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ABSTRACT

THERMOCHEMICAL PROPERTIES OF METHYL AND CHLORO-METHYL HYPOCHLORITES AND ETHERS AND REACTION OF METHYL RADICAL WITH CLO

Hypochlorites are formed from reactions of chlorine monoxide (ClO) addition to unsaturates and association with radicals. ClO is a prevalent and an important species in chemistry of the atmosphere and in combustion systems where chlorine is present. Thermochemical property data on these oxy-chlorocarbon species are important to understanding the reaction pathways and kinetics in these environments. Enthalpy, $\Delta H_f^\circ_{298}$, entropy, S°_{298} and heat capacities, $C_p(T)$ from 300 to 1500 K are determined for methyl hypochlorite and three chloro-methyl hypochlorites and formaldehyde-Cl atom complex radicals ($\text{CH}_2\text{O}\cdots\text{Cl}$, $\text{CHClO}\cdots\text{Cl}$, $\text{CCl}_2\text{O}\cdots\text{Cl}$) by density functional, and *ab initio* calculation methods. Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) density functional calculation level, with single point calculations for energy at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q levels of calculation. Enthalpies of formation are determined at each calculation level using the $\Delta H^\circ_{\text{rxn}}$ and known enthalpies of other reactants in each of several working reactions (up to seven). Barriers for intramolecule rotation are calculated and contributions to entropy and heat capacity from internal rotation in the chloro-methyl hypochlorite, chloro-dimethyl ether, chloro-methoxy and formaldehyde-Cl atom coupling radicals are determined. Evaluation of enthalpy data from reaction (up to seven) schemes and the statistical distribution of rotation conformers, result in $\Delta H_f^\circ_{298}$ values for CH_3OCl of -15.4 ± 1.5 , CH_2ClOCl of -22.1 ± 2 , CHCl_2OCl of -26.1 ± 4 and CCl_3OCl of -26.7 ± 5

kcal/mol in CBS-Q//B3LYP/6-31G(d,p) method. Evaluation of data from all 7 reaction schemes, and the statistical distribution analysis of rotation conformers, result in $\Delta H_f^\circ_{298}$ values for $\text{CH}_2\text{ClOCH}_3$ of -55.4 ± 1 , $\text{CHCl}_2\text{OCH}_3$ of -61.8 ± 2 , and CCl_3OCH_3 of -62.8 ± 3 kcal/mol at the CBS-Q//B3** level. Enthalpies of formation are determined at each calculation level using the $\Delta H^\circ_{\text{rxn}298}$ and known enthalpies of other reactants in each of 6 different working reactions. The statistical distribution analysis of rotation conformers is also considered; $\Delta H_f^\circ_{298}$ values for $\text{CH}_2\text{ClO}\bullet$ of -4.5 ± 0.3 , $\text{CHCl}_2\text{O}\bullet$ of -5.6 ± 0.3 , $\text{CCl}_3\text{O}\bullet$ of -7.5 ± 0.3 , $\text{CH}_2\text{O--Cl}$ of -2.1 ± 0.3 , CHClO--Cl of -17.5 ± 0.3 , and $\text{CCl}_2\text{O--Cl}$ of -24.7 ± 0.3 kcal/mol at the CBS-Q//B3**. The reaction system ($\text{CH}_3\text{Cl} + \text{ClO} \leftrightarrow \text{CH}_3\text{OCl} \leftrightarrow \text{Products}$) is very important to understanding the depletion effect of chlorine chemistry on stratospheric ozone layer. Monochlorine monoxide radical (ClO) is known the cause of ozone depletion and alkyl and alkyl halides are most abundant in atmosphere.. The kinetics for the reactions of monochlorine monoxide radical (ClO) with methyl radical are analyzed by using quantum Rice-Ramsperger-Kassel (QRRK) theory for $k(T)$ and a modified strong collision approach for falloff.

**THERMOCHEMICAL PROPERTIES OF METHYL AND CHLORO-METHYL
HYPOCHLORITES AND ETHERS AND REACTION OF
METHYL RADICAL WITH CLO**

**by
Dawoon Jung**

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APPROVAL PAGE

THERMOCHEMICAL PROPERTIES OF METHYL AND CHLORO-METHYL HYPOCHLORITES AND ETHERS AND REACTION OF METHYL RADICAL WITH CLO

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To my beloved family

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CHAPTER 1

INTRODUCTION

CH_3OCl has been considered an important atmospheric species since the severe depletions in stratospheric ozone were first observed during the Antarctic spring in 1985.

^{1,2} This ozone depletion is now believed to be the result from several reaction sequences involving the chlorine monoxide radical (ClO).^{3,4} At low temperature, methyl radical associates with chlorine monoxide radical (ClO) and produces methyl hypochlorite (CH_3OCl) but at higher temperature or low pressure, methoxy radical and Cl atom are dominant initial products from the association, with formaldehyde also observed.⁹

Chlorocarbons are widely used chemicals as solvents in synthesis and in cleaning agents, as synthesis starting materials and in polymer, pesticide and other product manufacture. Chlorocarbons and other halocarbon compounds are present in the atmosphere from evaporation of these solvents and other anthropogenic activities. They often exhibit relatively long tropospheric lifetimes due to their slow decay or low reaction rates with OH radical.⁵

Chlorocarbon radicals are the initial intermediates from reaction of chlorocarbons in atmospheric and combustion systems. Chlorine substitution on methyl and alkyl radicals results in decreased stability (and lower reactivity to products) of peroxy adducts formed from reaction of these radicals with O_2 . The slower reactions with O_2 permit the chlorinated methyl radicals to build up to higher concentrations in combustion environments, relative to CH_3 , where they are more likely to undergo reactions with the

radical pool, of which HO_2 , OH and ClO are major species. These association reactions result in oxychlorides or chloro-methoxy species. Chlorine monoxide radicals are also active in combustion inhibition (termination reactions) via cycles similar to that for thermal catalytic ozone destruction in the stratosphere.⁶

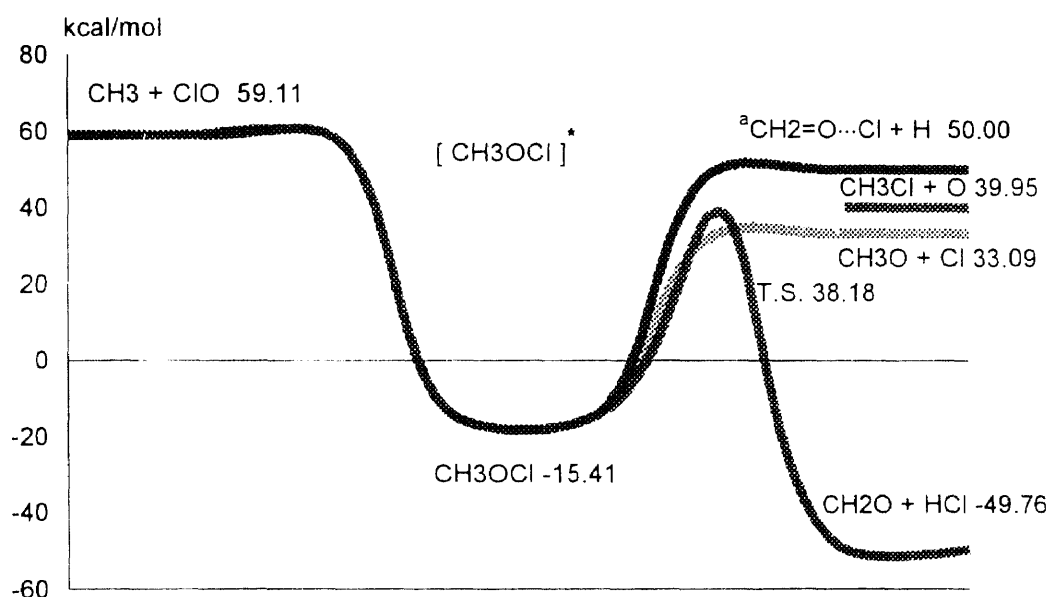
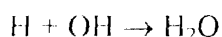
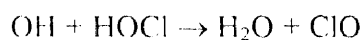
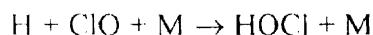


Figure 1.1 Overview schematic of CH_3OCl Formation and Dissociation Paths

^a Weakly bond (5kcal/mol), formaldehyde~Cl atom complete: this complete is lower in energy than $\text{C}\cdots\text{H}_2\text{OCl}$, hypochlorite-methyl radical.

Termination



A desired fate of Cl atoms is formation of HCl, but oxygen rich (fuel lean), high temperature environments of combustion and the upper atmosphere often shift the limited supply of hydrogen to O-H or H-OH bonds which are stronger than the H-Cl

bond. This often results in significant steady state levels of atomic and molecular chlorine as well as chlorine oxide in the combustion environment. Cl and ClO react rapidly with alkyl radicals, with ClO radicals undergoing association to form chemically activated oxychlorides that can be stabilized, or further react to new products. ClO also serves to convert CO to CO₂.⁷

Atomic chlorine is also frequently used to initiate oxidation reactions of hydrocarbons, oxychlorocarbons and halocarbons for studies relevant to atmospheric lifetimes and product formation in atmospheric photochemistry.^{11,12} ClO radical is formed in these studies via association reaction of Cl atoms with peroxy radicals with subsequent cleavage of the very weak O-O peroxide bond.¹³



Thermodynamic property data on the oxygenated chlorocarbon species are needed for evaluation of reaction paths, kinetic processes, as well as stability of intermediate adducts and the oxy-chlorocarbon species formed as products.^{9,10} These properties are also needed in kinetic modeling and in equilibrium computer codes (Examples: Chemkin, Nasa, Stanjan equilibrium codes, commercially available). There is very little or no thermodynamic data on these oxygenated chlorocarbons in the literature.¹⁵⁻¹⁷ Francisco et al. report a theoretical study on the excited states¹⁴ and ΔH_f° for methyl hypochlorite (CH₃OCl) of -13.5 ± 2 kcal/mol with CCSD(T)/6-311G(2df,2p) level¹⁵ of theory, which we convert to $\Delta H_f^\circ_{298}$ of -15.9 kcal/mol. Elrod et al. report Gaussian-2 *ab initio* study for $\Delta H_f^\circ_{298}$ of CH₃OCl as -17.7 kcal/mol¹⁶ and separately derive $\Delta H_f^\circ_{298}$ of CH₃OCl as -12.3 kcal/mol by bond additivity based on methods developed by Colussi.¹⁷ J. Espinosa-Garcia recently reported⁵³ $\Delta H_f^\circ_{298}$ for CH₃OCl of -

13.2 \pm 2.3 kcal/mol by the unweighted average of the results of MP4/6-31G(d,p)/MP2/6-31G(d), CCSD(T)/6-311G(3d,2p), CCSD/cc-pVTZ, and Truhlar's basis-set limit method. Melius includes unpublished BAC/MP4 $\Delta H_f^\circ_{298}$ for methyl hypochlorite on his web site -14.0 kcal/mol,¹⁸ and Crowley et al.¹⁹ used bond additivity values of Benson²⁰ to estimation of $\Delta H_f^\circ_{298}$ of -14.6 kcal/mol for CH₃OCl.

These estimates exhibit the wide range in enthalpy values at 298 K from -12.3 to -17.7 kcal/mol. There is, in addition, no literature data on thermodynamic properties of chloro-methyl hypochlorites (CH₂ClOCl, CHCl₂OCl, and CCl₃OCl). There is no published values for heat capacity or entropy on CH₃OCl or any of the chloro methyl hypochlorites, too.

This study estimates fundamental thermodynamic property data, $\Delta H_f^\circ_{298}$, S°_{298} and $C_p(T)$ and internal rotation barriers on the methyl hypochlorite, and chloro-methyl hypochlorites using *ab initio* and density functional calculations. The group additivity values of the O/C/Cl group, were determined for use in estimation of larger alkyl hypochlorites.

CHAPTER 2

VIBRATIONAL FREQUENCIES, GEOMETRIES, AND THERMODYNAMICS OF METHYL HYPOCHLORITE AND CHLORO-METHYLHYPOCHLORITES

2.1 Calculation Methods

2.1.1 Selection of Calculation Methods and Basic Sets

B3LYP/6-31G(d,p) is chosen because it is computationally economical and thus, possibly applicable to larger molecules, if it is accurate. It is also commonly used and is reported to yield accurate geometry and reasonable energies^{21,22} Comparison of calculation results from this level against data from higher calculation levels for ΔH_f° will provide some calibration of the B3LYP/6-31G(d,p) values (with similar working reactions) for larger molecules, where this may be one of the few calculation methods available. B3LYP/6-311+G(3df,2p) is chosen to see if this larger basic set results in an improvement to the above commonly used density functional calculation method.²² QCISD(T)/6-31G(d,p) is a configuration interaction method; but with a small, economical base set.^{23,24} CBS-Q//B3LYP/6-31G(d,p) calculation is a high level composite method with empirical corrections; it is reported to be comparable with QCISD(T)/6-311+G(3df,2p).^{29,30} This CBS-Q//B3LYP/6-31G(d,p) method similar to the Radom research group's CBS/RAD²⁵ method; it has B3LYP/6-31g(d,p) geometry, which they indicate is very close to QCISD(T) values and a QCISD(T) calculation in place of CCSD(T). These calculations are referred to as CBSQ//B3** in the present study for brevity.

2.1.2 Thermodynamic Properties Using *ab initio* Calculations

Enthalpy, $\Delta H_f^\circ_{298}$, entropy, S°_{298} and heat capacities $C_p(T)$, from 300 to 1500 K are determined for four chloro-methyl hypochlorites, CH_3OCl , CH_2ClOCl , CHCl_2OCl and CCl_3OCl using density functional B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p) and *ab initio* QCISD(T)/6-31G(d,p) and CBS-Q calculation methods.²⁵⁻³⁰

Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) density functional calculation level, with single point calculations for energy at the B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q levels of calculation. Vibration frequencies are scaled by 0.9806 for zero point energies (ZPVE) and for thermal corrections.³¹ Enthalpies of formation are determined at each calculation level using the enthalpy of reaction ($\Delta H_{rxn, 298}$) with known enthalpies of other reactants in each of the 7 different reaction series.³²⁻³⁵ Barriers for intramolecular rotation about the $\text{CH}_3\text{-OCl}$ bond are analyzed versus torsion angle using B3LYP/6-31G(d,p) density functional calculations.

2.1.3 Calculation of Hindered Rotation Contribution to Thermodynamic Parameters

A technique for the calculation of thermodynamic functions from hindered rotations with arbitrary potentials has been previously developed.³⁶⁻³⁸ This technique employs expansion of the hindrance potential in the Fourier series, calculation of the Hamiltonian matrix in the basis of the wave functions of free internal rotation, and subsequent calculation of energy levels by direct diagonalization of Hamiltonian matrix. In this work the torsion potential calculated at discrete torsion angles is represented by equation 1.

$$V(\theta) = a_0 + a_1 \cos(\theta) + a_2 \cos(2\theta) + a_3 \cos(3\theta) + b_1 \sin(\theta) + b_2 \sin(2\theta) + b_3 \sin(3\theta) \quad (2.1)$$

where value of the coefficients a_i were calculated to provide the true minimum and maximum of the torsion potentials with allowance of a shift of the theoretical extreme angular positions.

2.2 Results and Discussion

2.2.1 Vibrational Frequencies and geometries

Harmonic vibrational frequencies are calculated for the methyl and three chlorinated methyl hypochlorites at the B3LYP/6-31G(d, p) level of theory on the basis of optimized geometry at the same level of theory. The vibrational frequencies and rotational constants for the methyl hypochlorite are given in Table 2.1. They are in good agreement with other reported calculation^{15,18} and experimental report.^{10,46} The ClO stretching frequency mode of CH_3OCl shows 660 cm^{-1} in this work, 667 cm^{-1} in B3LYP/6-311++G(3df,3pd),¹⁵ 692 cm^{-1} in CCSD(T)/6-311G(2df,2p),¹⁵ 704 cm^{-1} in BAC/MP4 theory,¹⁸ and 680 cm^{-1} in the spectra of Crowley et al.¹⁰ The CO stretching frequency mode of CH_3OCl is 1019 cm^{-1} in this calculation, 1007 cm^{-1} in B3LYP/6-311++G(3df,3pd),¹⁵ 1046 cm^{-1} in CCSD(T)/6-311G(2df,2p),¹⁵ 1039 cm^{-1} in BAC/MP4 level,¹⁸ 1006 cm^{-1} in the spectra of Crowley¹⁰ et al. and 1002 cm^{-1} in the experiment of Jungkamp et al.⁴⁶ The CH_3 symmetric deformation mode of CH_3OCl is 1463 cm^{-1} in B3LYP/6-31G(d,p), 1458 cm^{-1} in B3LYP/6-311++G(3df,3pd),¹⁵ 1467 cm^{-1} in CCSD(T)/6-311G(2df,2p),¹⁵ 1447 cm^{-1} in BAC/MP4,¹⁸ and 1450 cm^{-1} in the spectra of Crowley et al.¹⁰ and 1456 cm^{-1} in the experiment of Jungkamp et al.⁴⁶ The CH_3 symmetric stretching frequency mode of CH_3OCl is 3026 cm^{-1} in this work, 3019 cm^{-1} in

TABLE 2.1-a. Vibrational Frequencies^a (cm⁻¹) for Methyl Hypochlorite

| CH ₃ OCl | Frequencies | B3LYP/ | B3LYP/6-311 | CCSD(T)/ | BAC/MP4 ^c | Expt. |
|----------------------|---------------------------|-----------|-------------------------|---------------------------|-----------------------------|-----------|
| Symm | | Mode type | 6-31G(d,p) ^a | ++G(3df,3pd) ^b | 6-311G(2df,2p) ^b | |
| Crowley ^d | Jungkamp ^e | | | | | |
| a'' | Torsion | 259 | 243 | 254 | 230 | |
| a' | COCl bend | 364 | 367 | 373 | 360 | |
| a' | ClO stretch | 660 | 677 | 692 | 704 | 680 |
| a' | CO stretch | 1019 | 1007 | 1046 | 1039 | 1006 1002 |
| a'' | CH ₃ rock | 1175 | 1172 | 1180 | 1150 | 1150 |
| a' | CH ₃ rock | 1198 | 1196 | 1201 | 1181 | 1190 1170 |
| a' | CH ₃ s-deform | 1463 | 1458 | 1467 | 1440 | 1450 1456 |
| a'' | CH ₃ d-deform | 1471 | 1466 | 1479 | 1454 | 1471 |
| a' | CH ₃ d-deform | 1523 | 1505 | 1516 | 1478 | |
| a' | CH ₃ s-stretch | 3026 | 3019 | 3040 | 2880 | 2998 2820 |
| a'' | CH ₃ d-stretch | 3104 | 3092 | 3117 | 2951 | 2920 |
| a' | CH ₃ d-stretch | 3125 | 3114 | 3144 | 2969 | 2904 |

TABLE 2.1-b. Rotation Constants (Ghz) for Methyl Hypochlorite

| CH ₃ OCl | Rotational constants (Ghz) | | |
|---------------------------|----------------------------|---------|---------|
| Calculation method | A | B | C |
| B3LYP/6-31G(d,p) | 41.97723 | 6.06531 | 5.48635 |
| B3LYP/6-311++G(3df,pd) | 43.101 | 6.177 | 5.596 |
| CCSD(T)/6-311G(2df,2p) | 41.484 | 6.280 | 5.651 |
| BAC/MP4 | 44.990 | 6.334 | 5.751 |
| Experimental ^f | 42.06435 | 6.29688 | 5.67062 |

TABLE 2.1-c. Vibrational Frequencies^a (cm⁻¹), Rotation Constants (Ghz) and Moment of Inertia (amu-Bohr) for Chloro-methyl hypochlorite

| CH ₂ ClOCl | B3LYP/6-31G(d,p) | CHCl ₂ OCl | B3LYP/6-31G(d,p) | CCl ₃ OCl | B3LYP/6-31G(d,p) |
|-----------------------|------------------------|-----------------------|------------------------|----------------------|------------------------|
| Freq. | Rotation. ^g | Freq. | Rotation. ^g | Freq. | Rotation. ^g |
| 124.47 | 11.39849 | 112.10 | 2.73563 | 115.01 | 1.80228 |
| 321.38 | 2.27446 | 182.46 | 2.01362 | 166.4 | 1.14561 |
| 447.79 | 1.99297 | 285.55 | 1.35547 | 247.33 | 1.09308 |
| 651.30 | | 384.15 | | 248.53 | |
| 691.70 | | 536.12 | | 316.21 | |
| 986.52 | | 628.16 | | 390.2 | |
| 1063.43 | | 732.07 | | 391.75 | |
| 1264.86 | | 767.69 | | 534.36 | |
| 1347.11 | | 1060.24 | | 689.1 | |
| 1466.7 | | 1217.93 | | 766.45 | |
| 3090.95 | | 1311.52 | | 839.81 | |
| 3171.11 | | 3144.99 | | 1036.88 | |

^a Nonscaled frequencies are calculated at the B3LYP/6-31G(d,p) level of theory. ^b Reference 15. ^c Reference 18. ^d Reference 10. ^e Reference 46. ^f Reference 47. ^g The rotational constant units are Ghz.

TABLE 2.2. Optimized Geometry of Chloro-methyl Hypochlorites^a

| Name | Definition | B3LYP/ 6-31G(d,p) ^a | CH ₃ OCl B3LYP/6-311 ++G(3df,3pd) ^b | CCSD(T)/ 6-311G(2df,2p) ^c | BAC/MP4 ^d | Exper. ^e |
|-----------------|------------|-----------------------------------|---|---|----------------------|---------------------|
| R1 | R(2,1) | 1.096 | 1.091 | 1.091 | 1.083 | 1.111 |
| R2 | R(3,1) | 1.096 | 1.091 | 1.091 | 1.083 | 1.111 |
| R3 | R(4,1) | 1.095 | 1.090 | 1.089 | 1.081 | 1.086 |
| R4 | R(5,1) | 1.425 | 1.425 | 1.425 | 1.411 | 1.389 |
| R5 | R(6,5) | 1.736 | 1.702 | 1.709 | 1.668 | 1.674 |
| R6 | R(6,4) | 3.531 | | | | |
| A1 ^f | A(2,1,3) | 109.97 | | | 110.1 | |
| A2 | A(2,1,4) | 109.63 | | | 109.9 | |
| A3 | A(3,1,4) | 109.63 | | | 109.9 | |
| A4 | A(2,1,5) | 111.96 | 111.3 | 111.4 | 111.1 | |
| A5 | A(3,1,5) | 111.96 | 111.3 | 111.4 | 111.0 | |
| A6 | A(4,1,5) | 103.48 | 104.0 | 104.4 | 104.7 | |
| A7 | A(1,5,6) | 110.44 | 111.2 | 109.2 | 112.1 | 112.8 |
| D1 ^g | D(6,5,1,2) | 62.02 | 61.7 | 61.5 | 61.4 | |
| D2 | D(6,5,1,3) | -62.02 | -61.7 | -61.5 | -61.4 | |
| D3 | D(6,5,1,4) | 180.00 | 180.0 | 180.0 | 180.0 | |

| CH ₂ ClOCl | | | CHCl ₂ OCl | | | CCl ₃ OCl | | |
|-----------------------|------------|--------------------|-----------------------|------------|--------------------|----------------------|------------|--------------------|
| Name | Definition | Value ^d | Name | Definition | Value ^d | Name | Definition | Value ^d |
| R1 | R(2,1) | 1.818 | R1 | R(2,1) | 1.803 | R1 | R(2,1) | 1.801 |
| R2 | R(3,1) | 1.091 | R2 | R(3,1) | 1.801 | R2 | R(3,1) | 1.801 |
| R3 | R(4,1) | 1.092 | R3 | R(4,1) | 1.091 | R3 | R(4,1) | 1.790 |
| R4 | R(5,1) | 1.390 | R4 | R(5,1) | 1.375 | R4 | R(5,1) | 1.383 |
| R5 | R(6,5) | 1.739 | R5 | R(6,5) | 1.738 | R5 | R(6,5) | 1.742 |
| R6 | R(6,4) | 3.523 | R6 | R(6,4) | 3.538 | R6 | R(6,4) | 4.150 |
| A1 | A(2,1,3) | 106.61 | A1 | A(2,1,3) | 110.51 | A1 | A(2,1,3) | 109.25 |
| A2 | A(2,1,4) | 106.98 | A2 | A(2,1,4) | 107.37 | A2 | A(2,1,4) | 110.22 |
| A3 | A(3,1,4) | 112.10 | A3 | A(3,1,4) | 107.49 | A3 | A(3,1,4) | 110.22 |
| A4 | A(2,1,5) | 114.07 | A4 | A(2,1,5) | 113.82 | A4 | A(2,1,5) | 112.72 |
| A5 | A(3,1,5) | 113.14 | A5 | A(3,1,5) | 113.81 | A5 | A(3,1,5) | 112.72 |
| A6 | A(4,1,5) | 103.88 | A6 | A(4,1,5) | 103.19 | A6 | A(4,1,5) | 101.51 |
| A7 | A(1,5,6) | 112.40 | A7 | A(1,5,6) | 115.05 | A7 | A(1,5,6) | 114.83 |
| D1 | D(6,5,1,2) | 74.68 | D1 | D(6,5,1,2) | -63.92 | D1 | D(6,5,1,2) | 62.13 |
| D2 | D(6,5,1,3) | -47.43 | D2 | D(6,5,1,3) | -63.92 | D2 | D(6,5,1,3) | -62.12 |
| D3 | D(6,5,1,4) | -169.23 | D3 | D(6,5,1,4) | -180.07 | D3 | D(6,5,1,4) | -180.00 |

^a Geometry is optimized in B3LYP/6-31g(d,p) density functional calculation level, ^b B3LYP/6-311++G(3df,3pd) level in reference 15, ^c CCSD(T)/6-311(2df,2p) level in reference 15, and ^d BAC/MP4 level in reference 18.

