54E+16   0.    60600.   ! Ar=14.14-0.192*2  deg=2  ****
 CYC8CL10+CL        = PRESTYR1+CL2   8.88E+13   0.    12780.   ! al               **
 CYC8CL10          = PRESTYR5+CL    1.83E+16   0.    59840.   ! Ar=14.14-0.192*3  deg=1
 CYC8CL10+CL        = PRESTYR5+CL2   4.44E+13   0.    11900.   ! al

 C4CL5.N+C4CL4      = LC8CL9T       8.00E+11   0.     4500.   !                   **
 LC8CL10          = LC8CL9T+CL     7.57E+15   0.    91430.   ! A=13.24-1.38*0 trend deg=2
 LC8CL10+CL         = LC8CL9T+CL2    8.88E+13   0.    32300.   ! al
 LC8CL9T          = PRESTYR2      8.00E+11   0.     4500.   !                   **
 PRESTYR2          = STYRENE+CL     8.20E+14   0.    39470.   ! Ar=14.14-0.15*2 trend

 C4CL5.N+C.#CC2CL3   = LC8CL8A        4.47E+13   0.      0.   ! A=13.88-0.23  trend
 C6CL5T+C2CL3       = LC8CL8A        4.47E+13   0.      0.   ! A=13.88-0.23  trend
 C6CL5B+C2CL3       = LC8CL8A        2.63E+13   0.      0.   ! A=13.88-0.23*2  trend
!styrene slightly lower
!LC8CL8A+CL        = LC8CL9T        6.92E+13   0.      0.   ! A=14.14-0.15*2 trend

 C6CL7N+C2CL        = LC8CL8N        1.55E+13   0.      0.   ! ch2cl+chcl2
 C6CL7N+C2CL2       = LC8CL9N        8.00E+11   0.     4500.

 C6CL7N+C2CL3       = LC8CL10        2.63E+13   0.      0.   ! A=13.88-0.23*2  trend
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C6CL8TE+C2CL3      = LC8CL11B        8.00E+11   0.     4500.   !                  **
LC8CL11B           = LC8CL10+CL      3.20E+15   0.    10250.   ! Ar=14.14-0.15*2  deg=2 **

C6CL7N+CCL3        = C7CL10TE        9.12E+12   0.        0.   ! A=13.88-0.23*4  trend
C6CL8TE+CCL3       = C7CL11          8.00E+11   0.     4500.
C7CL11             = C7CL10TE+CL     1.04E+15   0.     9730.   ! Ar=14.14-0.15*2 trend
C7CL10TE+CCL3      = C8CL13          8.00E+11   0.     4500.
C8CL13             = C8CL12B+CL      6.99E+14   0.    15170.   ! Ar=14.14-0.15*2 trend deg=2
C8CL12B            = C8CL11N+CL      3.12E+16   0.    67430.   ! Ar=14.14-0.192*2 trend deg=6
C8CL12B+CL         = C8CL11N+CL2     2.66E+14   0.    16610.   ! a1
C8CL11N            = CCJYDE13        8.00E+11   0.     4500.
CCJYDE13           = CYC8CL10+CL     3.23E+14   0.    11790.   ! Ar=14.14-0.15*3 trend

C6CL7N+C2CL4       = LC8CL11A        8.00E+11   0.     4500.   ! styrene no change
LC8CL10+CL         = LC8CL11A        9.80E+13   0.        0.   ! Af=14.14-0.15*3  trend deg=2 *
LC8CL11A           = CYC8CL11A       8.00E+11   0.     4500.                        *
CYC8CL11A          = CYC8CL10A+CL    4.29E+16   0.        0.   ! Ar=14.14-0.15*1 trend      *
CYC8CL10A          = PRESTYR2+CL     1.91E+16   0.    56290.   ! Ar=14.14-0.192*1 deg=2      ++
CYC8CL10A+CL       = PRESTYR2+CL2    8.88E+13   0.    10360.   ! a1
CYC8CL10A          = PRESTYR4+CL     7.96E+15   0.    69540.   ! Ar=14.14-0.15*1 trend
CYC8CL10A+CL       = PRESTYR4+CL2    8.88E+13   0.    18610.   ! a1
PRESTYR4           = STYRENE+CL      1.09E+15   0.    26210.   ! Ar=14.14-0.15*2 trend