^e Experimental value in reference 47. ^f Bond length or the distance between two atoms of number in Å. ^g Bond angle or the angle among three atoms of number in degree. ^h Dihedral angle among the four number atoms.

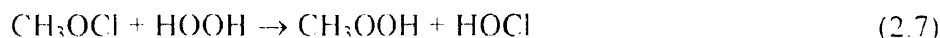
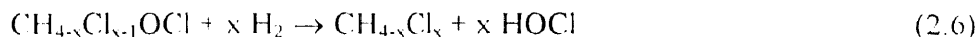
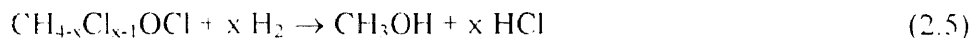
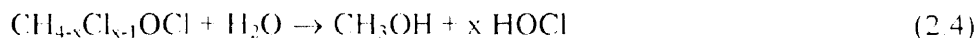
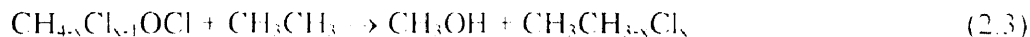
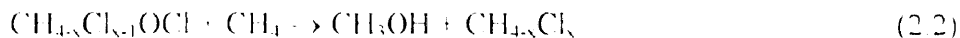
B3LYP/6-311++G(3df,3pd),¹⁵ 3040 cm^{-1} in CCSD(T)/6-311G(2df,2p),¹⁵ 2880 cm^{-1} in BAC/MP4,¹⁸ and 2998 cm^{-1} in the spectra of Crowley et al.¹⁹ and 2820 cm^{-1} by Jungkamp et al.⁴⁶ The vibrational frequencies and rotational constants for multiple chloro-methyl hypochlorites are given in Table 2.1.

The optimized B3LYP/6-31G(d, p) geometries for the methyl and three chlorinated methyl hypochlorites are illustrated in Table 2.2. Numerical values of the structural parameters including carbon-hydrogen, carbon-chlorine, carbon-oxygen, oxygen-hydrogen bond distances along with applicable bond angles are also listed in Table 2.2. Effects of chlorine α -substitution on molecular geometry can be seen from Table 2.2. The C-H and O-Cl bond lengths in the equilibrium conformations of four title molecules: CH_3OCl , CH_2ClOCl , CHCl_2OCl , and CCl_3OCl optimized at the B3LYP/6-31G(d, p) are similar, while the C-O bond lengths (R4) decrease in order; 1.425 Å in CH_3OCl , 1.390 Å in CH_2ClOCl , 1.375 Å in CHCl_2OCl , 1.383 Å in CCl_3OCl . The Cl-C bond lengths (R1) in the chloro-methyl hypochlorites also decrease with increase in number of chlorines; it is 1.818, 1.807, and 1.801 Å in CH_2ClOCl , CHCl_2OCl , and CCl_3OCl . The Cl-O bond length (R5) increases in this series at 1.736, 1.739, 1.738 and 1.742 Å in CH_3OCl , CH_2ClOCl , CHCl_2OCl , and CCl_3OCl . The geometry parameters of Melius were obtained by conversion of his cartesian coordinates. The geometry of CH_3OCl in this work is similar with values reported by Francisco,¹⁵ Melius,¹⁸ and experimental values of Rigden et al.⁴⁷ in Table 2.2. The C-O bond distance (R4) of CH_3OCl is 1.425 Å in this work and in Francisco's calculation, 1.411 Å in BAC/MP4, and 1.389 Å in the study of Rigden et al.. The O-Cl bond length (R4) of CH_3OCl is 1.736 Å in B3LYP/6-31G(d,p) level, 1.702 Å in B3LYP/6-311++G(3df,3pd) calculation,

1.709 Å in CCSD(T)/6-31G(2df, 2p) method, and 1.674 Å in the experiment.⁴⁷ We conclude that the geometry and frequencies of methyl hypochlorite optimized B3LYP/6-31G(d,p) is reliable, because higher level calculations with larger basis sets¹⁵ and experiments^{10,46,47} demonstrate consistent results with these. Distance between the hypochlorite chloride and hydrogen on the methyl group in the low energy conformers are 3.531, 3.523, 3.538 Å for CH₃OCl, CH₂ClOCl, and CHCl₂OCl, probably too long for significant hydrogen bonding.

2.2.2 Enthalpies of Formation ($\Delta H_f^\circ_{298}$)

Enthalpies of formation ($\Delta H_f^\circ_{298}$) for the chlorinated methyl hypochlorites are estimated using total energies obtained by the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) calculation methods and up to seven reactions. Total energies are corrected by zero-point vibration energies (ZPVE) which are scaled by 0.9806 as recommended by Scott et al.³¹ Thermal correction, 0 K to 298.15 K, is calculated to estimate $\Delta H_f^\circ_{298}$ at 298.15 K.²⁵ The following seven reaction schemes are selected to determine $\Delta H_f^\circ_{298}$ of each hypochlorite



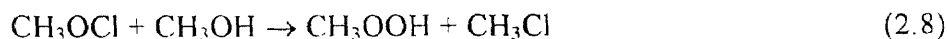


TABLE 2.3. Total Energies at Different Levels of Theory, Composite CBS-Q, Zero Point Vibrational Energies and Thermal Corrections (in Hartree)

| | B3lyp6-31 ^a | B3lyp6-311 ^b | Qcisd(t) ^c | CBS-Q//B3** ^d | ZPVE ^e | Therm.corr ^f |
|------------------------------------|------------------------|-------------------------|-----------------------|--------------------------|-------------------|-------------------------|
| CH ₃ OCl | -575.2592837 | -575.3390109 | -574.3841628 | -574.6295050 | 0.0410793 | 0.0048110 |
| CH ₂ ClOCl | -1034.8547193 | -1034.9680400 | -1033.4165982 | -1033.7901135 | 0.0326765 | 0.0054710 |
| CHCl ₂ OCl | -1494.4410880 | -1494.5892530 | -1492.4425490 | -1492.9531856 | 0.0231510 | 0.0064280 |
| CCl ₃ OCl | -1954.0177560 | -1954.2014662 | -1951.4608590 | -1952.0982319 | 0.0128272 | 0.0076190 |
| CH ₄ | -40.5240144 | -40.5367468 | -40.3895577 | -40.4053008 | 0.0441427 | 0.0038100 |
| CH ₃ Cl | -500.1125454 | -500.1588917 | -499.4146950 | -499.5567137 | 0.0371844 | 0.0039640 |
| CH ₂ Cl ₂ | -959.6989037 | -959.7802630 | -958.4390436 | -958.7102821 | 0.0288944 | 0.0045180 |
| CHCl ₃ | -1419.2803335 | -1419.3974234 | -1417.4600091 | -1417.8637645 | 0.0194826 | 0.0054130 |
| CCl ₄ | -1878.8542563 | -1879.0076351 | -1876.4749422 | -1877.0143867 | 0.0091235 | 0.0065880 |
| C ₂ H ₆ | -79.8387377 | -79.8614929 | -79.5855303 | -79.6247780 | 0.0734705 | 0.0044200 |
| CH ₃ CH ₂ Cl | -539.4330408 | -539.4896189 | -538.6171237 | -613.9098084 | 0.0655247 | 0.0049740 |
| CH ₃ CHCl ₂ | -999.0218923 | -999.1134044 | -997.6453262 | -997.9432661 | 0.0564894 | 0.0057830 |
| CH ₃ CCl ₃ | -1458.6031122 | -1458.7300519 | -1456.6676728 | -1457.0996327 | 0.0465540 | 0.0068200 |
| CH ₂ ClCCl ₃ | -1918.1859474 | -1918.3479613 | -1915.6904981 | -1916.2530975 | 0.0377806 | 0.0078380 |
| CH ₃ OH | -115.7239624 | -115.7729014 | -115.4123794 | -115.5342419 | 0.0503989 | 0.0042490 |
| CH ₃ OOH | -190.8563041 | -190.9322666 | -190.3649472 | -190.5872201 | 0.0536790 | 0.0052550 |
| H ₂ | -1.1785393 | -1.1800138 | -1.1651440 | -1.1625321 | 0.0099737 | 0.0033050 |
| H ₂ O | -76.4197367 | -76.4632487 | -76.2316386 | -76.3329532 | 0.0209515 | 0.0037790 |
| HCl | -460.8007820 | -460.8383783 | -460.2244702 | -460.3437852 | 0.0065994 | 0.0033040 |
| HOCl | -535.9488401 | -536.0211143 | -535.1952314 | -535.4175126 | 0.0128606 | 0.0038930 |
| HOOH | -151.5431913 | -151.6119014 | -151.1740042 | -151.3730998 | 0.0258741 | 0.0042040 |

^{a,b,c} Total energies are in Hartree at 0 K; all molecular geometries are optimized in B3LYP/6-31G(d,p). ^a B3LYP/6-31G(d,p). ^b B3LYP/6-311+G(3df,2p). ^c QCISD(T)/6-31G(d,p). ^d CBS-Q//B3LYP/6-31G(d,p) enthalpies are in Hartree, which include thermal correction and zero-point energy at 298 K. ^e ZPE is in Hartree and scaled by 0.9806. ^f Thermal corrections are in Hartree.

Density functional and ab initio calculations with ZPVE and thermal correction are performed for all four compounds in each reaction, and enthalpy of reaction $\Delta H_{\text{rxn}}^{\circ}{}_{298}$ is calculated. Since enthalpies of formation of three compounds have been experimentally determined or theoretically calculated, the unknown enthalpies of formation of CH₃OCl, CH₂ClOCl, CHCl₂OCl, and CCl₃OH are obtained. As example, $\Delta H_f^{\circ}{}_{298}$ (CH₃OCl) is calculated from

$$\Delta H_{\text{rxn}, 298} = \Delta H_f^{\circ}{}_{298} \{(\text{CH}_3\text{OH}) + (\text{CH}_3\text{Cl}) - (\text{CH}_3\text{OCl}) - (\text{CH}_4)\} \quad (2.9)$$

and the listed known enthalpies of CH_3OH , CH_3Cl and CH_4 .

The enthalpies of reaction are obtained by the reaction schemes tabulated in Tables

2.4. The ΔH_f° on the standard compounds in reaction sets are from literature in Table

2.5 and are used to determine ΔH_f° values in Table 2.6.

TABLE 2.4. Reaction Enthalpies (in kcal/mol) at 298 K^a

| Reaction Schemes | ΔH_{rxn} (Theory level ^b) | | | |
|---|---|--------------------------|------------------------|-----------------|
| | B3LYP/ 6-31G(d,p) | B3LYP6-311 +G(3df,2p) | QCISD(T) 6-31G(d,p) | CBS-Q //B3** |
| 1 $\text{CH}_3\text{OCl} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{Cl}$ | -32.16 | -33.94 | -32.25 | -35.23 |
| $\text{CH}_2\text{ClOCl} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{Cl}_2$ | -26.46 | -29.13 | -27.18 | -30.82 |
| $\text{CHCl}_2\text{OCl} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CHCl}_3$ | -23.33 | -26.55 | -24.07 | -28.83 |
| $\text{CCl}_3\text{OCl} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CCl}_4$ | -21.64 | -25.33 | -21.93 | -28.30 |
| 2 $\text{CH}_3\text{OCl} + \text{CH}_3\text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{CH}_2\text{Cl}$ | -36.15 | -38.06 | -36.67 | -40.22 |
| $\text{CH}_2\text{ClOCl} + \text{CH}_3\text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{CHCl}$ | -32.33 | -35.07 | -34.32 | -39.29 |
| $\text{CHCl}_2\text{OCl} + \text{CH}_3\text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{CCl}_2$ | -29.30 | -32.41 | -32.32 | -39.12 |
| $\text{CCl}_3\text{OCl} + \text{CH}_3\text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{ClCCl}_3$ | -32.31 | -35.12 | -34.24 | -40.37 |
| 3 $\text{CH}_3\text{OCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HOCl}$ | 4.39 | 5.66 | 5.63 | 6.72 |
| $\text{CH}_2\text{ClOCl} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 2\text{HOCl}$ | 45.87 | 50.17 | 48.68 | 54.44 |
| $\text{CHCl}_2\text{OCl} + 3\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 3\text{HOCl}$ | 82.17 | 90.29 | 88.13 | 99.67 |
| $\text{CCl}_3\text{OCl} + 4\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 4\text{HOCl}$ | 112.75 | 125.12 | 123.24 | 141.66 |
| 4 $\text{CH}_3\text{OCl} + \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{HCl}$ | -51.17 | -54.51 | -51.56 | -53.96 |
| $\text{CH}_2\text{ClOCl} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} + 2\text{HCl}$ | -65.25 | -70.18 | -65.69 | -66.91 |
| $\text{CHCl}_2\text{OCl} + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + 3\text{HCl}$ | -84.50 | -90.23 | -83.43 | -82.36 |
| $\text{CCl}_3\text{OCl} + 4\text{H}_2 \rightarrow \text{CH}_3\text{OH} + 4\text{HCl}$ | -109.49 | -115.58 | -105.50 | -101.04 |
| 5 $\text{CH}_3\text{OCl} + \text{H}_2 \rightarrow \text{CH}_4 + \text{HOCl}$ | -18.51 | -20.90 | -18.79 | -19.31 |
| $\text{CH}_2\text{ClOCl} + \text{H}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HOCl}$ | -13.59 | -15.99 | -13.62 | -13.54 |
| $\text{CHCl}_2\text{OCl} + \text{H}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \text{HOCl}$ | -13.06 | -15.56 | -12.15 | -11.61 |
| $\text{CCl}_3\text{OCl} + \text{H}_2 \rightarrow \text{CCl}_3\text{H} + \text{HOCl}$ | -15.66 | -18.28 | -13.37 | -12.87 |
| 6 $\text{CH}_3\text{OCl} + \text{HOOH} \rightarrow \text{CH}_3\text{OOH} + \text{HOCl}$ | -1.85 | -1.73 | -1.44 | -1.33 |
| 7 $\text{CH}_3\text{OCl} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OOH} + \text{CH}_3\text{Cl}$ | 8.75 | 12.74 | 10.32 | 12.43 |

^a Reaction enthalpies include thermal correction and zero-point energy correction at 298 K. ^b See foot notes of Table 2.3 for the explanation of theory levels.

TABLE 2.5. Enthalpy Data Used in Reactions to Determine $\Delta H_f^\circ_{298}$ of Target

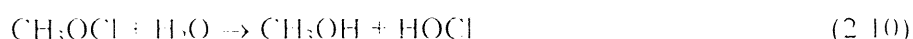
Oxychlorides

| Compound | $\Delta H_f^\circ_{298}$ ^a | source | uncertainty | source |
|------------------------------------|---------------------------------------|--------|-------------------|---------------------|
| CH ₄ | -17.89 | Ref.32 | ±0.1 | Ref.32 (48) |
| CH ₃ Cl | -19.60 | Ref.33 | ±0.2 | Ref.33 (49) |
| CH ₂ Cl ₂ | -22.83 | Ref.32 | ±0.3 | Ref.32 |
| CHCl ₃ | -24.20 | Ref.34 | ±0.3 | Ref.43 |
| CCl ₄ | -22.94 | Ref.32 | ±0.5 | Ref.32 |
| C ₂ H ₆ | -20.24 | Ref.34 | ±0.1 | Ref.34 (49) |
| CH ₃ CH ₂ Cl | -26.84 | Ref.33 | ±0.2 | Ref.33 (49) |
| CH ₃ CHCl ₂ | -31.09 | Ref.33 | ±0.3 | Ref.43 |
| CH ₃ CCl ₃ | -34.01 | Ref.33 | ±0.3 | Ref.33 (50) |
| CH ₂ ClCCl ₃ | -35.71 | Ref.33 | ±2.0 ^b | Ref.49 |
| CH ₃ OH | -48.08 | Ref.34 | ±0.1 | Ref.34 (52) |
| CH ₃ OOH | -31.80 | Ref.35 | ±0.9 | Ref.35 ^c |
| HCl | -22.06 | Ref.32 | ±0.1 | Ref.32 |
| HOCl | -17.80 | Ref.32 | ±0.5 | Ref.32 |
| HOOH | -32.53 | Ref.32 | | |
| H ₂ O | -57.80 | Ref.34 | ±0.01 | Ref.44 |

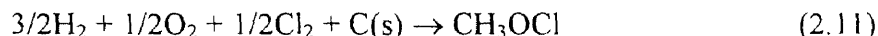
^a Units in kcal/mol. ^b The uncertainty comes from 1,1,2,2-tetrachloroethane (CHCl₂CHCl₂).

^c The standard deviation of Table 2.5 in reference 35.

Data in Table 2.6 shows that the enthalpy of formation of CH₃OCl, CH₂ClOCl, CHCl₂OCl, CCl₃OCl at the CBS-Q calculation level, for the reaction schemes is relatively consistent for each species except for values determined using reaction scheme (4),(2.5). The $\Delta H_f^\circ_{298}$ for CH₃OCl is -15.41 kcal/mol, using the CBS-Q method through all reaction schemes in Table 2.6, on the other hand, The $\Delta H_f^\circ_{298}$ for CH₃OCl is -15.91 kcal/mol, using the average of three different calculations, B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), and QCISD(T)/6-31g(d,p). Francisco et al.¹⁵ using CCSD(T)/6-311G calculation with a large basis set (2df,2p) determine enthalpy of formation for -13.5 ± 2 kcal/mol at 0 K from the reaction,



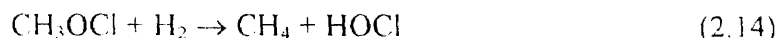
which we calculate as -15.9 kcal/mol at 298 K using the reaction below and data in this study.



Elord et al.¹⁶ report $\Delta H_f^\circ_{298}$ of CH_3OCl at -17.69 kcal/mol from G2 analysis on the isodesmic reaction:



They also calculated $\Delta H_f^\circ_{298}$ of CH_3OCl at -12.3 kcal/mol from bond additivity by Colussi's values.¹⁷ Espinosa-Garcia recently reported⁵³ $\Delta H_f^\circ_{298}$ for CH_3OCl of -13.2 ± 2.3 kcal/mol by the unweighted average of the results of MP4/6-31G(d,p)//MP2/6-31G(d), CCSD(T)/6-311G(3d,2p), CCSD/cc-pVTZ, and Truhlar's basis-set limit method using hydrogenation reactions.



Melius reports $\Delta H_f^\circ_{298}$ of -14.0 kcal/mol based on BAC/MP4¹⁸ calculation. The available literature data on CH_3OCl show a variation in standard enthalpies of formation, -12.3 to -17.7 kcal/mol at 298 K.

The accuracy of the enthalpies of formation obtained theoretically is controlled by several factors: the level of sophistication (method + basis set) applied to calculate the electronic energy, the reliability of the enthalpies of formation of the reference compounds, the uncertainty in the thermal corrections, and the extent to which error cancellation occurs in the working chemical reaction used in the evaluation.

The results for the B3LYP/6-31G(d, p), B3LYP/6-311+G(3df, 2p), and QCISD(T)/6-31G(d, p) calculation analysis show relatively uniform $\Delta H_f^\circ_{298}$ values through the

TABLE 2.6: Comparison of Enthalpies of Formation^a at 298 K (in kcal/mol)

| Species theory ^b | rxn 1 ^c | rxn 2 | rxn 3 | rxn 4 | rxn 5 | rxn 6 | rxn 7 | avg. ^d | overall. ^e |
|--------------------------------|--------------------|--------|---------------|---------------|--------|--------|--------|-------------------|-----------------------|
| CH₃OCi | | | | | | | | | |
| B3lyp6-31 | -17.63 | -18.53 | -12.47 | -18.97 | -17.19 | -15.22 | -12.07 | -16.01±2.82 | |
| B3lyp6-311 | -15.85 | -16.62 | -13.74 | -15.63 | -14.80 | -15.34 | -16.06 | -15.43±0.94 | |
| Qcisd(t) | -17.54 | -18.01 | -13.71 | -18.58 | -16.90 | -15.63 | -13.64 | -16.29±2.01 | |
| CBS-Q//B3* | -14.56 | -14.46 | -14.80 | -16.18 | -16.38 | -15.73 | -15.73 | -15.41±0.79 | -15.41±1.52 |
| Max Error ^f | ±0.29 | ±0.35 | ±0.56 | ±0.10 | ±0.58 | ±1.44 | ±1.15 | ±0.63 | |
| CH₂ClOCi | | | | | | | | | |
| B3lyp6-31 | -26.56 | -26.60 | <i>-13.95</i> | -26.95 | -23.81 | | | -25.98±1.46 | |
| B3lyp6-311 | -23.89 | -23.86 | <i>-18.25</i> | -22.02 | -21.41 | | | -22.80±1.27 | |
| Qcisd(t) | -25.84 | -24.61 | <i>-16.76</i> | -26.51 | -23.78 | | | -25.19±1.22 | |
| CBS-Q//B3* | -22.20 | -19.64 | -22.52 | -25.29 | -23.86 | | | -22.06±1.76 | -22.05±2.41 |
| Max Error | ±0.43 | ±0.45 | ±1.07 | <i>±0.15</i> | ±0.66 | | | ±0.65 | |
| CHCl₂OCi | | | | | | | | | |
| B3lyp6-31 | -31.06 | -32.55 | <i>-10.25</i> | -29.76 | -27.57 | | | -30.24±2.11 | |
| B3lyp6-311 | -27.84 | -29.44 | <i>-18.37</i> | -24.02 | -25.07 | | | -26.59±2.49 | |
| Qcisd(t) | -30.32 | -29.53 | <i>-16.21</i> | -30.83 | -28.48 | | | -29.79±1.02 | |
| CBS-Q//B3* | -25.56 | -22.73 | -27.75 | -31.90 | -29.02 | | | -26.27±2.76 | -26.02±3.59 |
| Max Error | ±0.44 | ±0.50 | ±1.58 | <i>±0.20</i> | ±0.80 | | | ±0.83 | |
| CCl₃OCi | | | | | | | | | |
| B3lyp6-31 | -31.48 | -31.24 | <i>-0.83</i> | -26.83 | -26.34 | | | -28.98±2.76 | |
| B3lyp6-311 | -27.80 | -28.43 | <i>-13.20</i> | -20.74 | -23.72 | | | -25.17±3.61 | |
| Qcisd(t) | -31.20 | -29.31 | <i>-11.32</i> | -30.82 | -28.63 | | | -29.99±1.22 | |
| CBS-Q//B3* | -24.83 | -23.18 | -29.74 | -35.28 | -29.13 | | | -26.72±3.22 | -26.72±4.65 |
| Max Error | ±0.63 | ±2.17 | ±2.09 | ±0.25 | ±0.81 | | | ±1.43 | |

^a Enthalpies of formation are calculated by different seven reactions in Table 2.3. ^b See Table 2.2 foot note for the explanation of theory levels. ^c See the reactions in Table 2.3. ^d Average values do not include bold italic data. ^e Average of CBS-Q//B3** values by all reaction schemes except reaction set 4 and adopted statistical conformer analysis. Uncertainty = the standard deviation of average (foot note d) + The average maximum error of all reaction schemes except reaction set 4. ^f The maximum error from uncertainty in values of the 3 standard molecules of reaction scheme. Values from Table 2.5

reaction schemes excluding data obtained from reaction scheme (3), (2.4). With the exception of CBS-Q//B3** level results, enthalpies calculated from use of reaction scheme (3), (2.4) are not consistent with data from the other six reaction schemes.

Deviation for $\Delta H_f^\circ_{298}$ across reaction scheme (3), (2.4) appears to scale linearly with the coefficient of H_2O and $HOCl$, suggesting a significant error in calculation of one or both of these species at all calculation levels except CBS-Q//B3** in Table 2.6.

The method of isodesmic reactions relies on the similarity of bonding environment in the reactants and products that leads to cancellation of systematic errors in the density functional and ab initio molecular orbital calculations. Reaction scheme (6), (2.7) is the only isodesmic reaction, but we can not apply reaction scheme (6), (2.7) to chloro-methyl hypochlorites because $\Delta H_f^\circ_{298}$ values for chloro-methyl peroxides are unknown. The values from all calculation levels using reaction scheme (6), (2.7) for CH_3OCl , where we can apply it, show good agreement.

2.2.3 Test of Calculation Method: Enthalpy of HOCl

Methyl hypochlorite and hypochlorous acid both have the oxy-chloride bond and an electron donor group, methyl and H atom respectively. We analyze $\Delta H_f^\circ_{298}$ of $HOCl$ by similar reaction sets to try and evaluate the accuracy of our calculation methods; data are illustrated in Table 2.7. The evaluated $\Delta H_f^\circ_{298}$ of $HOCl$ is $-17.8 \text{ kcal/mol}^{52}$, with a more recent value of -18.5 ± 0.5 recommended by Espinosa-Garcia⁵³. Our calculated $\Delta H_f^\circ_{298}$ for hypochlorous acid are $-19.2, -17.6, -17.6, -17.6, -17.5, -17.9 \text{ kcal/mol}$ using CBS-Q//B3** and reaction schemes 1 to 6 as shown in Table 2.7. Data from the reaction schemes in Table 2.7 obtained at the other calculation levels do not show this good agreement with the experimental value of $HOCl$. The next most reasonable values for $\Delta H_f^\circ_{298}$ of $HOCl$ are not the QCISD(T) but the density function values with the large basis set, in table 2.7.

Enthalpy values determined by B3LYP/6-311+G(3df,2p) method for the methyl- and chloromethyl- hypochlorites are also in good agreement with the values from CBS-Q calculations in Table 2.8; the data suggest this level of density functional theory is

TABLE 2.7. Enthalpies of formation at 298 K (in kcal/mol)^a

| Reaction Q//B3** | $\Delta H_f^{\circ}{}_{298}$ (Theory level ^b) | | | |
|--|--|------------|----------|--------|
| | B3lyp6-31 | B3lyp6-311 | Qcisd(1) | CBS- |
| 1 HOCl + H ₂ → H ₂ O + HCl | -24.27 | -19.69 | -22.68 | -19.69 |
| 2 HOCl + CH ₃ → CH ₃ Cl + H ₂ O | -22.95 | -19.90 | -21.63 | -17.56 |
| 3 HOCl + CH ₄ → CH ₃ OH + HCl | -19.59 | -18.64 | -19.49 | -17.49 |
| 4 HOCl + CH ₃ CH ₃ → CH ₃ CH ₂ OH + HCl | -19.85 | -19.38 | -19.65 | -17.61 |
| 5 HOCl + CH ₃ CH ₃ → CH ₃ CH ₂ Cl + H ₂ O | -23.85 | -20.68 | -22.10 | -17.46 |
| 6 HOCl + H ₂ O → HOOH + HCl | -11.29 | -17.24 | -13.67 | -17.87 |

^a Reaction enthalpies include thermal correction and zero-point energy correction at 298 K. ^b See foot notes of Table 2.3 for the explanation of theory levels

TABLE 2.8. Enthalpies of formation at 298 K (in kcal/mol) for B3LYP/6-311+G(3df,2p) and CBS-Q//B3LYP6-31G(d,p)

| | CH ₃ OCl ^a | CH ₂ ClOCl ^a | CHCl ₂ OCl ^a | CCl ₃ OCl ^a | HOCl ^b |
|-----------------------|----------------------------------|------------------------------------|------------------------------------|-----------------------------------|-------------------|
| B3LYP/6-311+G(3df,2p) | -15.43 | -22.8 | -26.59 | -25.17 | -17.24 |
| CBS-Q//B3** | -15.41 | -22.06 | -26.27 | -26.72 | -17.87 |

^a The average values from the selected reaction in Table 2.6. ^b value from working reaction (6) in Table 2.7.

reasonable for use in enthalpy determinations of oxy-halocarbons using the selected working reactions. Radom et al.⁵³ report that the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) provides reasonably accurate enthalpies. The CBS-Q//B3** and B3LYP/6-

311+G(3df,2p)//B3LYP/6-31G(d,p) both show good agreement for HOCl enthalpies in this study.

TABLE 2.9. Comparison of Enthalpies of Formation Calculated by Semiempirical Methods (in kcal/mol)

| Species | | | | | | | | | |
|-----------------------------|--------------------|--------|--------|--------|--------|--------|--------|---------------------|-------------|
| Theory overall ^c | rxn 1 ^a | rxn 2 | rxn 3 | rxn 4 | rxn 5 | rxn 6 | rxn 7 | output ^b | |
| CH₃OCl | | | | | | | | | |
| PM3 | -30.40 | -33.04 | -9.50 | -45.35 | -35.94 | -20.57 | -37.53 | -34.16 | -15.41±1.52 |
| AM1 | -1.30 | -11.72 | -7.25 | -12.40 | -29.05 | -18.83 | -29.60 | -18.71 | |
| CH₂ClOCl | | | | | | | | | |
| PM3 | -35.76 | -37.40 | 6.78 | -64.92 | -40.57 | -38.75 | | -38.75 | -22.05±2.41 |
| AM1 | -3.88 | -13.17 | -10.97 | -21.27 | -26.83 | -24.95 | | -24.95 | |
| CHCl₂OCl | | | | | | | | | |
| PM3 | -35.17 | -36.71 | 25.87 | -81.68 | -43.11 | -40.52 | | -40.52 | -26.14±3.59 |
| AM1 | -0.44 | -13.61 | -6.79 | -22.24 | -21.50 | -23.29 | | -23.29 | |
| CCl₃OCl | | | | | | | | | |
| PM3 | -34.72 | -44.32 | 40.83 | -102.6 | -46.64 | -46.42 | | -46.42 | -26.72±4.65 |
| AM1 | 1.81 | -8.73 | -2.40 | -23.01 | -17.85 | -21.42 | | -21.42 | |

^a Enthalpy of formation at 298 K calculated by reaction scheme ^b Enthalpy of formation at 298 K calculated by MOPAC program directly. ^c Average of CBS-Q//B3** values after statistical conformer analysis by all reaction schemes except reaction set 1.4. (see foot note c in Table 2.6)

2.2.4 Enthalpies of Rotational Conformers

There are two staggered structures, which show different enthalpies in CH₂ClOCl, and CHCl₂OCl as shown in Figures 2.2 and 2.3. We calculate the correction to enthalpy of formation using statistical analysis of the conformer values listed in Table 2.11. The $\Delta H_f^\circ_{298}$ of CH₃OCl, CH₂ClOCl, CHCl₂OCl, and CCl₃OCl are -15.4 ± 1.5 kcal/mol, -22.1 ± 2.4 kcal/mol, -26.1 ± 3.6 kcal/mol, and -26.7 ± 4.7 kcal/mol respectively. These are the average data using all reactions except reaction series 4 based on CBS-Q calculation level results and considering statistical distribution of rotation conformers in Table 2.11.

The error analysis is performed using the standard deviation in CBS-Q//B3** calculations and the average of maximum error over all reaction sets bar reaction scheme 4, (2.5).

There still exists a significant discrepancy in the $\Delta H_f^\circ_{298}$ for CH_3OCl . We did not intend to resolve this issue in this study. Our primary object is to obtain more complete ($\Delta H_f^\circ_{298}$, S°_{298} , and $C_p(T)$) thermodynamic properties and groups for group additivity of oxygenated chloro carbon species, i.e. for estimation of thermodynamic properties of higher molecular weight hypochlorites. The very high level *ab initio* calculation values of Espinosa-Garcia⁵⁴ with one working reaction are 2.2 kcal/mol above our value; but our values are close to other reported data.

2.2.5 Comparison to Semiempirical (MOPAC) Data

A comparison of enthalpies of formation calculated using density functional and *ab initio* theory with the semiempirical MO methods,⁵⁵ AM1^{56,57} and PM3,⁵⁸ is also performed. The results listed in Table 2.9 for PM3 are not acceptable. Reaction scheme 4 and direct output from AM1 are the most reasonable for the calculation of enthalpies of formation on alkyl hypochlorites among these semiempirical methods. We do not find AM1 to be accurate for other oxy – chlorocarbons and do not recommend these methods for enthalpies or Gibbs Free Energies.

2.2.6 Rotational Barriers

Potential barriers for internal rotations of CH_3OCl , CH_2ClOCl , CHCl_2OCl , and CCl_3OCl are calculated at the B3LYP/6-31G(d, p) level. Potential energy as function of torsion

angle is determined by varying the torsion angle at 15° intervals and allowing the remaining molecular structural parameters to be optimized. The geometry and harmonic vibrational frequencies are calculated for all rotational conformers at

Table 2.10. Total Energy^a (Hartree) of Molecules by Torsion angle

| Angle (degree) ^b | CH ₃ OCl | CH ₂ ClOCl | CHCl ₂ OCl | CCl ₃ OCl |
|-----------------------------|---------------------|-----------------------|-----------------------|----------------------|
| 0 | -575.2592837 | -1034.854719 | -1494.441088 | -1954.017756 |
| 15 | -575.2585261 | -1034.853574 | -1494.439493 | -1954.016222 |
| 30 | -575.2566273 | -1034.851042 | -1494.435627 | -1954.012615 |
| 45 | -575.2546614 | -1034.848626 | -1494.431417 | -1954.009123 |
| 60 | -575.2539522 | -1034.847569 | -1494.428546 | -1954.007689 |
| 75 | -575.2549882 | -1034.848042 | -1494.428116 | -1954.009172 |
| 90 | -575.2569937 | -1034.849121 | -1494.430153 | -1954.012799 |
| 105 | -575.2587273 | -1034.849702 | -1494.433764 | -1954.016478 |
| 120 | -575.2592694 | -1034.849164 | -1494.437250 | -1954.017717 |
| 135 | -575.2583500 | -1034.848085 | -1494.438995 | -1954.015570 |
| 150 | -575.2564308 | -1034.84756 | -1494.438501 | -1954.011659 |
| 165 | -575.2545660 | -1034.848547 | -1494.436908 | -1954.008467 |
| 180 | -575.2539661 | -1034.850925 | -1494.435881 | -1954.007808 |
| 195 | -575.2551159 | -1034.853483 | -1494.436282 | -1954.009976 |
| 210 | -575.2572001 | -1034.854718 | -1494.437768 | -1954.013720 |
| 225 | -575.2588711 | -1034.853402 | -1494.439006 | -1954.016948 |
| 240 | -575.2592268 | -1034.849569 | -1494.43835 | -1954.017622 |
| 255 | -575.2581205 | -1034.844698 | -1494.435412 | -1954.015341 |
| 270 | -575.2561859 | -1034.840762 | -1494.431367 | -1954.011681 |
| 285 | -575.2544925 | -1034.839233 | -1494.428445 | -1954.008641 |
| 300 | -575.2539551 | -1034.840640 | -1494.428296 | -1954.007717 |
| 315 | -575.2548617 | -1034.844495 | -1494.431153 | -1954.009336 |
| 330 | -575.2567292 | -1034.849365 | -1494.435563 | -1954.012737 |
| 345 | -575.2585378 | -1034.853282 | -1494.43949 | -1954.016227 |
| 360 | -575.2592838 | -1034.854720 | -1494.441088 | -1954.017756 |

^a Total energies are in Hartree in B3LYP/6-31G(d,p) theory ^b The torsion angle in degree

B3LYP/6-31G(d, p) level. The barriers for internal rotations are calculated from the differences between the total energy of each conformer as a function of torsion angle in 15 degree intervals. Potential energy vs. torsion angle diagrams for internal rotations about C-O bond of the methyl and chlorinated methyl hypochlorites are shown in Figure

2.1, 2.2, 2.3, and 2.4. The values of the coefficients of the Fourier expansion, a_i and b_i in equation 1 are listed in Table 2.12.

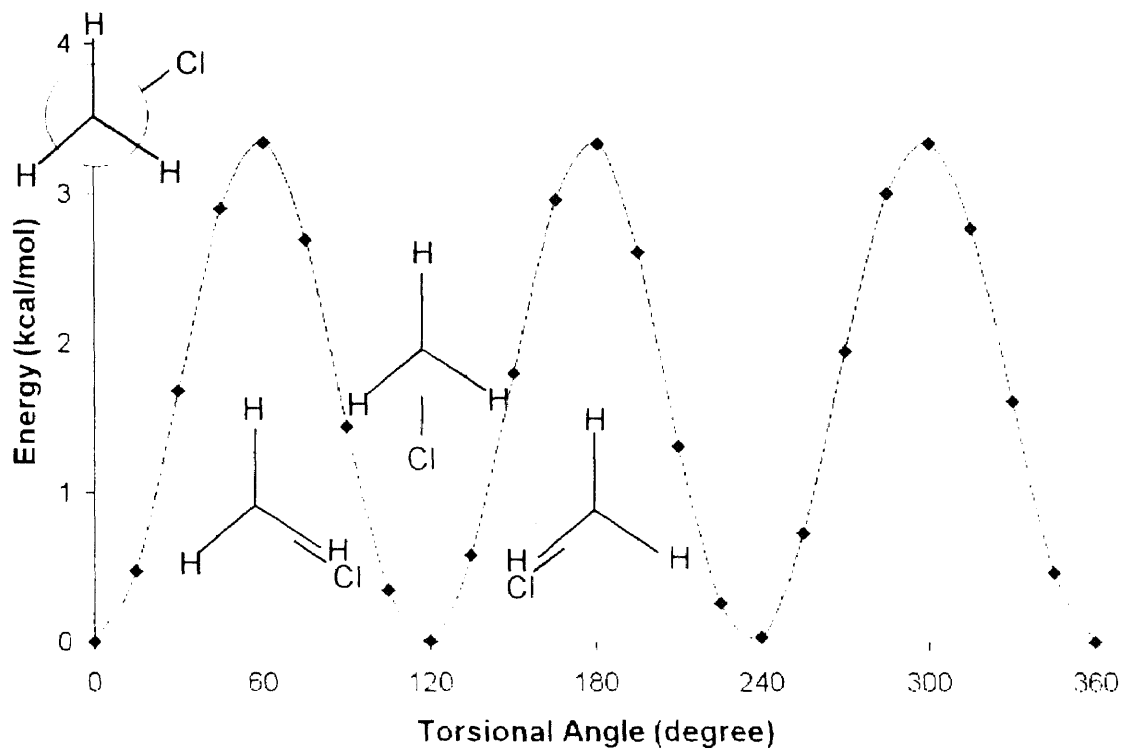


Figure 2.1. Potential energy for internal rotation about C-O bond of CH₃OCl versus torsion angle.

The calculated symmetric rotational barrier for methyl hypochlorite is shown in Figure 1.1. The calculation shows that the H-Cl eclipsed structure has a rotational barrier of 3.35 kcal/mol and that the barrier is uniform for the three hydrogens

Figure 2.2 shows calculated rotational barriers for 1-chloro-methyl hypochlorite. The Cl-Cl anti staggered structure is 3.2 kcal/mol higher in energy than the more stable H-Cl anti staggered conformer because of the Cl interaction with the oxygen atom's non

bonding electrons. The H-Cl eclipsed rotational barrier is 4.5 kcal/mol and the Cl-Cl eclipsed rotational barrier is 9.7 kcal/mol. The Cl/Cl interaction is stronger than H/Cl interaction across the oxygen link on 1-chloro-methyl hypochlorite.

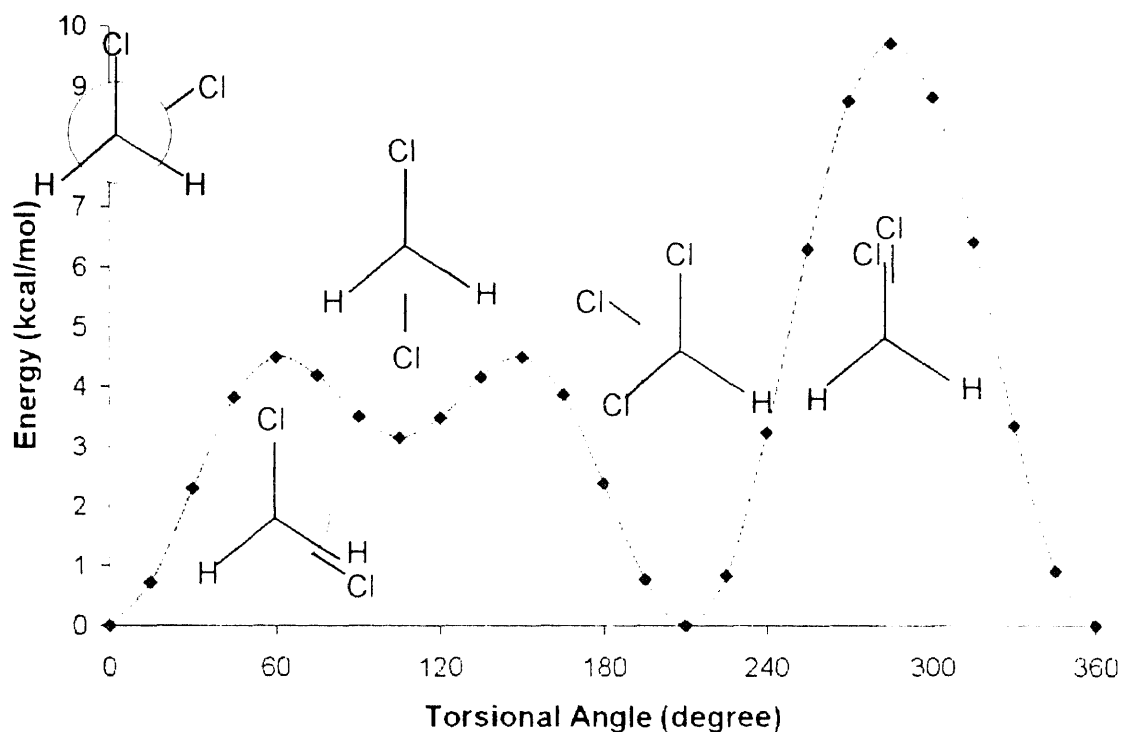


Figure 2.2. Potential energy for internal rotation about C-O bond of CH_2ClOCl versus torsion angle.

Calculated rotational barriers and conformer energies in 1,1-dichloro-methyl hypochlorite are shown in figure 2.3. The Cl-Cl anti staggered conformer has higher energy of 1.3 kcal/mol than the more stable H-Cl anti staggered conformer. The H-Cl eclipsed structure represents a rotational barrier of 3.3 kcal/mol and the Cl-Cl eclipsed structure represents a rotational barrier of 8.08 kcal/mol.

The rotational barriers for 1,1,1 trichloro-methyl hypochlorite are displayed in Figure 2.4. The Cl-Cl eclipsed structure shows a rotational barrier of 6.3 kcal/mol above the Cl-Cl anti staggered conformer.

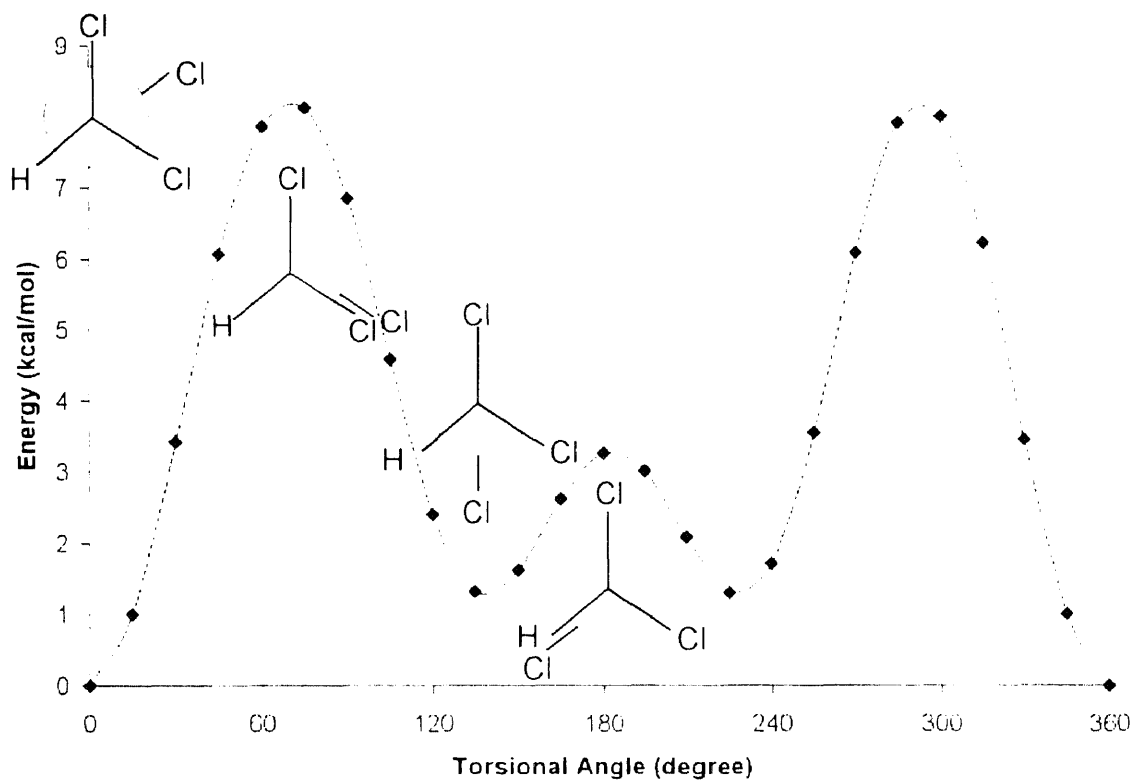


Figure 2.3. Potential energy for internal rotation about C-O bond of CHCl_2OCl versus torsion angle.

Table 2.11-a $\Delta H_f^\circ_{298}$ for Rotational Conformers, Relative fraction, and Overall $\Delta H_f^\circ_{298}$ Values

| Compound | energy(kcal/mol) ^c | relative (%) ^d | final value(kcal/mol) ^e |
|------------------------------------|-------------------------------|---------------------------|------------------------------------|
| CH ₃ OCl | -15.41 | 100.00 | -15.41±1.52 |
| CH ₂ ClOCl ^a | -22.06 | 99.76 | -22.05±2.41 |
| CH ₂ ClOCl ^b | -18.91 | 0.24 | |
| CHCl ₂ OCl ^a | -26.27 | 90.14 | -26.14±3.59 |
| CHCl ₂ OCl ^b | -24.96 | 9.86 | |
| CCl ₃ OCl | -26.72 | 100.00 | -26.72±4.65 |

^a H-Cl anti staggered. ^b Cl-Cl anti staggered. ^c Energy of conformer = overall value in Table 2.6 + energy barrier; Energy barrier = energy of conformer- energy of most stable conformer ^d Relative (%) = conformer fraction ÷ total fraction; Conformer fraction = $e^{(-\Delta E/RT)}$; ΔE = Energy difference, $R = 1.987$ (cal/mol·K), $T = 298$ K. ^e Final value = $\Sigma(\text{Energy} \times \text{relative fraction})$; Uncertainty is the value in foot note e in Table 2.6.