 CJC*CC+C2CL3      = C6CL10E14       1.55E+13   0.        0.   ! Af=13.88-0.23*3  trend
 CJC*CC+C2CL4      = C6CL11E4        8.00E+11   0.        0.   ! est
 C6CL11E4          = C6CL10E14+CL    1.52E+15   0.    20130.   ! cl+c2cl4=rev
 CC*CJ+CJC*C       = C6CL10E14       1.55E+13   0.        0.   ! Af=13.88-0.23*3  trend
 LC3CL6+CJC*C      = C6CL11E5        8.00E+11   0.     4500.
 C6CL11E5          = C6CL10E14+CL    2.45E+14   0.    12380.   ! CL+C2CL4 = REV
 C6CL10E14+CL      = C6CL9DE14+CL2   1.33E+14   0.    16610.   ! a1
 C6CL10E14         = C6CL9DE14+CL    4.62E+15   0.    67330.   ! Ar=14.14-0.192*3 deg=3 trend
 C6CL9DE14         = CYC6CL9A        8.00E+11   0.     4500.
 CYC6CL9A          = CYC6CL8+CL      1.23E+15   0.        0.   ! Ar=14.14-0.15*2 deg=2 trend  dHrxn(-)
C6CL10E14          = C6CL9E14N+CL    8.69E+12   0.    86420.   ! Af=13.24-1.38*3 trend deg=2
C6CL10E14+CL       = C6CL9E14N+CL2   8.88E+13   0.    28890.   ! a1
C6CL9E14N+C2CL3    = LC8CL12         2.63E+13   0.        0.   ! Af13.88-.23*2 trend

C2CL3+CC*CJ        = C5CL8DE13       2.63E+13   0.        0.   ! Af=13.88-0.23*2  trend
C5CL8DE13          = C5CL7DE13+CL    8.41E+15   0.    67520.   ! Ar=14.14-0.192*2  deg=3 trend
C5CL8DE13+CL       = C5CL7DE13+CL2   1.33E+14   0.    16450.   ! a1
C5CL7DE13+CC*CJ    = LC8CL12         1.55E+13   0.        0.   ! Af=13.88-0.23*3

C6CL9V+C2CL2       = CYC8CL11B       8.00E+11   0.     4500.   !
CYC8CL11B          = CYC8CL10+CL     5.80E+15   0.      440.   ! Ar=trend
C4CL6DE13+C4CL5.N  = CYC8CL11B       8.00E+11   0.     4500.   !

2CJ*C*C            = C6CL6A          9.12E+12   0.        0.
C6CL6A+CL          = C6CL7B          1.38E+14   0.        0.
C6CL7B             = CYC6CL7         8.00E+11   0.     4500.

!CCL2+O            = CCL2O           1.00E13    0.        0.   ! from chcl3 mechanism
END
! a1:  Trend plot abstraction of Cl from RCl, see ref.
! a2:  Association to ROCl then cleavage of weak Cl-O to alkooxy radical
! a3:  Abstraction of Cl by R. from ClO
! a4:  Cl+ROO->ROOCl->RO+Cl, formation of ROOCl, dissociation to lower energy products RO+ClO
! a5:  From QRRK table 12 and corresponding figure
! a6:  Chemical activation reaction, Cl addition, dissociation of adduct to products, Cl addition from a7
! a7:  Addition of Cl to olefin, see a1
! a8:  Elimination, reverse from Wang and Frenhlach (see QRRK table 3)
! a9:  Chemical activation reaction, A from Oxygen atom association to alkyl radical, Ea=0, elimination of weaker C-Cl bond
! a10: Chemical activation reaction, A, Ea from a9. Cl atom shift from Skell et al. (see QRRK talbe 2), then elimination of CO
! a11: Cl shift (see QRRK table 2). Elimination Eaf=dH+Ear
! a12: Addition of Cl to olefin, see a1. ClO molecular elimination Eaf=dH+Ear
! a13: Chemical activation reaction. A from a12. Elimination of Cl from weaker C-Cl bond.
! a14: Chemical activation reaction, similar to a5
! a15: R. abstraction of Cl from RCl, Ea from a1, A from alkyl radical abstraction data in NIST database.
! a16: Chiang, H. M., Ph.D. dissertation NJIT May,1995, pp.176
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