Table 2.11-b. Adjustments for Entropy of Mixing – Rotational Conformers

| Entropy correction | |
|------------------------------------|--|
| CH ₂ ClOCl ^a | $-R\{0.9976 \times \ln(0.9976) + 0.0024 \times \ln(0.0024)\} = 0.03$ |
| CHCl ₂ OCl ^b | $-R\{0.9014 \times \ln(0.9014) + 0.0986 \times \ln(0.0986)\} = 0.64$ |

^a Entropy for CH₂ClOCl at 298K. Entropy (CH₂ClOCl) = Entropy (C/Cl/H2/O) + Entropy (O/C/Cl) + Entropy correction (CH₂ClOCl) ^b Entropy for CHCl₂OCl at 298K. Entropy (CHCl₂OCl) = Entropy (C/Cl2/H/O) + Entropy (O/C/Cl) + Entropy correction (CHCl₂OCl)

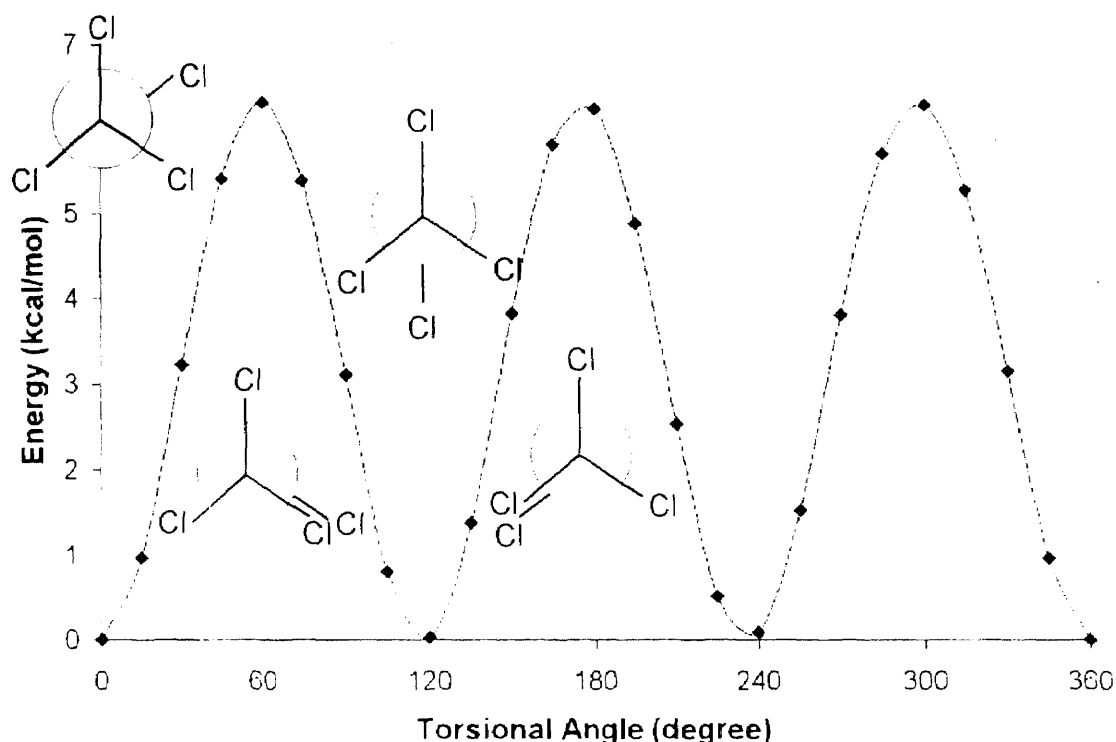


Figure 2.4. Potential energy for internal rotation about C-O bond of CHCl_2OCl versus torsion angle.

2.2.7 Entropy, S°_{298} and Heat Capacity, $C_p(T)$ from 300 to 1500 K

S°_{298} and $C_p(T)$ calculations use the B3LYP/6-31g(d, p) determined geometry and frequencies with values summarized in Table 2.13. TVR represents the sum of the contributions from translations, external rotations and vibrations for S°_{298} and $C_p(T)$. The torsion frequency corresponding to the internal rotor is not included in TVR. Instead, a more exact contribution from the hindered rotation is calculated and listed under I.R. in Table 2.13. I.R. represents the contributions from internal rotation about C-O bond for S°_{298} and $C_p(T)$'s.

TABLE 2.12. Coefficients^a (kcal/mol) of Truncated Fourier Series Representation
Expansion for Internal Rotation Potentials

| C-O rotors | a0 | a1 | a2 | a3 | b1 | | |
|-----------------------|-------|--------|--------|--------|--------|--------|--------|
| b2 | b3 | | | | | | |
| CH ₃ OCl | 1.653 | 0.024 | -0.036 | -1.660 | -0.045 | -0.056 | 0.176 |
| CH ₂ ClOCl | 3.715 | 0.317 | -2.474 | -1.506 | -1.180 | -1.463 | 1.450 |
| CHCl ₂ OCl | 3.905 | 0.903 | -2.391 | -2.498 | -0.163 | -0.063 | -0.211 |
| CCl ₃ OCl | 3.220 | -0.005 | -0.113 | -3.118 | -0.009 | -0.167 | 0.349 |

^a Unit in kcal/mol. Values of rotational barriers computed using the B3LYP/6-31G(d,p) theory. Coefficients are calculated as follows: $V(\theta) = a_0 + a_1 \cos(\theta) + a_2 \cos(2\theta) + a_3 \cos(3\theta) + b_1 \sin(\theta) + b_2 \sin(2\theta) + b_3 \sin(3\theta)$.

TABLE 2.13. Ideal Gas Phase Thermodynamic Properties^a at 298 K

| Species | $\Delta H_f^\circ_{298}$ ^b | S°_{298} ^c | C_{p300} ^e | C_{p400} | C_{p500} | C_{p600} | C_{p800} | C_{p1000} | C_{p1500} |
|--|---------------------------------------|------------------------------|-------------------------|------------|------------|------------|------------|-------------|-------------|
| CH ₃ OCl TVR ^d | | 60.92 | 11.46 | 13.54 | 15.52 | 17.25 | 20.02 | 22.09 | 25.31 |
| (3) ^l Internal ^e | | 4.27 | 2.13 | 2.19 | 2.11 | 1.98 | 1.71 | 1.52 | 1.26 |
| Total | -15.41 | 65.19 | 13.59 | 15.73 | 17.63 | 19.23 | 21.73 | 23.61 | 26.57 |
| Colussi ^f | -12.26 | | | | | | | | |
| Francisco ^g | -15.9 | | | | | | | | |
| Elord ^h | -17.69 | | | | | | | | |
| Espinosa ⁱ | -13.2 | | | | | | | | |
| Crowley ^j | -14.58 | | | | | | | | |
| Melius ^k | -14.00 | 65.40 | 13.44 | | 17.72 | | 21.89 | 23.82 | 26.85 |
| CH ₂ ClOCl TVR | | 68.98 | 13.85 | 16.37 | 18.44 | 20.08 | 22.47 | 24.11 | 26.54 |
| (1) Internal | | 5.52 | 2.24 | 2.41 | 2.41 | 2.28 | 1.86 | 1.48 | 0.88 |
| Total | -22.05 | 74.50 | 16.09 | 18.78 | 20.85 | 22.36 | 24.33 | 25.59 | 27.42 |
| CHCl ₂ OCl TVR | | 75.19 | 17.34 | 19.98 | 21.91 | 23.31 | 25.16 | 26.31 | 27.87 |
| (1) Internal | | 5.21 | 3.84 | 3.27 | 2.65 | 2.18 | 1.62 | 1.29 | 0.81 |
| Total | -26.14 | 80.40 | 21.18 | 23.25 | 24.56 | 25.49 | 26.78 | 27.60 | 28.68 |
| CCl ₃ OCl TVR | | 79.11 | 21.70 | 24.23 | 25.82 | 26.85 | 28.02 | 28.62 | 29.26 |
| (3) Internal | | 6.26 | 1.84 | 1.76 | 1.72 | 1.67 | 1.51 | 1.29 | 0.81 |
| Total | -26.72 | 85.37 | 23.54 | 25.99 | 27.54 | 28.52 | 29.53 | 29.91 | 30.07 |

^a Thermodynamic properties are referred to standard state of an ideal gas of pure enantiomer at 1 atm. Units: enthalpy in kcal/mol; entropy and heat capacity in cal/mol·K. ^b $\Delta H_f^\circ_{298}$ is the average value of CBS-Q level considering the statistical contribution of rotational conformers in kcal/mol excluding reaction scheme 4. (see footnote e in Table 2.6 and final value in Table 2.8) ^c Units in cal/mol K. ^d The sum of contributions from translations, external rotations, and vibrations. ^e Contributions from internal rotation about C-O bond. ^f Reference 17. ^g -15.9 kcal/mol, which we convert to 298 K by this reaction using ΔH_f° of reference 15 and thermal energies of this study: $3/2\text{H}_2 + 1/2\text{O}_2 + 1/2\text{Cl}_2 + \text{C(s)} \rightarrow \text{CH}_3\text{OCl}$. ^h Reference 16. ⁱ Reference 54. ^j Reference 19 and ^k Reference 18-b. ^l Symmetry number is taken into account for S°_{298} . Entropy corrections for CH₂ClOCl, and CHCl₂OCl mixing σ -0.03 and -0.64 respectively are not included above.

There is no published data on entropy and heat capacity values for CH_3OCl , CH_2ClOCl , CHCl_2OCl or CCl_3OCl . There is one data set, *ab initio* calculation, in the web site of C. Melius for methyl hypochlorite.¹⁸ Our calculation results show a good agreement for the entropy and heat capacity with the BAC/MP4 values of Melius¹⁸ for CH_3OCl ; the BAC/MP4 method uses HF/6-31G* structures and frequencies. Table 2.1 shows a comparison of frequencies among B3LYP/6-31G(d,p), BAC/MP4¹⁸ theory along with experimental data,^{10,46} and calculated rotation constants.

2.2.8 Group Values and Group Additivity Correction Terms

Hypochlorite groups are estimated in order to extend the current data to larger molecules by use of group additivity. Conventional group additivity does not work well for chlorocarbons or other halocarbons, as group additivity does not incorporate effects of non-next nearest neighbors.³⁹

In this paper, we define the O/C/Cl group and a limited set of interaction terms which can be used with Benson type group additivity scheme for calculation of the thermodynamic properties of multichloro-hypochlorites.⁴⁵ Previous studies report and explain the use of interaction terms for chloro^{39,40} and fluoro^{41,42} hydrocarbons. We have recently reported new groups for chloro and fluoro carbons and developed interaction terms to allow more accurate thermodynamic property estimation of these molecules.³⁸⁻⁴²

The group value for thermodynamic properties of C/H3/O are from existing literature.^{20,59} Values for C/Cl/H2/O, C/Cl2/H/O and C/Cl3/O are taken from recent work in this research group on chlorinated methanols³⁸ and ethers.⁶⁰ The properties of the C/Cl/H2/O, C/Cl2/H/O and C/Cl3/O groups for example, are derived from chloro-

methanol (CH_2ClOH), 1,1-dichloro-methanol (CHCl_2OH), and 1,1,1-trichloro-methanol (CCl_3OH), respectively and from chloro-dimethyl ether ($\text{CH}_2\text{ClOCH}_3$), 1,1-dichloro-dimethyl ether ($\text{CHCl}_2\text{OCH}_3$), and 1,1,1-trichloro-dimethyl ether (CCl_3OCH_3), respectively. In the present work, we estimate group values for O/C/Cl and chlorine interaction terms across the oxygen link on methyl oxychlorides of OCl/Cl, OCl/Cl₂, and OCl/Cl₃. There are no chlorines, other halogens, or bulky groups/fragments on the carbon atom adjacent to the oxygen atom containing the chlorine in the defining O/C/Cl group for methyl hypochlorite (CH_3OCl). Enthalpy of formation ($\Delta H_f^{\circ 298}$) and heat capacities, $C_p(T)$ of the O/C/Cl group are calculated on the basis of the equation 2.15

$$(\text{CH}_3\text{OCl}) = (\text{C/H}_3/\text{O}) + (\text{O/C/Cl}) \quad (2.15)$$

S°_{298} of O/C/Cl is calculated on the basis of the equation 2.16

$$(\text{CH}_3\text{OCl}) = (\text{C/H}_3/\text{O}) + (\text{O/C/Cl}) - R \ln(\sigma) \quad (2.16)$$

$R = 1.987$ (cal/mol K), and σ is symmetry number, which is 3 for CH_3OCl .

Thermodynamic properties of methyl hypochlorite with no chlorine on the carbon atom adjacent to the $-\text{OCl}$ are now accurately predicted; but an adjustment needs to be made for chloro-oxychlorides where there are chlorine atoms on the adjacent carbon, such as chloro-methyl hypochlorite, dichloro-methyl hypochlorite or trichloro-methyl hypochlorite. This adjustment comes in the form of an interaction term to count the total number of chlorine atoms on the adjacent carbon atom. The assumption is based on the known accuracy and validity of group additivity for hydrocarbon and oxyhydrocarbons with gauche interactions.^{20,37}

The interaction values between chlorine(s) on the methyl and the chlorine attached to the oxygen (OCl/Cl, OCl/Cl₂, and OCl/Cl₃) are calculated from differences

between the sum of defined chlorinated oxyhydrocarbon group values and the determined thermodynamic properties of the parent compounds. For example, $\Delta H_f^{\circ}_{298}$ and C_p 's for the OCl/Cl₂ interaction term are estimated by the equation 2.17 and $\Delta H_f^{\circ}_{298}$ for CHCl₂OCl.

$$(\text{CHCl}_2\text{OCl}) = (\text{C/Cl}_2\text{/H/O}) + (\text{O/C/Cl}) + (\text{OCl/Cl}_2) \quad (2.17)$$

$$(\text{CHCl}_2\text{OCl}) = (\text{C/Cl}_2\text{/H/O}) + (\text{O/C/Cl}) - R \ln(\sigma) + (\text{OCl/Cl}_2) \quad (2.18)$$

S°_{298} for the OCl/Cl₂ interaction term is calculated from equation 2.18 using the S for the parent molecule. Equation 4 and 5 both use the CCl₂/H/O group from dichloromethanol and 1,1 dichloro methylether and the O/C/Cl group from CH₃OCl. $R = 1.987$ (cal/mol K), and σ is symmetry number, which is 1 for CHCl₂OCl. Entropy of mixing = $-R \sum \{(n_i) \times \ln(n_i)\}$; where n_i is fraction of conformer i. Mixing entropy is included in the (C/Cl₂/H/O) group, as it is in hydrocarbon and other molecular groups. For CHCl₂OCl, the mixing term is: $-R \{0.9014 \times \ln(0.9014) + 0.0986 \times \ln(0.0986)\} = 0.64$ cal/mol K in Table 2.11-b. The other interaction values are also estimated in the same manner.

The group values for enthalpy of formation and entropy of C/H₃/O at 298 K are -10.1 kcal/mol and 30.41 cal/mol-K respectively from Cohen^{39,40} and Benson.²⁰ Thermodynamic properties of the C/Cl/H₂/O, C/Cl₂/H/O, and C/Cl₃/O groups are calculated from the average of data from chloro-methanols and chloro-dimethyl ethers; group values for enthalpy of formation of C/Cl/H₂/O, C/Cl₂/H/O, and C/Cl₃/O are -20.9, -27.3, and -28.1 at 298 K; group values for entropy are 37.1, 42.5 and 51.1 cal/mol-K and group values for heat capacity at 300 K are 8.6, 12.7, 16.2 cal/mol-K, also listed in Table 2.14. Thermodynamic properties of the O/C/Cl groups are derived from

methyl hypochlorite (CH_3OCl) in this work by equations 2.15 and equation 2.16; The enthalpy, entropy at 298 K, and heat capacity at 300 K values are -5.41 kcal/mol, 37.0 and 7.4 cal/mol·K.

Interaction term values are also listed in Table 2.14 and are significant; they indicate a several kcal/mol increase in enthalpy due to destabilizing interaction of chlorine(s) on the methyl group with the hypochlorite group. The group additivity corrections for enthalpy of formation at 298 K are 4.2, 6.5, and 6.7 kcal/mol for OCl/Cl , OCl/Cl_2 , and OCl/Cl_3 , respectively. Interaction terms for entropies at 298 K and heat capacities are relatively small. Entropy terms are 0.8, 1.7, and -0.5 cal/mol·K for OCl/Cl , OCl/Cl_2 , and OCl/Cl_3 , respectively at 298 K. The interaction values for heat capacity at 300 K are 0.1, 1.0, and -0.1 cal/mol·K for OCl/Cl , OCl/Cl_2 , and OCl/Cl_3 , respectively. These low values for entropy and heat capacity interaction terms are encouraging. They suggest reasonable accuracy and consistency throughout our calculations and that the interaction terms are primarily needed for enthalpies.

Interaction values are calculated from the defined group values for methyl hypochlorite and thermodynamic properties of three chlorinated methyl hypochlorites as illustrated by equation 4 and 5. Table 2.15 lists groups and interaction terms for use in estimating thermodynamic property of oxychlorocarbons by modified group additivity method.

TABLE 2.14-a: Thermodynamic Properties of Chlorine Groups

| Groups | $\Delta H_f^\circ_{298}$ ^a | S°_{298} ^b | C_{p300} ^b | C_{p400} | C_{p500} | C_{p600} | C_{p800} | C_{p1000} | C_{p1500} | Ref |
|-----------|---------------------------------------|------------------------------|-------------------------|------------|------------|------------|------------|-------------|-------------|-------------------------|
| C/H3/O | -10.00 | 30.41 | 6.19 | 7.84 | 9.40 | 10.79 | 13.03 | 14.77 | 17.58 | 59 |
| C/Cl/H2/O | -21.09 | 37.05 | 8.64 | 10.62 | 12.49 | 13.89 | 15.59 | 16.79 | 19.19 | Other work ^c |
| C/Cl2/H/O | -27.71 | 42.19 | 12.74 | 15.50 | 17.43 | 18.44 | 19.05 | 19.34 | 20.60 | Other work ^c |
| C/Cl3/O | -28.75 | 51.11 | 16.24 | 18.08 | 19.30 | 19.96 | 20.36 | 20.55 | 21.46 | Other work ^c |
| O/C/Cl | -5.41 | 36.96 | 7.40 | 7.89 | 8.23 | 8.44 | 8.70 | 8.84 | 8.99 | This work |

^a Units in kcal/mol. ^b Units in cal/mol-K. ^c The average of group value from chloromethanols (reference 38) and chloro ethers (reference 60).

TABLE 2.14-b: Thermodynamic Properties of OCl-Cl_x interactions

| | $\Delta H_f^\circ_{298}$ ^a | S°_{298} ^b | C_{p300} ^b | C_{p400} | C_{p500} | C_{p600} | C_{p800} | C_{p1000} | C_{p1500} | Ref |
|---------|---------------------------------------|------------------------------|-------------------------|------------|------------|------------|------------|-------------|-------------|-----------|
| OCl/Cl | 4.45 | 0.78 | 0.05 | 0.27 | 0.13 | 0.02 | 0.04 | -0.05 | -0.77 | This work |
| OCl/Cl2 | 6.98 | 1.70 | 1.03 | -0.14 | -1.10 | -1.39 | -0.97 | -0.58 | -0.91 | This work |
| OCl/Cl3 | 7.44 | -0.52 | -0.10 | 0.02 | 0.01 | 0.12 | 0.47 | 0.52 | -0.38 | This work |

^a Units in kcal/mol. ^b Units in cal/mol-K. Groups include entropy of mixing corrections.

TABLE 2.15. Groups and Interaction Terms for Four Oxychlorides

| Compounds | CH ₃ OCl | CH ₂ ClOCl | CHCl ₂ OCl | CCl ₃ OCl |
|-------------|---------------------|-----------------------|-----------------------|----------------------|
| | C/H3/O | C/Cl/H2/O | C/Cl2/H/O | C/Cl3/O |
| | O/C/Cl | O/C/Cl | O/C/Cl | O/C/Cl |
| interaction | OCl/Cl | OCl/Cl2 | OCl/Cl3 | |

2.3 Summary

Thermochemical Properties of CH_3OCl and three chlorinated methyl hypochlorites are calculated using density functional *ab initio* calculations. Enthalpies, $\Delta H_f^\circ_{298}$ are presented as average data from the selected reaction schemes (up to seven) based on CBS-Q calculation level results considering statistical distribution of rotational conformers. CBS-Q calculation values of $\Delta H_f^\circ_{298}$ show consistency for all reaction schemes, which is not observed in the B3LYP/6-31G(d, p), B3LYP/6-311+G (3df, 2p), QCISD(T)/6-31G(d, p) calculations. Entropies, S°_{298} and heat capacities, $C_p(T)$ from 300 K to 1500 K are reported along with groups and oxychloride-chloride interaction group values for use in group additivity. Torsion potentials are presented for intramolecular rotations. Semiempirical methods do not seem satisfactory for estimation of oxy – chlorocarbon thermochemical properties.

CHAPTER 3

GEOMETRIES, VIBRATIONAL FREQUENCIES AND THERMODYNAMIC PROPERTIES OF CHLORO-ETHERS

3.1 Overview

Chloro-carbons are widely used chemicals as solvents in synthesis and in cleaning agents, as synthesis starting materials and in polymer, pesticide and other product manufacture. Chloro-carbons and other halocarbon compounds are present in the atmosphere from evaporation of these solvents and other anthropogenic activities. They often exhibit relatively long tropospheric lifetimes due to their slow decay in the atmosphere or low reaction rates with OH radical.⁶¹ Initial reactions of saturated and unsaturated alkyl chlorides in both atmospheric and in combustion chemistry result in alkyl radical intermediates. Saturated chloro-carbons undergo loss of H atom via abstraction with OH,^{5,62} while unsaturated chloro-carbons undergo addition. These radicals rapidly react with oxygen,⁸ that is present at high levels, and form a myriad of oxygenated chloro-carbon species.

Thermodynamic properties of chloro-dimethyl ethers provide data for understanding the stability, reaction pathways and products of oxygenated chloro-carbons in the combustion and atmospheric environments. The data also allows determination of oxy-chloro-carbon groups for group additivity of the mono, di and trichloro-methyl oxygen species, and thus thermodynamic property estimation on larger oxychlorocarbons. There is little or no literature data available on thermodynamic

properties of chlorinated oxygenated hydrocarbons with the exception of acid chlorides and methyl hypochlorites. The thermodynamic values for dimethyl ether are well known⁶³ but surprisingly there is no literature data, to our knowledge, for any chlorinated ether.

This research estimates fundamental thermodynamic property data on these species using *ab initio* and density functional calculations. These thermodynamic properties on chloro-dimethyl ethers allow estimation of C/Cl/H₂/O, C/Cl₂/H/O, C/Cl₃/O groups for use in group additivity on larger hydrocarbons.

3.2 Method

3.2.1 Computational Methods

All *ab initio* calculations are performed using the Gaussian 94 program suite.⁶⁴ The structural parameters 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 optimized geometry parameters are used to obtain total electronic energies in B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) single point calculations.^{30,65,66}

B3LYP/6-31G(d,p) is chosen because it is commonly used and is reported to yield accurate geometry and reasonable energies.²¹⁻²² Curtiss et al.⁶⁷ reported that B3LYP/6-31G(d,p) provides highly accurate structures for compounds with elements up to atomic number 10. Durant^{21,68} has compared density functional calculations BHandH and B3LYP with MP2 and Hartree-Fock methods for geometry and vibration frequencies. He reports that these density functional methods provide excellent geometry and

vibration frequencies, relative to MP2 at reduced computation expense. Petersson et al.⁶⁹ currently examines density functional methods of B3LYP/6-311+G(3df,2p)//B3LYP/6-31G with G2 study, and his CBS calculation methods and report that they have been the most successful for a wide range of molecules⁶⁹. Wong and Radom^{23,53} indicated the B3LYP/6-31G(d,p) geometry corresponds closely to QCISD(T)/6-31G(d,p) and they prefer ZPVE (Zero point vibrational Energy) of B3LYP/6-31G(d,p) to that of QCISD(T)/6-31G(d,p). Comparison of calculation results from B3LYP/6-31G(d,p) against data from higher calculation levels in use of working reaction for $\Delta H_f^\circ_{298}$, will provide some calibration of the B3LYP/6-31G(d,p) values with similar working reactions, for larger molecules, where this may be one of the few available calculation methods.

B3LYP/6-311+G(3df,2p) is chosen to evaluate if this large basic set results in an improvement to the above commonly used density functional calculation method. QCISD(T)/6-31G(d,p) is a configuration interaction method; but with a small, economical basis set.^{23,53} CBS-Q calculation is a high level composite method with empirical correction; it is reported to be nearly equivalent to QCISD(T)/6-311+G(3df,2p).^{23,30} The CBS-Q method⁷⁰ attempts to approximate the energy of a species at the infinite basis set limit by an extrapolation of the energies of pair natural orbital at the MP2 level. The effects of going from MP2 to QCISD(T) are accounted for with an additivity scheme. The geometry is obtained at the MP2 /6-31G level of theory, while the ZPE used is the scaled (by 0.9135) HF/6-31G value. For the open-shell systems, there is also a correction for spin contamination in the unrestricted Hartree-

Fock wave function. The CBS-Q method has been shown to yield reliable $\Delta H_f^\circ_{298}$ values for small molecules.⁵³⁻⁷⁰

The CBS-Q//B3LYP/6-31G(d,p) method used here, differs from CBS-Q in that it employs an improved geometry and ZPVE. The CBS-Q//B3LYP/6-31G(d,p) employs geometry optimized at B3LYP/6-31G(d,p) and a ZPVE calculation from B3LYP/6-31G(d,p) harmonic vibrational frequencies scaled (by 0.9806)³¹. This is very similar to the Radom research group's CBS/RAD²³ method; it has B3LYP/6-31g(d,p) geometry, which they indicate is very close to QCISD(T) values and a QCISD(T) calculation in place of CCSD(T). These calculations are referred to as CBSQ//B3** in the present study.

3.2.2 Thermodynamic Properties Using *ab initio* Calculations

Enthalpy, $\Delta H_f^\circ_{298}$, entropy, S°_{298} and heat capacities $C_p(T)$, ($300 < T/K < 1500$) are determined for three chloro-dimethyl ethers, $\text{CH}_2\text{ClOCH}_3$, $\text{CHCl}_2\text{OCH}_3$ and CCl_3OCH_3 using density functional B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p) and *ab initio* QCISD(T)/6-31G(d,p) and CBS-Q/B3** calculation methods.

Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) density functional calculation level, with single point calculations for energy at the B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q levels of calculation. Vibration frequencies are scaled³¹ by 0.9806 for zero point energies (ZPVE). Enthalpies of formation are determined at each calculation level using the enthalpy of reaction ($\Delta H_r^\circ_{298}$) with known enthalpies of other reactants in each of the 7 different reaction series.³²⁻³⁴ Barriers for intramolecular rotation about the two carbon-oxygen

bonds of chloro-dimethyl ethers are analyzed versus torsion angle using B3LYP/6-31G(d,p).

3.2.3 Calculation of Hindered Rotation Contribution to Thermodynamic

Parameters

A technique for the calculation of thermodynamic functions from hindered rotations with arbitrary potentials has been previously developed.³⁶⁻³⁷ This technique employs expansion of the hindrance potential in the Fourier series, calculation of the Hamiltonian matrix in the basis of the wave functions of free internal rotation, and subsequent calculation of energy levels by direct diagonalization of Hamiltonian matrix. In this work the torsion potential calculated at discrete torsion angle is represented by equation 3.1

$$V(\vartheta) = a_0 + a_1 \cos(\vartheta) + a_2 \cos(2\vartheta) + a_3 \cos(3\vartheta) + b_1 \sin(\vartheta) + b_2 \sin(2\vartheta) + b_3 \sin(3\vartheta) \quad (3.1)$$

where value of the coefficients a_i were calculated to provide the true minimum and maximum of the torsion potentials with allowance of a shift of the theoretical extreme angular positions.

Table 3.1 Vibrational Frequencies^a (cm⁻¹)^a, and moments of inertia (amu·Bohr²)^b

| CH ₃ OCH ₂ Cl | | CH ₃ OCHCl ₂ | | CH ₃ OCCL ₃ | |
|-------------------------------------|--------|------------------------------------|---------|-----------------------------------|---------|
| Freq | I | Freq | I | Freq | I |
| 145.44 | 125.88 | 106.90 | 554.68 | 99.90 | 973.41 |
| 187.44 | 540.54 | 179.64 | 642.99 | 188.21 | 1117.00 |
| 350.14 | 615.92 | 245.44 | 1030.71 | 206.94 | 1243.34 |
| 450.49 | | 286.60 | | 244.18 | |
| 636.57 | | 376.67 | | 278.00 | |
| 951.90 | | 506.19 | | 330.28 | |
| 1010.37 | | 669.08 | | 382.23 | |
| 1162.94 | | 730.70 | | 425.67 | |
| 1184.46 | | 942.92 | | 502.60 | |
| 1228.94 | | 1174.23 | | 713.75 | |
| 1307.75 | | 1190.93 | | 837.99 | |
| 1354.44 | | 1230.71 | | 976.58 | |
| 1480.56 | | 1234.06 | | 1171.49 | |
| 1498.64 | | 1366.68 | | 1182.51 | |
| 1514.21 | | 1485.75 | | 1211.39 | |
| 1520.76 | | 1500.15 | | 1483.26 | |
| 3019.38 | | 1515.16 | | 1498.36 | |
| 3059.57 | | 3061.84 | | 1512.40 | |
| 3097.21 | | 3142.64 | | 3068.13 | |
| 3159.16 | | 3177.92 | | 3153.12 | |
| 3180.26 | | 3189.44 | | 3187.26 | |

^a Nonscaled frequencies are calculated at the B3LYP/6-31G(D,P) level of theory. ^b The moment of inertia units are amu·Bohr².

3.3 Results and Discussion

3.3.1 Vibrational frequencies and geometry

Harmonic vibrational frequencies are calculated for three chloro-dimethyl ethers at the B3LYP/6-31G(d, p) level of theory on the basis of optimized geometry at the same level of theory. The vibrational frequencies and the moment of inertia (amu·Bohr²) for the multiple chlo-dimethyl ethers are given in Table 3.1.

The fully optimized geometry at the B3LYP/6-31G(d, p) density functional calculation level for the methyl and three chlorinated dimethyl ethers are presented in Table 3.2. The numerical values of the structural parameters including carbon-hydrogen, carbon-chlorine, carbon-oxygen, oxygen-hydrogen bond distance along with applicable bond

Table 3.2. Optimized geometry of chlorinated ethers.^a

| CH ₂ ClOCH ₃ | | | CHCl ₂ OCH ₃ | | |
|------------------------------------|------------|--------|------------------------------------|------------|---------|
| Name | Definition | Value | Name | Definition | Value |
| R(O-C) ^b | R(2,1) | 1.3656 | R(O-C) | R(2,1) | 1.3453 |
| R(C-O) | R(3,2) | 1.4262 | R(C-O) | R(3,2) | 1.4362 |
| R(Cl-C) | R(4,1) | 1.8626 | R(Cl-C) | R(4,1) | 1.8347 |
| R(H-C) | R(5,1) | 1.0952 | R(Cl-C) | R(5,1) | 1.8347 |
| R(H-C) | R(6,1) | 1.0987 | R(H-C) | R(6,1) | 1.0863 |
| R(H-C) | R(7,3) | 1.0905 | R(H-C) | R(7,3) | 1.0893 |
| R(H-C) | R(8,3) | 1.0952 | R(H-C) | R(8,3) | 1.0931 |
| R(H-C) | R(9,3) | 1.0987 | R(H-C) | R(9,3) | 1.0931 |
| A(C-O-C) ^c | A(1,2,3) | 114.97 | A(C-O-C) | A(1,2,3) | 118.56 |
| A(O-C-Cl) | A(2,1,4) | 113.41 | A(O-C-Cl) | A(2,1,4) | 113.47 |
| A(O-C-H) | A(2,1,5) | 113.59 | A(O-C-Cl) | A(2,1,5) | 113.47 |
| A(Cl-C-H) | A(4,1,5) | 103.94 | A(Cl-C-Cl) | A(4,1,5) | 108.50 |
| A(O-C-H) | A(2,1,6) | 108.48 | A(O-C-H) | A(2,1,6) | 108.61 |
| A(Cl-C-H) | A(4,1,6) | 105.08 | A(Cl-C-H) | A(4,1,6) | 106.15 |
| A(H-C-H) | A(5,1,6) | 112.02 | A(Cl-C-H) | A(5,1,6) | 106.15 |
| A(O-C-H) | A(2,3,7) | 106.48 | A(O-C-H) | A(2,3,7) | 105.34 |
| A(O-C-H) | A(2,3,8) | 110.92 | A(O-C-H) | A(2,3,8) | 110.49 |
| A(H-C-H) | A(7,3,8) | 109.67 | A(H-C-H) | A(7,3,8) | 110.14 |
| A(O-C-H) | A(2,3,9) | 110.99 | A(O-C-H) | A(2,3,9) | 110.49 |
| A(H-C-H) | A(7,3,9) | 109.48 | A(H-C-H) | A(7,3,9) | 110.14 |
| A(H-C-H) | A(8,3,9) | 109.25 | A(H-C-H) | A(8,3,9) | 110.15 |
| D(C-O-C-Cl) ^d | D(3,2,1,4) | -72.47 | D(C-O-C-Cl) | D(3,2,1,4) | -62.21 |
| D(C-O-C-H) | D(3,2,1,5) | 45.93 | D(C-O-C-Cl) | D(3,2,1,5) | 62.23 |
| D(C-O-C-H) | D(3,2,1,6) | 171.19 | D(C-O-C-H) | D(3,2,1,6) | 180.01 |
| D(H-C-C-C) | D(7,3,2,1) | 185.73 | D(H-C-O-C) | D(7,3,2,1) | -179.96 |
| D(H-C-O-C) | D(8,3,2,1) | 66.46 | D(H-C-O-C) | D(8,3,2,1) | 61.12 |
| D(H-C-O-C) | D(9,3,2,1) | -55.19 | D(H-C-O-C) | D(9,3,2,1) | -61.04 |

| CCl ₂ OCClH ₃ | | | The structure of molecules |
|-------------------------------------|------------|--------|----------------------------|
| Name | Definition | Value | |
| R(O-C) | R(2,1) | 1.3405 | |
| R(C-O) | R(3,2) | 1.4414 | |
| R(Cl-C) | R(4,1) | 1.8339 | |
| R(Cl-C) | R(5,1) | 1.8338 | |
| R(Cl-C) | R(6,1) | 1.7908 | |
| R(H-C) | R(7,3) | 1.0888 | |
| R(H-C) | R(8,3) | 1.0924 | |
| R(H-C) | R(9,3) | 1.0924 | |
| A(C-O-C) | A(1,2,3) | 118.83 | |
| A(O-C-Cl) | A(2,1,4) | 112.53 | |
| A(O-C-Cl) | A(2,1,5) | 112.53 | |
| A(Cl-C-Cl) | A(4,1,5) | 107.19 | |
| A(O-C-Cl) | A(2,1,6) | 106.72 | |
| A(Cl-C-Cl) | A(4,1,6) | 108.89 | |
| A(Cl-C-Cl) | A(5,1,6) | 108.90 | |
| A(O-C-H) | A(2,3,7) | 104.78 | |
| A(O-C-H) | A(2,3,8) | 110.34 | |
| A(H-C-H) | A(7,3,8) | 110.40 | |
| A(O-C-H) | A(2,3,9) | 110.34 | |
| A(H-C-H) | A(7,3,9) | 110.40 | |
| A(H-C-H) | A(8,3,9) | 110.45 | |
| D(C-O-C-Cl) | D(3,2,1,4) | -60.63 | |
| D(C-O-C-Cl) | D(3,2,1,5) | 60.61 | |
| D(C-O-C-Cl) | D(3,2,1,6) | 179.99 | |
| D(H-C-O-C) | D(7,3,2,1) | 179.97 | |
| D(H-C-O-C) | D(8,3,2,1) | 61.13 | |
| D(H-C-O-C) | D(9,3,2,1) | -61.19 | |

^a Geometry is optimized at B3LYP/6-31g(d,p) density functional calculation level. ^b Bond length or the distance between two atoms of number in Å. ^c Bond angle or the angle among three atoms of number in degree. ^d The dihedral angle among the four number atoms.

angles are also listed in Table 3.2. Effects of chlorine α -substitution on molecular geometry can be seen from Table 3.2. The C-H, C-Cl and O-C bond lengths in the equilibrium conformations of three title molecules, $\text{CH}_2\text{ClOCH}_3$, $\text{CHCl}_2\text{OCH}_3$, and CCl_3OCH_3 optimized at the B3LYP/6-31G(d, p) are similar, while the O-C bond lengths, $R(2,1)$ decrease in order: 1.3656 Å in $\text{CH}_2\text{ClOCH}_3$, 1.3453 Å in $\text{CHCl}_2\text{OCH}_3$, 1.3405 Å in CCl_3OCH_3 . The Cl-C bond lengths, $R(4,1)$ in the chloro-dimethyl ethers also decrease with increase in number of chlorines; It is 1.8626, 1.8347, and 1.8339 Å in $\text{CH}_2\text{ClOCH}_3$, $\text{CHCl}_2\text{OCH}_3$, and CCl_3OCH_3 . In contrast, the C-O bond length, $(R3,2)$ increases slightly in this series at 1.4262, 1.4362, and 1.4414 Å in $\text{CH}_2\text{ClOCH}_3$, $\text{CHCl}_2\text{OCH}_3$, and CCl_3OCH_3 , because the more chlorinated, the more electron withdrawing. The optimized geometry is the staggered form; the eclipsed geometry has a higher energy. Geometry will be further discussed when we present the intramolecular rotational energies versus torsion angle.

3.3.2 Enthalpies of Formation ($\Delta H_f^\circ_{298}$)

Enthalpies of formation ($\Delta H_f^\circ_{298}$) are estimated using total energies in Table 3.3, and calculated $\Delta H_{\text{rxn}(298)}$ for the seven reaction series in Table 3.4. The calculated $\Delta H_{\text{rxn}(298)}$ and known $\Delta H_f^\circ_{298}$ of reference species are utilized to estimate $\Delta H_f^\circ_{298}$ of the target chlorinated dimethyl ethers in each of the reaction schemes. $\Delta H_f^\circ_{298}$ for the reference species comes from literature thermodynamic properties, reported in Table 3.5.

Enthalpies of reaction ($\Delta H_{\text{rxn}(298)}$) are estimated using total energies obtained by the density functional and *ab initio* calculations. Zero-point energies (ZPVE's) and thermal correction to 298 K are taken into account. The total energies at 0 K, scaled ZPVE's,

TABLE 3.3. Total Energies at Different Levels of Theory, Composite CBS-Q, Zero Point Vibrational Energy and Thermal Correction (in Hartree)

| | Total energies | | | | ZPE ^e | Therm.cor ^f |
|-------------------------------------|------------------------|-------------|-----------------------|--------------------|------------------|------------------------|
| | B3lyp6-31 ^a | B3lyp6-311b | Qcisd(t) ^c | CBS-Q ^d | | |
| CH ₃ OCH ₃ | -155.03297 | -155.08851 | -154.60021 | -154.74287 | 0.07836 | 0.00525 |
| CH ₃ OCH ₂ Cl | -614.63432 | -614.72296 | -613.63747 | -613.90981 | 0.07037 | 0.00595 |
| CH ₃ OCHCl ₂ | -1074.22552 | -1074.34833 | -1072.66748 | -1073.07056 | 0.06102 | 0.00694 |
| CH ₃ OCCL ₃ | -1533.80436 | -1533.96260 | -1531.68768 | -1532.22325 | 0.05061 | 0.00809 |
| CH ₄ | -40.52401 | -40.53675 | -40.38956 | -40.40530 | 0.04414 | 0.00381 |
| CH ₃ Cl | -500.11255 | -500.15889 | -499.41470 | -499.55671 | 0.03718 | 0.00396 |
| CH ₃ OH | -115.72396 | -115.77290 | -115.41238 | -115.53424 | 0.05040 | 0.00425 |
| CH ₂ ClOH | -575.32655 | -575.40766 | -574.45020 | -574.69874 | 0.04270 | 0.00463 |
| CHCl ₂ OH | -1034.91935 | -1035.03410 | -1033.48138 | -1033.85979 | 0.03341 | 0.00542 |
| CCl ₃ OH | -1494.49745 | -1494.64736 | -1492.50060 | -1493.01115 | 0.02285 | 0.00657 |
| CH ₂ Cl ₂ | -959.69890 | -959.78026 | -958.43904 | -958.71028 | 0.02889 | 0.00452 |
| CHCl ₃ | -1419.28033 | -1419.39742 | -1417.46001 | -1417.86376 | 0.01948 | 0.00541 |
| CCl ₄ | -1878.85426 | -1879.00764 | -1876.47494 | -1877.01439 | 0.00912 | 0.00659 |
| C ₂ H ₆ | -79.83874 | -79.86149 | -79.58553 | -79.62478 | 0.07347 | 0.00442 |
| CH ₃ CH ₂ Cl | -539.43304 | -539.48962 | -538.61712 | -613.90981 | 0.06552 | 0.00497 |
| CH ₃ CHCl ₂ | -999.02189 | -999.11340 | -997.64533 | -997.94327 | 0.05649 | 0.00578 |
| CH ₃ CCl ₃ | -1458.60311 | -1458.73005 | -1456.66767 | -1457.09963 | 0.04655 | 0.00682 |
| C ₂ H ₅ OH | -155.96282 | -155.02100 | -154.53264 | -154.76284 | 0.07867 | 0.00518 |
| H ₂ | -1.17854 | -1.18001 | -1.16514 | -1.16253 | 0.00997 | 0.00331 |
| H ₂ O | -76.41974 | -76.46325 | -76.23164 | -76.33295 | 0.02095 | 0.00378 |
| HCl | -460.80078 | -460.83838 | -460.22447 | -460.34379 | 0.00660 | 0.00330 |
| HOCl | -535.94884 | -536.02111 | -535.19523 | -535.41751 | 0.01286 | 0.00389 |

^{a,b,c} Total energies are in Hartree at 0K; ^a B3LYP/6-31G(d,p), ^b B3LYP/6-311+G(3df,2p), ^c QCISD(T)/6-31G(d,p).

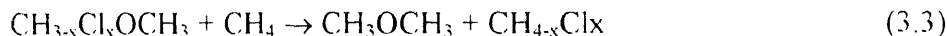
^d CBS-Q enthalpies are in Hartree, which include thermal correction and zero-point energy at 298.15 K. ^e ZPE is in Hartree and scaled by 0.9806. ^f Thermal corrections are in Hartree.

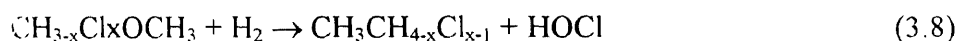
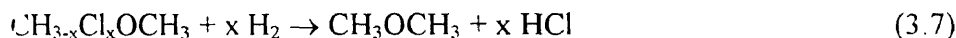
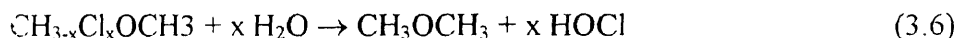
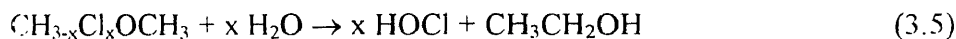
thermal corrections to 298 K from the B3LYP/6-31G(d, p), and the total energies at 298 K from B3LYP/6-311+G(3df+2p), QCISD(T)/6-31G(d, p) and CBS-Q/B3** calculation levels are listed in Table 3.33.

As example; ΔH_f° (CH₂ClOCH₃) is calculated from reaction scheme (1),

$$\Delta H_{rxn(298)} = \Delta H_f^\circ \{ (CH_3OCH_3) + (CH_3Cl) - (CH_2ClOCH_3) - (CH_4) \} \quad (3.2)$$

and the listed known enthalpies of CH₃OCH₃, CH₃Cl and CH₄.





The enthalpies of reaction are obtained by the reaction schemes tabulated in Tables 3.4.

The $\Delta H_f^\circ_{298}$ on the standard compounds in the reaction sets are from literature and are listed in Table 3.5; these are used to determine $\Delta H_f^\circ_{298}$ values in Table 3.6.

The accuracy of the enthalpies of formation obtained theoretically is controlled by several factors; The level of sophistication (method + basis set) applied to calculate the electronic energy, the reliability of the enthalpies of formation of the reference compounds, the uncertainty in the thermal corrections, and the extent to which cancellation of errors occurs in the working chemical reaction used in the evaluation.

3.3.3 Test of Calculation Method: Enthalpy of HOCl

In earlier chapter, we compared the reaction schemes for the enthalpy of formation at 298 K on methyl hypochlorite and observed that working reaction with the reactant of hydrogen and product of hydrochloric acid did not result in accurate $\Delta H_f^\circ_{298}$ of target molecule in CE S-Q//B3** method. A similar trend is observed in the calculation analysis of HOCl as shown in Table 3.7. The recommended $\Delta H_f^\circ_{298}$ for HOCl is -17.8 kcal/mol²⁰

TABLE 3.4. Reaction Enthalpies (in kcal/mol) at 298.15 K^a

| Reaction ^b | ΔH_{rxn} (Theory level ^b) | | | |
|--|---|---------------------------|-------------------------|-----------------|
| | B3LYP /6-31G(d,p) | B3LYP/6-311 +G(3df,2p) | QCISD(t) /6-31G(d,p) | CBS-Q //B3** |
| 1 $\text{CH}_2\text{ClOCH}_3 + \text{CH}_4 \rightarrow \text{CH}_3\text{OCH}_3 + \text{CH}_3\text{Cl}$ | 8.35 | 8.02 | 7.91 | 9.74 |
| $\text{CHCl}_2\text{OCH}_3 + \text{CH}_4 \rightarrow \text{CH}_3\text{OCH}_3 + \text{CH}_2\text{Cl}_2$ | 11.78 | 10.93 | 11.86 | 14.25 |
| $\text{CCl}_3\text{OCH}_3 + \text{CH}_4 \rightarrow \text{CH}_3\text{OCH}_3 + \text{CHCl}_3$ | 10.62 | 9.58 | 11.84 | 13.75 |
| 2 $\text{CH}_2\text{ClOCH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{OCH}_3 + \text{CH}_3\text{CH}_2\text{Cl}$ | 4.36 | 3.90 | 3.49 | 4.75 |
| $\text{CHCl}_2\text{OCH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{OCH}_3 + \text{CH}_3\text{CHCl}_2$ | 5.92 | 4.98 | 4.71 | 5.77 |
| $\text{CCl}_3\text{OCH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{OCH}_3 + \text{CH}_3\text{CCl}_3$ | 4.65 | 3.72 | 3.59 | 3.47 |
| 3 $\text{CH}_2\text{ClOCH}_3 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{CH}_3\text{CH}_2\text{OH}$ | 36.46 | 37.52 | 35.73 | 39.16 |
| $\text{CHCl}_2\text{OCH}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{HOCl} + \text{CH}_3\text{CH}_2\text{OH}$ | 75.67 | 80.13 | 77.66 | 86.97 |
| $\text{CCl}_3\text{OCH}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{HOCl} + \text{CH}_3\text{CH}_2\text{OH}$ | 107.68 | 116.33 | 113.98 | 129.73 |
| 4 $\text{CH}_2\text{ClOCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OCH}_3 + \text{HOCl}$ | 44.90 | 47.62 | 45.79 | 51.69 |
| $\text{CHCl}_2\text{OCH}_3 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OCH}_3 + 2\text{HOCl}$ | 84.11 | 90.23 | 87.71 | 99.50 |
| $\text{CCl}_3\text{OCH}_3 + 3\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OCH}_3 + 3\text{HOCl}$ | 116.13 | 126.43 | 124.04 | 142.26 |
| 5 $\text{CH}_2\text{ClOCH}_3 + \text{H}_2 \rightarrow \text{CH}_3\text{OCH}_3 + \text{HCl}$ | -10.69 | -12.56 | -11.40 | -8.98 |
| $\text{CHCl}_2\text{OCH}_3 + 2\text{H}_2 \rightarrow \text{CH}_3\text{OCH}_3 + 2\text{HCl}$ | -27.07 | -30.13 | -26.66 | -21.85 |
| $\text{CCl}_3\text{OCH}_3 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OCH}_3 + 3\text{HCl}$ | -50.65 | -54.10 | -47.52 | -39.77 |
| 6 $\text{CH}_2\text{ClOCH}_3 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3 + \text{HOCl}$ | 19.00 | 15.95 | 16.88 | 18.86 |
| $\text{CHCl}_2\text{OCH}_3 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{HOCl}$ | 17.66 | 14.83 | 16.50 | 19.73 |
| $\text{CCl}_3\text{OCH}_3 + \text{H}_2 \rightarrow \text{CH}_3\text{CHCl}_2 + \text{HOCl}$ | 12.09 | 9.51 | 12.12 | 15.69 |
| 7 $\text{CH}_2\text{ClOCH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{CH}_2\text{ClOH}$ | -0.80 | -0.22 | -0.37 | 1.53 |
| $\text{CHCl}_2\text{OCH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{CHCl}_2\text{OH}$ | -1.89 | -0.97 | -1.19 | 1.34 |
| $\text{CCl}_3\text{OCH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{CCl}_3\text{OH}$ | -1.51 | -0.43 | -0.67 | 2.17 |

^a Reaction enthalpies include thermal correction and zero-point energy correction at 298K. ^b See Table 3.3 foot note for the explanation of theory levels. Reactions 1, 2 & 7 \equiv isodesmic.

and the calculated enthalpy of formation for hypochlorous acid is -19.2, -17.6, -17.6, -17.6, -17.5, -17.9 kcal/mol in CBS-Q/B3** level by the reaction schemes 1 to 6 in Table 3.7. In Table 3.6, The $\Delta H_f^\circ_{298}$ ($\text{CHCl}_2\text{OCH}_3$, CCl_3OCH_3) by reaction scheme five using the reactant of hydrogen and the product of hydrochloric acid also shows low and inconsistent values. We exclude reaction scheme (5), (3.7) in calculation of $\Delta H_f^\circ_{298}$ for $\text{CHCl}_2\text{OCH}_3$, and CCl_3OCH_3 . The CBS-Q//B3** method shows energies through the

reaction sets that are more consistent and thus it is deemed more accurate. B3LYP/6-31G(d, p), B3LYP/6-311+G(3df, 2p), and QCISD(T)/6-31G(d, p) calculate slightly lower values for HOCl than CBS-Q//B3** values. This same phenomenon is shown in the study of ΔH_f° of chloro-dimethyl ethers.

TABLE 3.5: Enthalpy Data Used in Reactions to Determine ΔH_f° of Target Ethers

| Compound | ΔH_f° ^a | source | uncertainty | source |
|------------------------------------|---------------------------------|--------|-------------|-------------|
| CH ₄ | -17.89 | Ref.32 | ±0.1 | Ref.32 (74) |
| CH ₃ Cl | -19.60 | Ref.33 | ±0.2 | Ref.33 (75) |
| CH ₂ Cl ₂ | -22.83 | Ref.32 | ±0.3 | Ref.32 |
| CHCl ₃ | -24.20 | Ref.33 | ±0.3 | Ref.33 (77) |
| C ₂ H ₆ | -20.24 | Ref.32 | ±0.1 | Ref.32 (74) |
| CH ₃ CH ₂ Cl | -26.84 | Ref.33 | ±0.2 | Ref.33 (74) |
| CH ₃ CHCl ₂ | -31.09 | Ref.33 | ±0.3 | Ref.33 (73) |
| CH ₃ CCl ₃ | -34.01 | Ref.33 | ±0.3 | Ref.33 (76) |
| CH ₃ OH | -48.08 | Ref.34 | ±0.1 | Ref.33 (77) |
| CH ₂ ClOH | -58.00 | Ref.34 | ±0.5 | Ref.34 |
| CHCl ₂ OH | -64.42 | Ref.34 | ±2.3 | Ref.34 |
| CCl ₃ OH | -65.01 | Ref.34 | ±2.3 | Ref.34 |
| CH ₃ CH ₂ OH | -56.12 | Ref.33 | ±0.4 | Ref.33 (77) |
| HCl | -22.06 | Ref.32 | ±0.1 | Ref.32 |
| HOCl | -17.80 | Ref.33 | ±0.5 | Ref.33 |
| HOOH | -32.53 | | | Ref.32 |
| H ₂ O | -57.80 | Ref.34 | ±0.01 | Ref.34 |

^a Units in kcal/mol

TABLE 3.6. Comparison of Enthalpies of Formation^a (in kcal/mol)

| Species | | | | | | | | | |
|--|-------------|-------------|---------------|---------------|---------------|-------------|-------------|--------------------|----------------------|
| Theory ^b | rxn 1 | rxn 2 | rxn 3 | rxn 4 | rxn 5 | rxn 6 | rxn 7 | avg. ^d | recomm. ^e |
| CH₂ClOCH | | | | | | | | | |
| ³ | | | | | | | | | |
| B3lyp6-31 ^f | -54.05 | -54.91 | -52.58 | -48.89 | -55.36 | -57 | -53.11 | -54.50±1.61 | |
| B3lyp6-311 ^g | -53.72 | -54.45 | -53.64 | -51.61 | -53.5 | -53.95 | -53.69 | -53.83±0.34 | |
| Qcisd(t) ^h | -53.61 | -54.04 | -51.85 | -49.78 | -54.66 | -54.88 | -53.54 | -53.76±1.08 | |
| CBS-Q ⁱ | -55.44 | -55.3 | -55.28 | -55.68 | -57.07 | -56.86 | -55.44 | -55.87±0.76 | -55.39±1.17 |
| Overall ^j | -54.21±0.84 | -54.68±0.55 | -53.34±1.49 | | -55.15±1.49 | -55.67±1.50 | -53.95±1.03 | | |
| Max Err | | | | | | | | | |
| Stds. ^k | ±0.36 | ±0.44 | ±0.91 | ±0.63 | ±0.17 | ±0.62 | ±0.78 | ±0.56 ^l | |
| CHCl₂OCH | | | | | | | | | |
| ⁴ | | | | | | | | | |
| B3lyp6-31 ^f | -60.71 | -60.76 | -51.79 | -48.1 | -61.04 | -62.26 | -58.44 | -60.64±1.37 | |
| B3lyp6-311 ^g | -59.86 | -59.82 | -56.25 | -54.22 | -57.98 | -59.43 | -59.36 | -59.29±0.77 | |
| Qcisd(t) ^h | -60.79 | -59.55 | -53.78 | -51.7 | -61.45 | -61.1 | -59.14 | -60.41±1.00 | |
| CBS-Q ⁱ | -63.18 | -60.61 | -63.09 | -63.49 | -66.26 | -64.33 | -61.67 | -62.73±1.30 | -61.79±2.21 |
| Overall ^j | -61.14±1.43 | -60.19±0.59 | | | -60.16±1.90 | -61.78±2.06 | -59.65±1.40 | | |
| Max Err | | | | | | | | | |
| Stds. ^k | ±0.38 | ±0.54 | ±1.42 | ±1.14 | ±0.22 | ±0.68 | ±2.19 | ±1.06 | |
| CCH₂OCCH₃ | | | | | | | | | |
| B3lyp6-31 ^f | -60.92 | -62.41 | -43.8 | -40.12 | -59.52 | -60.98 | -59.41 | -60.65±1.08 | |
| B3lyp6-311 ^g | -59.88 | -61.48 | -52.45 | -50.42 | -56.07 | -58.4 | -60.49 | -59.26±2.25 | |
| Qcisd(t) ^h | -62.14 | -61.35 | -50.1 | -48.03 | -62.65 | -61.01 | -60.25 | -61.48±0.73 | |
| CBS-Q ⁱ | -64.05 | -61.23 | -65.85 | -66.25 | -70.4 | -64.58 | -63.09 | -64.18±1.63 | -62.79±3.00 |
| Overall ^j | -61.75±1.79 | -61.62±0.54 | | | -59.41±1.90 | -61.24±2.54 | -60.81±1.59 | | |
| Max Err | | | | | | | | | |
| Stds. ^k | ±0.50 | ±0.57 | ±1.93 | ±1.65 | ±0.27 | ±0.80 | ±3.05 | ±1.42 | |

^a Enthalpies of formation are calculated by seven different reactions in Table 3.3. ^b See Table 3.2 footnote for the explanation of theory levels. ^c See the reactions in Table 3.3. Reaction 1, 2, and 7 are isodesmic. ^d Average values do not include bold italic data.

^e average of values in CBS-Q level by isodesmic reaction 1, 2, 7 sets with statistical analysis of conformers; the uncertainty is the addition of CBS-Q's standard deviation and maximum error standard deviation of isodesmic reaction 1, 2, 7 sets. ^f B3LYP/6-31G(d,p). ^g B3LYP/6-311+G(3df,2p). ^h QCISD(T)/6-31G(d,p) and ⁱ CBS-Q//B3** method. ^j Average of overall theory's enthalpies of formation; Average values do not include bold italic data. ^k The maximum error from uncertainty in values of the 3 standard molecules of reaction scheme; values from Table 3.5.

TABLE 3.7. Enthalpies of formation^a (in kcal/mol) at 298.15 K for HOCl

| Reaction Schemes | $\Delta H_f^{\circ}_{298}$ (Theory level ^b) | | | |
|--|---|---------------------------|-------------------------|-----------------|
| | B3LYP /6-31G(d,p) | B3LYP/6-311 +G(3df,2p) | QCISD(t) /6-31G(d,p) | CBS-Q //B3** |
| 1 HOCl + H ₂ → H ₂ O + HCl | -24.27 | -19.69 | -22.68 | -19.69 |
| 2 HOCl + CH ₄ → CH ₃ Cl + H ₂ O | -22.95 | -19.90 | -21.63 | -17.56 |
| 3 HOCl + CH ₄ → CH ₃ OH + HCl | -19.59 | -18.64 | -19.49 | -17.49 |
| 4 HOCl + CH ₃ CH ₃ → CH ₃ CH ₂ OH + HCl | -19.85 | -19.38 | -19.65 | -17.61 |
| 5 HOCl + CH ₃ CH ₃ → CH ₃ CH ₂ Cl + H ₂ O | -23.85 | -20.68 | -22.10 | -17.46 |
| 6 HOCl + H ₂ O → HOOH + HCl | -11.29 | -17.24 | -13.67 | -17.87 |

^a Reaction enthalpies include thermal correction and zero-point energy correction at 298K. ^b See foot notes of Table 3.3 for the explanation of theory levels. ^c B3LYP/6-31G(d,p), ^d B3LYP/6-311+G(3df,2p), ^e QCISD(T)/6-31G(d,p) and ^f CBS-Q//B3** method.

3.3.4 Analysis of Data Trends by Isodesmic versus Non isodesmic Reaction

Reaction schemes (1, 2, 7) are isodesmic reactions, which conserve bond type on both sides of the reaction and in principle should show more consistent enthalpy values over the calculation methods, resulting from a more optimum cancellation of error(s). Reaction 7 also includes group balance; but it may have errors due to the uncertainty in $\Delta H_f^{\circ}(298)$ of the di and tri chloromethanols. The isodesmic reactions (1, 2, 7) show good, uniform results for 1 chloro-methyl ether and 1,1 dichloro-methyl ether; while the non isodesmic reactions show significantly higher error. The average error values over the 3 isodesmic reactions are ± 0.8 , 1.1 and 1.3 kcal/mol for CH₂ClOCH₃, CHCl₂OCH₃, and CCl₃OCH₃, respectively. For 1,1,1 trichloro-methyl ether, only Rxn 2 shows good consistency through all calculation levels where the average value over the 4 calculation levels is 2.5 kcal/mole above the CBS-Q results averaged over all reactions. Isodesmic

reactions 1 and 7 also show good consistency among the non – composite calculations methods. Non isodesmic reactions 3 and 4, which use H₂O and HOCl are completely unacceptable for the non composite calculation methods for the di and tri chloro ethers.

3.3.5 Recommended values

The $\Delta H_f^\circ_{298}$ of CH₂ClOCH₃, CHCl₂OCH₃, and CCl₃OCH₃ are -55.4 kcal/mol, -61.8 kcal/mol, -62.8 kcal/mol, respectively before statistical analysis of conformers. These enthalpies are the average value of $\Delta H_f^\circ_{298}$ by the 3 isodesmic reactions at the CBS-Q/B3** calculation level for all three chloro dimethyl ethers. The two conformers of CH₂ClOCH₃, and CHCl₂OCH₃ are illustrated in Figures 3.1 and 3.3 show differences in enthalpies of 5.1 and 2.6 kcal/mole respectively. In our analysis of energy by torsion angle, the most stable conformer in Table 3.9 is the optimized geometry when Cl (4) and H (8) or Cl(5) and H(7) is almost parallel because of the lone electron pair of oxygen; the dihedral angle, D(3,2,1,6) among C-O-C-H or C-O-C-Cl and D(7,3,2,1) among H-C-O-C is close to 180 degree.

The $\Delta H_f^\circ_{298}$ considering statistical distribution of rotational conformers of CH₂ClOCH₃, CHCl₂OCH₃, and CCl₃OCH₃ are -55.4±1 kcal/mol, -61.8 ± 2 kcal/mol, -62.8 ± 3.0 kcal/mol, respectively. The uncertainty in Table 3.6 is the standard deviation of the reaction sets plus the average of maximum error from standard compounds in the reaction schemes.

3.3.6 Comparison to Semiempirical (MOPAC) data

The AM1^{56,57} and PM3⁵⁸ methods in the MOPAC 6.0 package⁵⁵ are used to perform the semiempirical MO calculations. The enthalpy of formation of three title molecules are calculated with AM1 and PM3 parameters and compared to those obtained from the density functional and *ab initio* studies. Direct results from the MOPAC calculations, as well as results from reaction analysis with MOPAC data are presented. The results, listed

TABLE 3.8. Comparison of Enthalpies of Formation calculated by semiempirical methods (in kcal/mol)

| Species | | rxn 1 ^a | rxn 2 | rxn 3 | rxn 4 | rxn 5 | rxn 6 | rxn 7 | output ^b | CBS- |
|--|---------------------|--------------------|--------|--------|---------|--------|--------|--------|---------------------|-------|
| Theory | Q//B** ^c | | | | | | | | | |
| CH₂ClOCH₃ | | | | | | | | | | |
| PM3 | -49.77 | -52.36 | -30.58 | -28.86 | -64.72 | -53.02 | -53.29 | -54.05 | -55.39 | ±1.17 |
| AM1 | -43.49 | -53.86 | -50.51 | -49.43 | -54.58 | -65.13 | -53.71 | -61.12 | | |
| CHCl₂OCH₃ | | | | | | | | | | |
| PM3 | -55.92 | -57.57 | -15.10 | -13.38 | -85.08 | -61.07 | -62.55 | -59.43 | -61.79 | ±2.21 |
| AM1 | -42.84 | -52.13 | -51.01 | -49.93 | -60.23 | -70.11 | -64.18 | -64.15 | | |
| CCl₃OCH₃ | | | | | | | | | | |
| PM3 | -57.21 | -58.76 | 2.11 | 3.83 | -103.72 | -52.32 | -59.37 | -63.08 | -62.79 | ±3.00 |
| AM1 | -36.84 | -50.02 | -44.28 | -43.19 | -58.65 | -57.13 | -60.48 | -59.03 | | |

^a Enthalpy of formation at 298K calculated by reaction scheme.^b Enthalpy of formation at 298K calculated by MOPAC program directly ^c Average values in CBS-Q calculations by all reaction schemes except reaction 5 with statistical analysis of conformers

in Table 3.8, indicate that the PM3 method, without use of working reactions appears to be a preferred alternative for the calculation of enthalpies of formation for chloro-dimethyl ethers among these two semiempirical methods. Use of MOPAC results obtained from isodesmic or other working reactions is less satisfactory.

Table 3.9. Total Energy^a (Hartrees) of Molecules by Torsion angle.^b

| Angl ^e | CH ₂ Cl- OCH ₃ ^c | CH ₂ ClO- CH ₃ ^d | CHCl ₂ - OCH ₃ ^c | CHCl ₂ O- CH ₃ ^d | CCl ₃ - OCH ₃ ^c | CCl ₃ O- CH ₃ ^d |
|-------------------|--|--|--|--|---|---|
| 0 | -614.63432 | -614.63432 | -1074.2255 | -1074.2255 | -1074.2255 | -1533.8044 |
| 15 | -614.63306 | -614.63393 | -1074.2244 | -1074.2253 | -1074.2253 | -1533.8034 |
| 30 | -614.62977 | -614.63292 | -1074.2214 | -1074.2246 | -1074.2246 | -1533.8008 |
| 45 | -614.62586 | -614.63186 | -1074.2178 | -1074.2238 | -1074.2238 | -1533.7984 |
| 60 | -614.62294 | -614.63141 | -1074.2152 | -1074.2235 | -1074.2235 | -1533.7975 |
| 75 | -614.62213 | -614.63189 | -1074.2144 | -1074.2238 | -1074.2238 | -1533.7983 |
| 90 | -614.62373 | -614.63295 | -1074.2155 | -1074.2246 | -1074.2246 | -1533.8006 |
| 105 | -614.62714 | -614.63393 | -1074.2179 | -1074.2253 | -1074.2253 | -1533.8032 |
| 120 | -614.63104 | -614.63432 | -1074.2203 | -1074.2255 | -1074.2255 | -1533.8044 |
| 135 | -614.63376 | -614.63389 | -1074.2213 | -1074.2252 | -1074.2252 | -1533.8035 |
| 150 | -614.63418 | -614.63286 | -1074.2207 | -1074.2245 | -1074.2245 | -1533.801 |
| 165 | -614.63245 | -614.63181 | -1074.2193 | -1074.2237 | -1074.2237 | -1533.7986 |
| 180 | -614.62979 | -614.63142 | -1074.2187 | -1074.2235 | -1074.2235 | -1533.7975 |
| 195 | -614.62744 | -614.63196 | -1074.2191 | -1074.2239 | -1074.2239 | -1533.7982 |
| 210 | -614.62614 | -614.63303 | -1074.2204 | -1074.2247 | -1074.2247 | -1533.8005 |
| 225 | -614.62586 | -614.63398 | -1074.2213 | -1074.2253 | -1074.2253 | -1533.8032 |
| 240 | -614.62609 | -614.63431 | -1074.2206 | -1074.2255 | -1074.2255 | -1533.8044 |
| 255 | -614.6262 | -614.63385 | -1074.2184 | -1074.2252 | -1074.2252 | -1533.8033 |
| 270 | -614.626 | -614.63284 | -1074.2157 | -1074.2245 | -1074.2245 | -1533.8007 |
| 285 | -614.62587 | -614.63183 | -1074.2144 | -1074.2237 | -1074.2237 | -1533.7983 |
| 300 | -614.62645 | -614.63141 | -1074.2151 | -1074.2235 | -1074.2235 | -1533.7975 |
| 315 | -614.62813 | -614.63185 | -1074.2178 | -1074.2238 | -1074.2238 | -1533.7984 |
| 330 | -614.63071 | -614.63287 | -1074.2213 | -1074.2246 | -1074.2246 | -1533.8008 |
| 345 | -614.63321 | -614.63388 | -1074.2243 | -1074.2253 | -1074.2253 | -1533.8033 |
| 360 | -614.63432 | -614.63432 | -1074.2255 | -1074.2255 | -1074.2255 | -1533.8044 |

^a The unit of total energies is Hartree in B3LYP/6-31G(d,p) theory. ^b The torsion angle of D(4123) or D(8321)^d in Table 2

3.3.7 Rotational Barriers

Potential barriers for the two internal rotations of CH₂ClOCH₃, CHCl₂OCH₃, and CCl₃OCH₃ are calculated at the B3LYP/6-31G(d, p) level. Potential energy as function of dihedral angle is determined by varying the torsion angle at 15° intervals and allowing the remaining molecular structural parameters to be optimized. The geometry and harmonic vibrational frequencies are calculated for all rotational conformers at

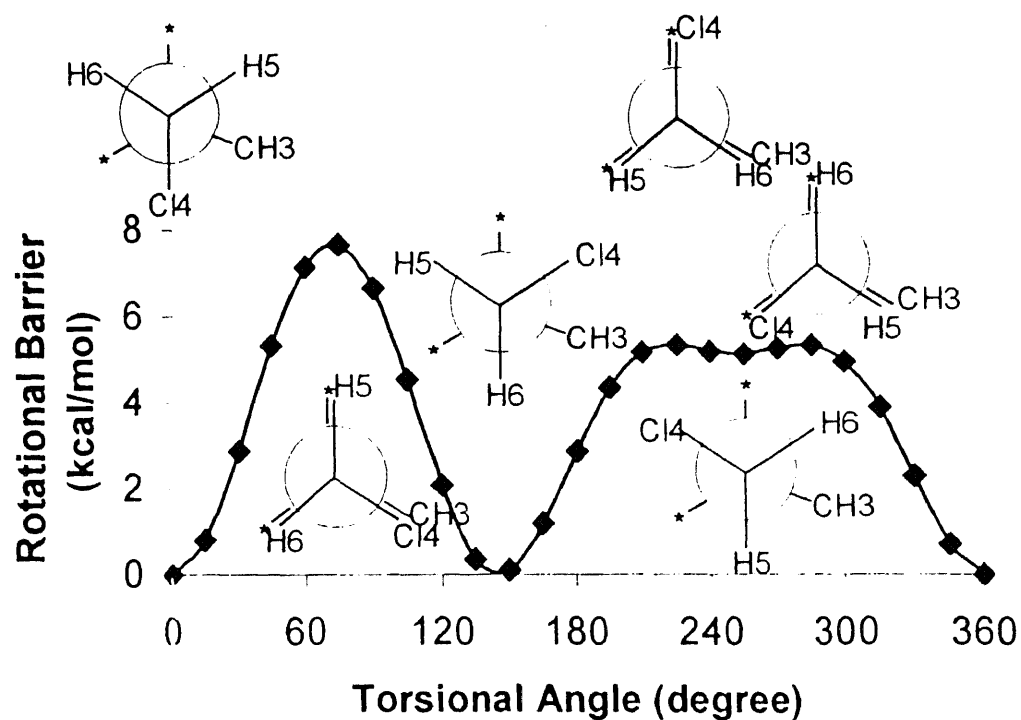


Figure 3.1. Potential energy for internal rotation about $\text{CH}_2\text{Cl}-\text{OCH}_3$ bond by torsional angle.

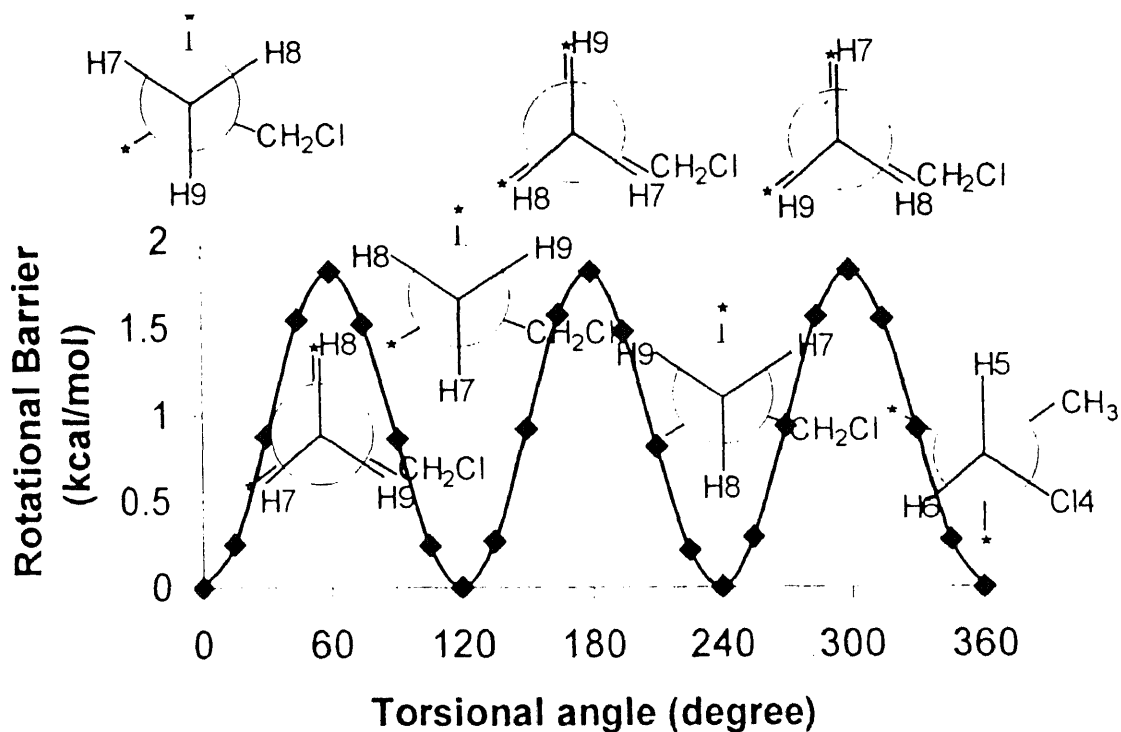


Figure 3.2. Potential energy for internal rotation about $\text{CH}_2\text{ClO}-\text{CH}_3$ bond by torsional angle.

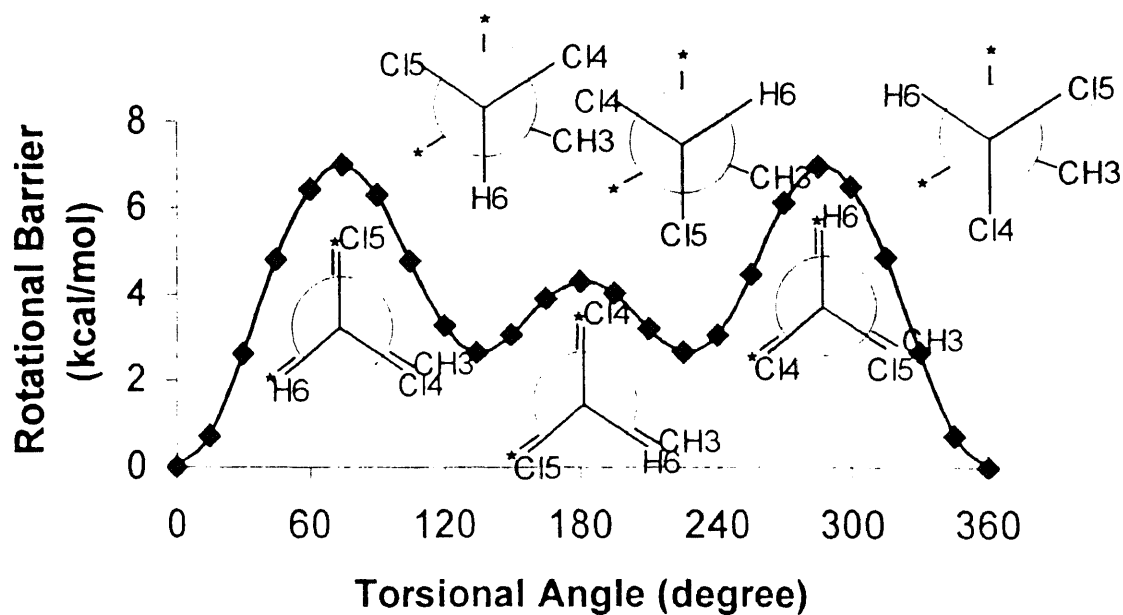


Figure 3.3 Potential energy for internal rotation about $\text{CHCl}_2\text{-OCH}_3$ bond by torsional angle.

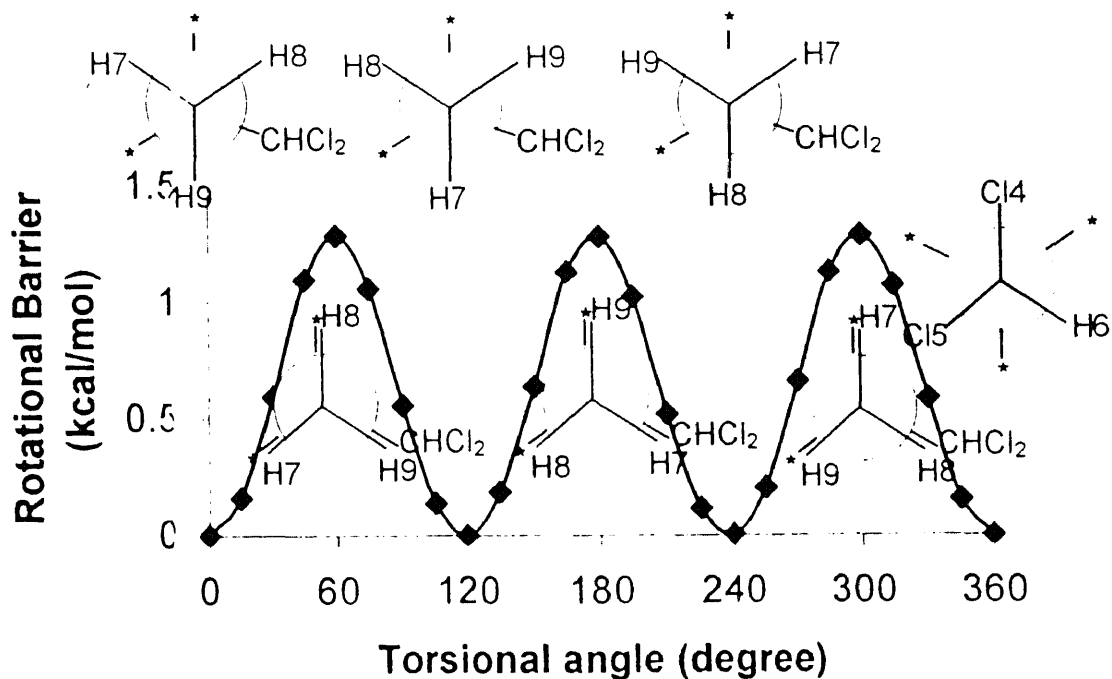


Figure 3.4 Potential energy for internal rotation about $\text{CHCl}_2\text{-O-CH}_3$ bond by torsional angle.

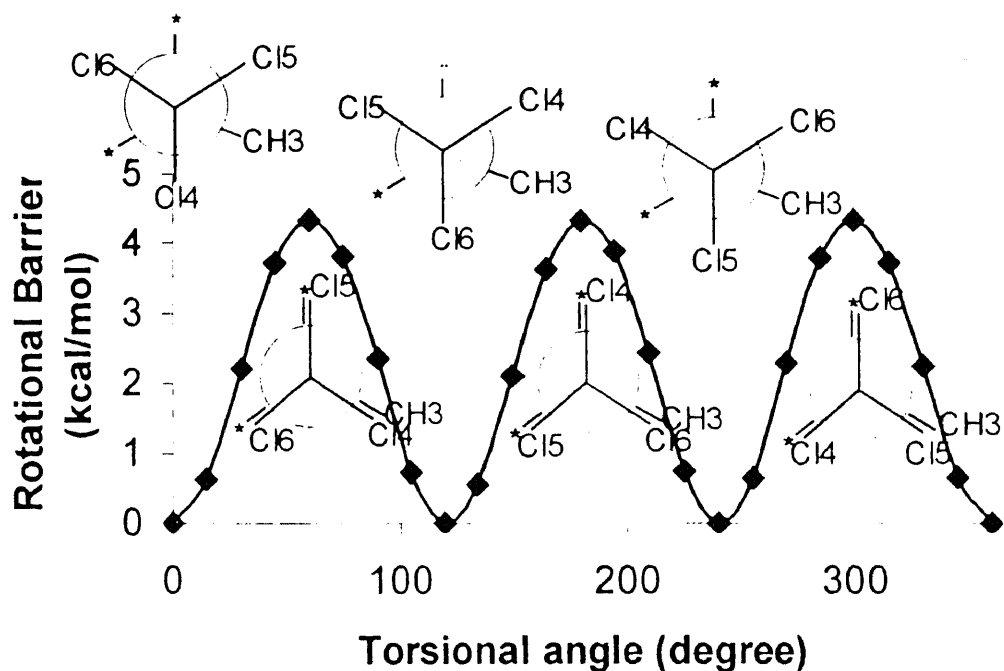


Figure 3.5. Potential energy for internal rotation about $\text{CCl}_3\text{-OCH}_3$ bond by torsional angle.

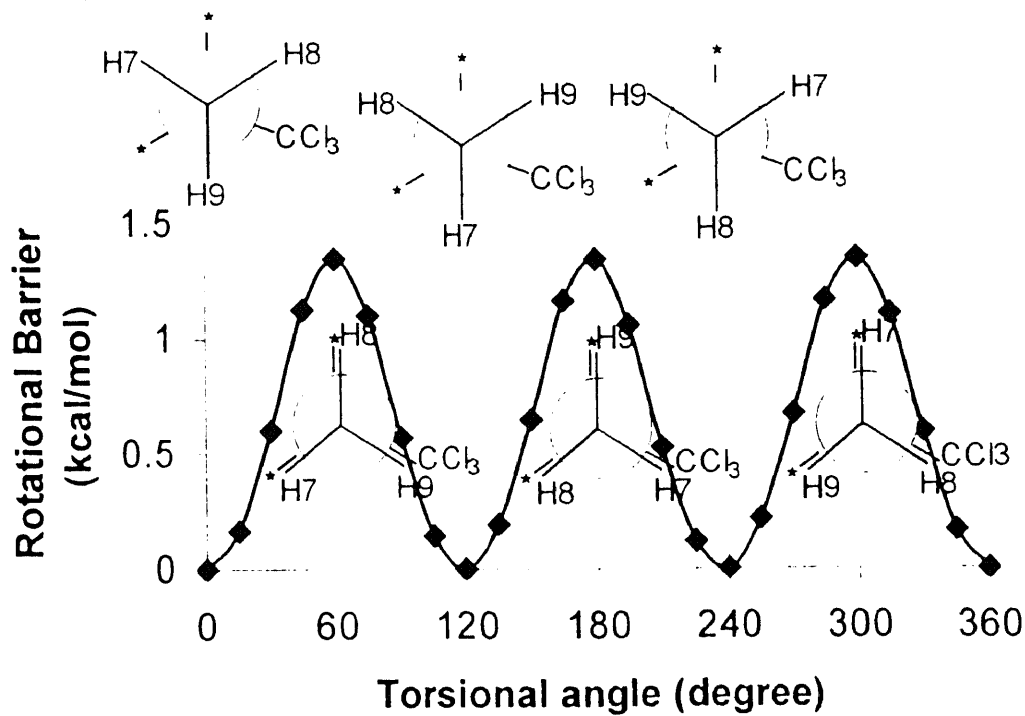


Figure 3.6. Potential energy for internal rotation about $\text{CCl}_3\text{O-CH}_3$ bond by torsional angle.

Table 3.10. $\Delta H_f^\circ_{298}$ for Rotational Conformers, Relative, Overall $\Delta H_f^\circ_{298}$ Values and Entropy correction^b

| Compound | energy(kcal/mol) ^c | relative (%) ^f | final value(kcal/mol) ^g |
|---|-------------------------------|---------------------------|------------------------------------|
| CH ₂ ClOCH ₃ (1) ^a | -55.39 | 99.99 | |
| CH ₂ ClOCH ₃ (2) ^b | -50.30 | 0.01 | -55.39±1.17 |
| CHCl ₂ OCH ₃ (1) ^a | -61.82 | 98.84 | |
| CHCl ₂ OCH ₃ (2) ^b | -60.10 | 1.16 | -61.79±2.21 |
| CCl ₃ OCH ₃ | -62.79 | 100.00 | -62.79±3.00 |

^a CH₃-H anti staggered, and ^b CH₃-Cl anti staggered conformer in Figure 1. ^c CH₂Cl-H anti staggered, and ^d CH₂Cl-Cl anti staggered conformer in Figure 3. ^e Energy of conformer = overall value in Table 6 + energy barrier, Energy barrier = energy of conformer- energy of most stable conformer ^f Relative = conformer fraction ÷ total fraction; Conformer fraction = $e^{(-B/RT)}$, B = Energy difference, R = 1.987 (cal/mol·K), T = 298K. ^g Final value = $\Sigma(\text{Energy} \times \text{relative fraction})$; Uncertainty is the value in foot note e in Table 6. ^h Entropy correction for CHCl₂OCH₃ = $-R\{0.9884 \cdot \ln(0.9884) + 0.0116 \cdot \ln(0.0116)\} = 0.13 \text{ cal/mol·K}$.

TABLE 3.11 Coefficients^a (kcal/mol) of Truncated Fourier Series Representation Expansion for Internal Rotation Potentials

| Rotors | a0 | a1 | a2 | a3 | b1 | b2 | b3 |
|-------------------------------------|-------|--------|--------|--------|--------|--------|--------|
| CH ₂ Cl-OCH ₃ | 3.692 | -0.089 | -2.254 | -1.288 | -0.265 | 1.578 | -0.981 |
| CH ₂ ClO-CH ₃ | 0.896 | 0.010 | -0.006 | -0.908 | -0.006 | -0.019 | 0.024 |
| CHCl ₂ -OCH ₃ | 3.971 | -0.298 | -1.996 | -1.821 | 0.034 | -0.021 | -0.061 |
| CHCl ₂ O-CH ₃ | 0.620 | 0.005 | -0.007 | -0.642 | -0.007 | -0.015 | 0.039 |
| CCl ₃ -OCH ₃ | 2.218 | -0.011 | -0.026 | -2.178 | -0.021 | 0.043 | -0.070 |
| CCl ₃ O-CH ₃ | 0.641 | 0.006 | -0.008 | -0.670 | -0.007 | -0.017 | 0.040 |

^a Unit in kcal/mol. Values of rotational barriers computed using the B3LYP/6-31G(d,p) theory. Coefficients are calculated as follows. $V(\theta) = a_0 + a_1 \cos(\theta) + a_2 \cos(2\theta) + a_3 \cos(3\theta) + b_1 \sin(\theta) + b_2 \sin(2\theta) + b_3 \sin(3\theta)$.

B3LYP/6-31G(d, p) level. The values of the coefficients of the Fourier expansion, a_i and b_i ($i=1,2,3$) in equation 1 are listed in Table 3.11.

Figure 3.1 shows calculated rotational barriers of CH₂Cl-OCH₃ versus torsion angle. The double asterisks, * * signify a lone electron pair on oxygen. 1 chloro-dimethyl ether (CH₂Cl-OCH₃) has two conformers. The CH₃-Cl anti staggered is 5.09 kcal/mol higher in energy than the more stable CH₃-H anti staggered conformer because of the Cl interaction with the oxygen atom's non bonding electrons. The CH₃-Cl eclipsed

rotational barrier is 7.65 kcal/mol and the $\text{CH}_3\text{-H}$ eclipsed rotational barrier is 5.30 kcal/mol. The $\text{CH}_3\text{-Cl}$ eclipsed barrier is 2.35 kcal/mol higher in energy than the $\text{CH}_3\text{-H}$ eclipsed barrier. The interaction of chlorine and a methyl group appears to exhibit more repulsion or strain compared to that of a methyl interaction with hydrogen.

Calculated rotational barriers and conformer energies in 1,1 dichloro-dimethyl ether ($\text{CHCl}_2\text{-OCH}_3$) are shown in figure 3.3. The $\text{CH}_3\text{-H}$ staggered conformer has 2.63 kcal/mol lower energy than the $\text{CH}_3\text{-Cl}$ staggered conformer due to the interaction between an electron lone pair of oxygen and chlorine. The $\text{CH}_3\text{-Cl}$ eclipsed structure represents a rotational barrier of 7.00 kcal/mol and the $\text{CH}_3\text{-H}$ eclipsed structure represents a barrier of 4.30 kcal/mol. The $\text{CH}_3\text{-Cl}$ eclipsed barrier shows higher energy than $\text{CH}_3\text{-H}$ eclipsed because the interaction of methyl group and chlorine has more repulsion and strain compared to that of methyl group and hydrogen.

The symmetric rotational barrier of 1,1,1 trichloro-dimethyl ether ($\text{CCl}_3\text{-OCH}_3$) is illustrated in Figure 3.3. The $\text{CH}_3\text{-Cl}$ eclipsed structure shows a rotational barrier of 4.33 kcal/mol above the $\text{CH}_3\text{-Cl}$ staggered conformer.

The calculated symmetric rotational barriers for methyl (CH_3) rotations in the chlorinated dimethyl ethers are shown in Figures 3.2, 3.4, 3. 6. The calculations show that the hydrogen and chloromethyl ($\text{H-CH}_2\text{-Cl}$) staggered structure has a rotational barrier of 1.82 kcal/mol in $\text{CH}_2\text{ClO-CH}_3$, 1.28 kcal/mol in $\text{CHCl}_2\text{O-CH}_3$, and 1.34kcal/mol in $\text{CCl}_3\text{O-CH}_3$.

TABLE 3.12: Ideal Gas Phase Thermodynamic Properties^a

| Species | | ΔH_f° ^b ₂₉₈ | S° ₂₉₈ ^c | $C_{p,300}$ ^c | $C_{p,400}$ | $C_{p,500}$ | $C_{p,600}$ | $C_{p,800}$ | $C_{p,1000}$ | $C_{p,1500}$ |
|------------------------------------|--------------------------|--|---------------------------------------|--------------------------|-------------|-------------|-------------|-------------|--------------|--------------|
| CH ₂ ClOCH ₃ | TVR ^d | | 64.89 | 13.90 | 17.54 | 21.02 | 24.07 | 28.91 | 32.48 | 38.01 |
| (3) ^l | Internal(1) _e | | 4.93 | 2.15 | 2.33 | 2.48 | 2.52 | 2.36 | 2.02 | 1.26 |
| | Internal(2) _f | | 4.65 | 1.93 | 1.73 | 1.55 | 1.42 | 1.26 | 1.18 | 1.08 |
| | Total | -55.39 | 74.47 | 17.99 | 21.60 | 25.05 | 28.02 | 32.53 | 35.68 | 40.35 |
| | Group add. _k | -54.65 | 73.96 | 18.23 | 22.16 | 25.59 | 28.48 | 33.02 | 36.16 | |
| CHCl ₂ OCH ₃ | TVR | | 71.23 | 17.50 | 21.25 | 24.58 | 27.36 | 31.61 | 34.66 | 39.29 |
| (3) | Internal(1) _g | | 3.64 | 3.03 | 3.85 | 4.09 | 3.89 | 3.04 | 2.27 | 1.17 |
| | Internal(2) _h | | 4.65 | 1.93 | 1.73 | 1.55 | 1.42 | 1.26 | 1.18 | 1.08 |
| | Total | -61.79 | 79.65 | 22.47 | 26.83 | 30.23 | 32.67 | 35.92 | 38.10 | 41.54 |
| | Group add. | -61.06 | 79.29 | 22.33 | 27.04 | 30.53 | 33.03 | 36.48 | 38.71 | |
| CCl ₃ OCH ₃ | TVR | | 73.78 | 21.78 | 25.48 | 28.50 | 30.93 | 34.51 | 37.01 | 40.71 |
| (18) | Internal(1) ⁱ | | 5.93 | 2.22 | 2.27 | 2.20 | 2.05 | 1.66 | 1.30 | 0.73 |
| | Internal(2) ^j | | 5.31 | 1.73 | 1.50 | 1.35 | 1.26 | 1.15 | 1.10 | 1.04 |
| | Total | -62.79 | 85.02 | 25.72 | 29.25 | 32.06 | 34.24 | 37.32 | 39.41 | 42.48 |
| | Group add. | -61.85 | 84.45 | 25.83 | 29.62 | 32.40 | 34.55 | 37.79 | 39.92 | |

^a Thermodynamic properties are referred to standard state of an ideal gas of pure enantiomer at 1atm. One torsion frequency is excluded in the calculation of entropies and heat capacities; instead, the contributions from hindered rotations about the C-O bond are calculated. ^b ΔH_f° is the average value of CBS-Q level considering the statistical contribution of rotational conformers in kcal/mol. (see footnote c in Table 6 and final value in Table 8) ^c Units in cal/mol K; mixing of -0.13 cal/mol-K for entropy correction of CHCl₂OCH₃ is included (see footnote h in Table 10). ^d The sum of contributions from translations, external rotations, and vibrations. ^e Contributions from internal rotation about C-O bond of CH₂Cl-OCH₃. ^f CH₂ClO-CH₃. ^g CHCl₂-OCH₃. ^h CHCl₂O-CH₃. ⁱ CCl₃-OCH₃ and ^j CCl₂O-CH₃. ^k Group additivity; C/H3/O and O/C2 come from ref.36; C/C1/H2/O, C/C12/H1/O and C/C13/O comes from the average of chloro-methanols (ref.37) and chloro-dimethyl ethers (this work). ^l Symmetry number is taken into account for S° ₂₉₈.

3.3.8 Entropy, S° ₂₉₈ and Heat Capacity, $C_p(T)$ from 300 to 1500 K

S° ₂₉₈ and $C_p(T)$ calculations use the B3LYP/6-31G(d, p) determined geometry and frequencies with values summarized in Table 3.12. TVR represents the sum of the contributions from translations, external rotations and vibrations for S° ₂₉₈ and $C_p(T)$. The torsion frequency corresponding to the internal rotor is not included in TVR. Instead, a more exact contribution from the hindered rotation is calculated and listed under I.R. in Table 3.12. I.R. represents the contributions from internal rotation about C-O bond for

S_{298}° and $C_p(T)$'s. There are 2 rotors in the chloro-dimethyl ethers and we calculate their contribution individually in Table 3.12.

3.3.9 Group Values and Group Additivity Estimation

The group values for thermodynamic properties of C/H3/O and O/C2 are from existing literature.^{20,59} In the present work, we improve the group value for C/Cl/H2/O, C/Cl2/H/O, C/Cl3/O. Enthalpy of formation ($\Delta H_f^{\circ}_{298}$) and heat capacities, $C_p(T)$ of the O/C/H group are calculated on the basis of the equation 3.9 for each of the thermodynamic properties.

$$(\text{CH}_2\text{ClOCH}_3) = (\text{C/H}_3/\text{O}) + (\text{O/C/2}) + (\text{C/Cl/H}_2/\text{O}) \quad (3.10)$$

Values for C/Cl/H2/O, C/Cl2/H/O and C/Cl3/O are taken from recent work in this laboratory on chlorinated methanols³⁸ and this study. The properties of the C/Cl/H2/O, C/Cl2/H/O and C/Cl3/O groups for example, are derived from chloro-methanol (CH_2ClOH), 1,1-dichloro-methanol (CHCl_2OH), and 1,1,1-trichloro-methanol (CCl_3OH), respectively and from chloro-dimethyl ether ($\text{CH}_2\text{ClOCH}_3$), 1,1-dichloro-dimethyl ether ($\text{CHCl}_2\text{OCH}_3$), and 1,1,1-trichloro-dimethyl ether (CCl_3OCH_3), respectively. Group values for of C/Cl/H2/O, C/Cl2/H/O, C/Cl3/O are -20.9, -27.3, -28.1 kcal/mol for enthalpy of formation at 298 K. The group additivity determined $\Delta H_f^{\circ}_{298}$ values for $\text{CH}_2\text{ClOCH}_3$ of -54.7, $\text{CHCl}_2\text{OCH}_3$ of -61.1, and CCl_3OCH_3 of -61.9 kcal/mol. These enthalpy values are slightly higher than our recommended CBS-Q//B3** values in Table 3.12. The reason is that the oxygenated chlorocarbon groups are an average of values from alcohols and ethers. The recommended $\Delta H_f^{\circ}_{298}$ values

determined in this study for $\text{CH}_2\text{ClOCH}_3$, $\text{CHCl}_2\text{OCH}_3$, and CCl_3OCH_3 are -55.4 ± 1 , -61.8 ± 2 , and -62.8 ± 3 kcal/mol.

The entropy, S°_{298} of the C/Cl/H₂/O is calculated on the basis of the equation 3.10.

$$(\text{CHCl}_2\text{OCH}_3) = (\text{C/H}_3/\text{O}) + (\text{O/C/2}) + (\text{C/Cl}_2/\text{H/O}) - R \ln(\sigma) \quad (3.11)$$

$R = 1.987$ cal/mol K, and σ is symmetry number, which is 3 for $\text{CH}_2\text{ClOCH}_3$. Entropy of mixing = $-R \sum \{(n_i) \times \ln(n_i)\}$; where n_i is fraction of conformer i . Mixing entropy is included in the (C/Cl₂/H/O) group, as it is in hydrocarbon and other molecular groups. For $\text{CHCl}_2\text{OCH}_3$, the mixing term for entropy is: $-R \{0.9884 \times \ln(0.9884) + 0.1161 \times \ln(0.1161)\} = 0.13$ cal/mol K in Table 3.10. Thermodynamic properties of the C/Cl/H₂/O, C/Cl₂/H/O, and C/Cl₃/O groups are calculated using two sets of thermodynamic property data; where the two data from chloro-methanols and chloro-dimethyl ethers are listed in Table 3.13-a. Table 3.13-b lists the average of group values in Table 3.13-a. Group values of C/Cl/H₂/O, C/Cl₂/H/O, C/Cl₃/O are 37.1, 42.4, 51.1 cal/mol·K for entropy at 298 K and 8.6, 12.7, 16.2 cal/mol·K for heat capacity at 300 K, respectively in Table 3.13-b which are values we recommend. Table 3.14 lists groups for use in oxychlorocarbon by our modified group additivity method.

There are no published data for entropy and heat capacity values of $\text{CH}_2\text{ClOCH}_3$, $\text{CHCl}_2\text{OCH}_3$ or CCl_3OCH_3 . We calculate and compare data with the group additivity. The group additivity shows good agreement for the entropy and heat capacity for all chloro-dimethyl ethers. The entropy at 298 K of $\text{CH}_2\text{ClOCH}_3$, $\text{CHCl}_2\text{OCH}_3$, and CCl_3OCH_3 is 74.5, 79.7, 85.0 cal/mol·K in this work and 74.0, 79.3, 84.5 cal/mol by the group additivity, respectively. The heat capacity of $\text{CH}_2\text{ClOCH}_3$, $\text{CHCl}_2\text{OCH}_3$,

TABLE 3.13-a. Thermodynamic Properties of C/Cl_x/H_{3-x}/O from chloro-methanol and from this work

| Groups | H _f [°] ₂₉₈ ^a | S [°] ₂₉₈ ^b | C _{p300} ^b | C _{p400} | C _{p500} | C _{p600} | C _{p800} | C _{p1000} | C _{p1500} | Ref |
|----------------------------------|---|--|--------------------------------|-------------------|-------------------|-------------------|-------------------|--------------------|--------------------|-----------------|
| C/Cl/H ₂ /O | -20.10 | 36.55 | 8.88 | 11.18 | 13.02 | 14.35 | 16.09 | 17.27 | 19.19 | 37 ^c |
| C/Cl/H ₂ /O | -21.59 | 37.56 | 8.40 | 10.06 | 11.95 | 13.43 | 15.10 | 16.31 | | this work |
| C/Cl ₂ /H/O | -26.52 | 42.03 | 12.61 | 15.71 | 17.73 | 18.80 | 19.62 | 19.94 | 20.60 | 37 |
| C/Cl ₂ /H/O | -27.99 | 42.74 | 12.88 | 15.29 | 17.13 | 18.08 | 18.49 | 18.73 | | this work |
| C/Cl ₃ /O | -27.11 | 50.54 | 16.34 | 18.45 | 19.65 | 20.28 | 20.82 | 21.06 | 21.46 | 37 |
| C/Cl ₃ /O | -28.99 | 51.67 | 16.13 | 17.71 | 18.96 | 19.65 | 19.89 | 20.04 | | this work |
| C/H ₃ /O ^d | -10.00 | 30.41 | 6.19 | 7.84 | 9.40 | 10.79 | 13.03 | 14.77 | 17.58 | 36 |
| O/C2 ^e | -23.80 | 8.68 | 3.40 | 3.70 | 3.70 | 3.80 | 4.40 | 4.60 | | 36 |

^a Units in kcal/mol. ^b Units in cal/mol-K. ^c The group value from chloro-methanols (reference. 37). ^{d, e} Oxy-hydrocarbon groups of Cohen and Benson used in GA.

TABLE 3.13-b: Averaged Thermodynamic Properties of Oxy-Chlorocarbon Groups

| Groups | H _f [°] ₂₉₈ ^a | S [°] ₂₉₈ ^b | C _{p300} ^b | C _{p400} | C _{p500} | C _{p600} | C _{p800} | C _{p1000} | C _{p1500} | Ref |
|------------------------|---|--|--------------------------------|-------------------|-------------------|-------------------|-------------------|--------------------|--------------------|-----------|
| C/Cl/H ₂ /O | 20.85 | 37.05 | 8.64 | 10.62 | 12.49 | 13.89 | 15.59 | 16.79 | 19.19 | this work |
| C/Cl ₂ /H/O | 27.26 | 42.38 | 12.74 | 15.50 | 17.43 | 18.44 | 19.05 | 19.34 | 20.60 | this work |
| C/Cl ₃ /O | 28.05 | 51.11 | 16.24 | 18.08 | 19.30 | 19.96 | 20.36 | 20.55 | 21.46 | this work |

^a Units in kcal/mol ^b Units in cal/mol-K. ^c The average of the values in Table 13-a.

TABLE 3.14: Group for use in Group Additivity of Chloro-ethers

| Compounds | CH ₂ ClOCH ₃ | CHCl ₂ OCH ₃ | CCl ₃ OCH ₃ |
|-----------|------------------------------------|------------------------------------|-----------------------------------|
| Group 1 | C/H ₃ /O | C/H ₃ /O | C/H ₃ /O |
| Group 2 | O/C2 | O/C2 | O/C2 |
| Group 3 | C/Cl/H ₂ /O | C/Cl ₂ /H/O | C/Cl ₃ /O |

C_p(T) or All[°]₂₉₈ of compounds = All[°]₂₉₈ of Group 1 + All[°]₂₉₈ of Group 2 + All[°]₂₉₈ of Group 3. S[°]₂₉₈ of compounds = S[°]₂₉₈ of Group 1 + S[°]₂₉₈ of Group 2 + S[°]₂₉₈ of Group 3 - Rln(symmetry); R = 1.987 cal/mol-K, Symmetry = see the foot note 1 in the Table 12. Entropy of mixing = -R Σ{(n_i) × ln(n_i)}; where n_i is fraction of conformer i. For CHCl₂OCH₃, the mixing term is: -R {0.9014 × ln(0.9014) + 0.0986 × ln(0.0986)} = 0.64 cal/mol K in Table 3.10.

and CCl_3OCH_3 is 18.0, 22.5, 25.7 cal/mol·K at 300 K, and 25.1, 30.2, 32.1 cal/mol at 500 K from B3LYP/6-31G(d,p) calculation. The comparison values from group additivity are 18.2, 22.3, 25.8 cal/mol·K at 300 K, 25.6, 30.5, 32.4 cal/mol·K at 500 K.

3.4 Summary

Structure, torsion potentials and thermodynamic properties of three chlorinated dimethyl ethers are calculated using density function and *ab initio* calculations. Enthalpies, $\Delta H_f^\circ_{298}$ are presented as average data using up to seven reaction schemes based on CBS-Q//B3** theory and considering statistical distribution of rotational conformers. CBS-Q//B3** calculation values of $\Delta H_f^\circ_{298}$ show consistency for all reaction schemes except the reaction: $\text{CHCl}_2\text{OCH}_3 + 2\text{H}_2 \rightarrow 2\text{HCl} + \text{CH}_3\text{OCH}_3$. Enthalpy of formation at 298 K, $\Delta H_f^\circ_{298}$, entropies, S°_{298} and heat capacities, $C_p(T)$ from 300 K to 1500 K are reported along with values of thermodynamic properties on C/Cl/H₂/O, C/Cl₂/H/O, C/Cl₃/O groups needed for use in group additivity.

CHAPTER 4

THERMODYNAMIC PROPERTIES, VIBRATIONAL FREQUENCIES AND GEOMETRY OF CHLOROMETHOXY AND FORMALDEHYDE – CHLORINE, COMPLEX RADICALS

4.1 Overview

The initial product of chlorocarbon reaction in atmospheric chemistry and in combustion is a chlorocarbon (ClC) radical. One of the important reaction of these ClC radicals is reaction with O_2 then the NO in atmosphere to form ClCO \cdot radical or reaction in high temperature combustion with O_2 to RClO \cdot + $O\cdot$ (chain branching).

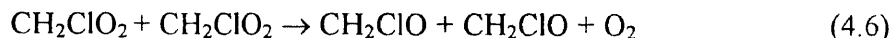
Enthalpy, $\Delta H_f^\circ_{298}$, entropy, S°_{298} and heat capacities, $C_p(T)$ from 300 to 1500K of chloro methoxy radicals ($CH_2ClO\cdot$, $CHCl_2O\cdot$, $CCl_3O\cdot$) and that of formaldehyde – Cl atom complex radicals ($CH_2O\cdots Cl$, $C^*HClO\cdots Cl$, $CCl_2O\cdots Cl$) are determined using density functional B3LYP/6-31g(d,p) optimized geometries and its single point calculations for energy at the B3LYP/6-311+G(3df,2p), and *ab initio* calculations of QCISD(T)/6-31G(d,p) and CBS-Q//B3LYP/6-31G(d,p) levels of calculation (defined as CBSQ//B3**). Enthalpies of formation are determined at each calculation level using the $\Delta H^\circ_{rxn(298)}$ and known enthalpies of other reactants in each of 6 different working reactions. The statistical distribution analysis of rotation is also considered; $\Delta H_f^\circ_{298}$ values for $CH_2ClO\cdot$ of -4.5 ± 0.3 , $CHCl_2O\cdot$ of -5.6 ± 0.3 , $CCl_3O\cdot$ of -7.5 ± 0.3 , $CH_2O\cdots Cl$ of -2.1 ± 0.3 , $CHClO\cdots Cl$ of -17.5 ± 0.3 , and $CCl_2O\cdots Cl$ of -24.7 ± 0.3 kcal/mol at the CBS-Q//B3** Contributions to entropy and heat capacity from internal rotation about Cl-O bond of formaldehyde and chlorine atom complex radicals are also

determined. Rotational barrier of formaldehyde and chlorine atom complex radicals are analyzed by versus torsion angle using density functional B3LYP/6-31G(d,p) method.

Initial products from pyrolysis, oxidation, or photochemical reactions of saturated and unsaturated chlorinated hydrocarbons are the corresponding radicals. Important reactions of these alkyl radicals in combustion and in atmospheric photochemistry are combination reactions with molecular oxygen, chlorine or hydrogen to form energized adducts (from the chemical activation process of the new bond formation) which can undergo further reaction or be stabilized. These reactions are complex, difficult to study experimentally and present a source of controversy with regard to both pathway and reaction rates. The reaction system, ($\text{ClO} + \text{CH}_3 \rightarrow \text{CH}_3\text{OCl}^* \rightarrow \text{Products}$) is important to understanding the depletion effect that chlorine chemistry has on the stratospheric ozone after the nocturnal winters in the ann-artic and artic. The thermodynamic propeties of methoxy ($\text{CH}_3\text{O}\bullet$), chloro-methoxy radical ($\text{CH}_2\text{ClO}\bullet$, $\text{CHCl}_2\text{O}\bullet$, $\text{CCl}_3\text{O}\bullet$) or formaldehyde – chlorine atom complex radicals ($\text{CH}_2\text{O}\cdots\text{Cl}$), chloro-formaldehyde – chlorine atom complex radicals ($\text{CHClO}\cdots\text{Cl}$, $\text{C}\bullet\text{Cl}_2\text{O}\cdots\text{Cl}$) are needed for the understanding this ozone depletion reaction chemistry.

The source of chlorine to the stratosphere includes the man-made chlorofluorocarbons as well as naturally occurring species; the most abundant natural species is methyl chloride.^{3,4} The atmospheric oxidation of methyl chloride leads to the formation of the chloro-methoxy radical, $\text{CH}_2\text{ClO}\bullet$ radical in atmosphere.





One important requirement for modeling and simulation of these systems is accurate thermodynamic property data for molecules, intermediate radicals and reaction transition states. These data allow determination of equilibrium, and reverse rate constants from forward rate and equilibrium constants. *Ab initio* and density functional calculations with a reasonable computational resource provide an opportunity to accurately estimate thermodynamic properties of reactants, intermediate radicals, and products, plus estimate properties for transition states which are often nearly impossible to obtain through (experiment) observation. Thermodynamic property data on the oxygenated chlorocarbon species are needed for evaluation of reaction paths, kinetic processes, as well as stability of intermediate adducts and the oxy-chlorocarbon species formed as products.^{9,10} These properties are also needed in kinetic modeling and in equilibrium calculations. There is very little or no thermodynamic data of these oxygenated chlorocarbon radicals in the literature.

In this study, we calculate $\Delta H_f^\circ_{298}$ using the composite CBS-Q//B3** *ab initio* method. Entropy and heat capacity from 300 to 1500 K are determined using the density functional method, B3LYP/6-31G(d,p) for chloro methoxy radicals ($\text{CH}_2\text{ClO}\bullet$, $\text{CHCl}_2\text{O}\bullet$, $\text{CCl}_3\text{O}\bullet$) and that of intermediate radical adducts ($\text{CH}_2\text{O}\cdots\text{Cl}$, $\text{CHClO}\cdots\text{Cl}$ and $\text{CCl}_2\text{O}\cdots\text{Cl}$). These are weakly bound formaldehyde – chlorine atom complexes; they are not hypochlorite methyl radicals because the newly formed PI bond in the formaldehyde is some 20 to 30 kcal/mole stronger than the $\text{C}\cdot\text{H}_2\text{O}-\text{Cl}$ bond. Thus the

loss of a hydrogen on CH_3OCl (formation of $\text{C}\cdot\text{H}_2\text{OCl}^*$) results in rapid cleavage of the weak $\text{O}-\text{Cl}$ bond and formation of the PI (double) bond of $\text{CH}_2=\text{O}$.

We also analyze the rotational barrier versus torsion angle in 15 degree increments using the B3LYP/6-31G(d,p), density functional method for the formaldehyde ($\text{CH}_2=\text{O} \cdots \text{Cl}$) weakly bound (ca 7 kcal/mole) complexes ($\text{CH}_2\text{O} \cdots \text{Cl}$, $\text{C}\cdot\text{HClO} \cdots \text{Cl}$ and $\text{CCl}_2\text{O} \cdots \text{Cl}$).

4.2 Methods

4.2.1 Selection of Calculation Methods and Basic Sets

B3LYP/6-31G(d,p) is chosen because it is computationally economical and thus possibly applicable to larger molecules, if it is accurate. It is also commonly used and is reported to yield accurate geometry and reasonable energies.^{21,22} Comparison of calculation results from this level against data from higher calculation levels for $\Delta H^\circ_{f,298}$, will provide some calibration of the B3LYP/6-31G(d,p) values (with similar working reactions) for larger molecules, where this may be one of the few calculation methods available. B3LYP/6-311+G(3df,2p) is chosen to see if this larger basic set results in an improvement to the above commonly used density functional calculation method.²² QCISD(T)/6-31G(d,p) is a configuration interaction method; but with a small, economical base set.^{23,24} CBS-Q//B3LYP/6-31G(d,p) calculation is a high level composite method with empirical corrections; it is reported to be comparable with QCISD(T)/6-311+G(3df,2p).^{29,30} This CBS-Q//B3LYP/6-31G(d,p) method is similar to the Radom research group's CBS/RAD²³ method; it has B3LYP/6-31g(d,p) geometry, which they indicate is very close to QCISD(T) values and a QCISD(T) calculation in

place of CCSD(T). These calculations are referred to as CBSQ//B3** in the present study for brevity.

4.2.2 *Ab Initio*, Density Functional and Composite Calculations

Geometry optimizations and frequency calculations for chloro methoxy radicals ($\text{CH}_2\text{ClO}\bullet$, $\text{CHCl}_2\text{O}\bullet$, $\text{CCl}_3\text{O}\bullet$) and that of formaldehyde ($\text{CH}_2=\text{O} \cdots \text{Cl}$) atom complex radicals ($\text{CH}_2\text{O}\cdots\text{Cl}$, $\text{CHClO}\cdots\text{Cl}$, $\text{CCl}_2\text{O}\cdots\text{Cl}$) are performed using B3LYP/6-31G(d,p) density functional theory and the enthalpy of formation for radicals are analyzed using 6 isodesmic and non isodesmic reactions with B3LYP/6-31G(d,p) geometries and single point calculations for energy at the B3LYP/6-311 +G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q levels of calculation. Zero-point vibrational energies (ZPVE), vibrational frequencies and thermal contributions to enthalpy and entropy from harmonic frequencies are scaled with factor, 0.9806 as recommended by Scott et al.³¹ Entropies and heat capacities are calculated from scaled vibrational degrees of freedom. The numbers of optical isomers, conformers, and spin degeneracy of unpaired electrons are also incorporated in entropy value. The molecular orbital calculations are performed using the Gaussian94.

4.2.3 Calculation of Hindered Rotation Contribution to Thermodynamic Parameters

A technique for the calculation of thermodynamic functions from hindered rotations with arbitrary potentials has been previously developed.²⁵⁻²⁹ This technique employs expansion of the hindrance potential in the Fourier series, calculation of the Hamiltonian matrix in the basis of the wave functions of free internal rotation, and

subsequent calculation of energy levels by direct diagonalization of Hamiltonian matrix.

In this work the torsion potential calculated at discrete torsion angle is represented by equation 4.7.

$$V(\vartheta) = a_0 + a_1 \cos(\vartheta) + a_2 \cos(2\vartheta) + a_3 \cos(3\vartheta) + b_1 \sin(\vartheta) + b_2 \sin(2\vartheta) + b_3 \sin(3\vartheta) \quad (4.7)$$

where value of the coefficients, a_i , were calculated to provide the true minimum and maximum of the torsion potentials with allowance of a shift of the theoretical extreme angular positions

TABLE 4.1-a. Vibrational Frequencies^a (cm⁻¹) for Methoxy Radical

| Frequencies | B3LYP/6-3 | HF/6-31G* | Experimenta | | |
|-------------|-----------|-----------|-------------|--------|--------|
| | G(d,p) | | Powers | Chiang | Ramond |
| v(1) | 737.5599 | 728 | 662 | 657 | 630 |
| v(2) | 970.4561 | 990 | 929 | | |
| v(3) | 1125.1782 | 1082 | | | |
| v(4) | 1381.2903 | 1414 | 1289 | 1308 | 1210 |
| v(5) | 1381.9685 | 1423 | 1403 | 1410 | 1465 |
| v(6) | 1535.7183 | 1487 | | | |
| v(7) | 2910.8135 | 2842 | | | |
| v(8) | 2978.4791 | 2901 | 2948 | 3077 | 2895 |
| v(9) | 3018.5080 | 2918 | | | |

TABLE 4.1-b. Rotation Constants (amu·Bohr²) for Methoxy Radical

| CH ₃ O• | Rotational constants (Ghz) | | |
|--------------------|----------------------------|-------|-------|
| Calculation method | A | B | C |
| B3LYP/6-31G(d,p) | 11.46 | 64.94 | 65.45 |
| BAC/MP4 | 11.26 | 65.39 | 5.751 |

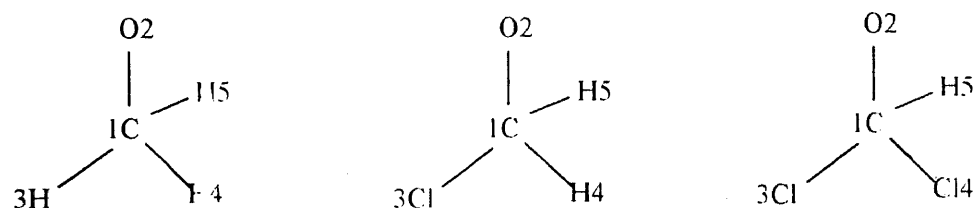
TABLE 4.1-c. Vibrational Frequencies^a (cm⁻¹), for Chloro-methoxy and Formaldehyde (CH₂=O) -- Cl complex Radicals

| | CH ₂ ClO• | CHCl ₂ O• | CCl ₃ O• | CH ₂ O--Cl | CHClO--Cl | CCl ₂ O--Cl |
|------|----------------------|----------------------|---------------------|-----------------------|-----------|------------------------|
| ν(1) | 381.7501 | 267.7132 | 197.7111 | 166.9031 | 67.5346 | 23.9588 |
| ν(2) | 654.3567 | 316.0065 | 227.8455 | 246.5912 | 102.7923 | 50.3990 |
| ν(3) | 663.0435 | 403.5839 | 319.183 | 280.6221 | 147.1607 | 94.0606 |
| ν(4) | 1048.7153 | 609.0035 | 361.2422 | 1197.1603 | 474.0943 | 306.0639 |
| ν(5) | 1161.3478 | 658.6866 | 362.7363 | 1241.0339 | 757.2484 | 454.5173 |
| ν(6) | 1263.0952 | 1053.3824 | 462.2841 | 1507.1104 | 944.4957 | 573.1060 |
| ν(7) | 1328.2493 | 1125.993 | 55.80651 | 1796.6157 | 1341.8297 | 581.7725 |
| ν(8) | 2937.3126 | 1141.0219 | 741.7952 | 2968.4959 | 1811.434 | 857.1454 |
| ν(9) | 2977.7799 | 2905.9089 | 1198.5441 | 3068.6775 | 3078.9726 | 1838.9103 |

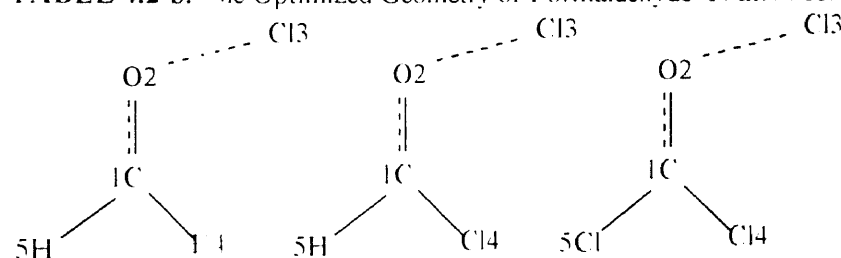
TABLE 4.1-d. Moment of Inertia (amu·Bohr) for Chloro-methoxy and Formaldehyde (CH₂=O)--Cl complex Radicals

| M. I | CH ₃ O• | CH ₂ ClO• | CHCl ₂ O• | CCl ₃ O• | CH ₂ O--Cl | CHClO--Cl | CCl ₂ O--Cl |
|------|--------------------|----------------------|----------------------|---------------------|-----------------------|-----------|------------------------|
| A | 11.46392 | 36.7832 | 250.7278 | 717.614 | 35.8181 | 232.1405 | 422.9114 |
| B | 64.94634 | 323.2344 | 571.6234 | 752.4084 | 446.585 | 903.7393 | 1741.88 |
| C | 65.44784 | 348.6029 | 794.2554 | 1115.45 | 482.403 | 1135.876 | 2164.76 |

^a Nonscaled, frequencies are calculated at the B3LYP/6-31G(d,p) level of theory. ^b Reference 15. ^c Reference 18. ^d Reference 10. ^e Reference 46. ^f Reference 47 ^g The rotational constant units are Ghz.

TABLE 4.2-a. The Optimized Geometry of Chloro-methoxy radicals

| Definition | $\text{CH}_3\text{O}\bullet^{\text{a}}$ | $\text{CH}_2\text{O}\bullet^{\text{b}}$ | $\text{CH}_2\text{ClO}\bullet^{\text{b}}$ | $\text{CHCl}_2\text{O}\bullet^{\text{b}}$ | $\text{CCl}_3\text{O}\bullet^{\text{b}}$ |
|------------|---|---|---|---|--|
| | H/6-31G* | B3LYP/6-31G(d,p) | | | |
| R(2,1) | 1.11 | 1.368 | 1.315 | 1.302 | 1.299 |
| R(3,1) | 1.33 | 1.100 | 1.850 | 1.828 | 1.805 |
| R(4,1) | 1.33 | 1.103 | 1.105 | 1.828 | 1.858 |
| R(5,1) | 1.33 | 1.103 | 1.105 | 1.110 | 1.805 |
| A(2,1,3) | 116.522 | 113.682 | 116.932 | 114.884 | 114.527 |
| A(2,1,4) | 108.522 | 110.920 | 110.553 | 114.886 | 97.639 |
| A(3,1,4) | 101.589 | 106.202 | 105.457 | 109.666 | 110.186 |
| A(2,1,5) | 116.522 | 113.392 | 110.555 | 105.480 | 114.657 |
| A(3,1,5) | 101.589 | 106.186 | 105.456 | 105.469 | 109.128 |
| A(4,1,5) | 101.591 | 105.420 | 107.328 | 105.467 | 110.153 |

TABLE 4.2-b. The Optimized Geometry of Formaldehyde-Cl atom complex radicals^b

| Definition | $\text{CH}_2\text{O}\cdots\text{Cl}^{\text{b}}$ | $\text{CHClO}\cdots\text{Cl}^{\text{b}}$ | $\text{CCl}_2\text{O}\cdots\text{Cl}^{\text{b}}$ |
|------------|---|--|--|
| | B3LYP/6-31G(d,p) | | |
| R(2,1) | 1.213 | 1.195 | 1.189 |
| R(3,2) | 2.479 | 2.612 | 2.693 |
| R(4,1) | 1.101 | 1.765 | 1.750 |
| R(5,1) | 1.105 | 1.098 | 1.759 |
| A(1,2,3) | 108.002 | 121.664 | 123.941 |
| A(2,1,4) | 121.973 | 124.857 | 124.581 |
| A(2,1,5) | 120.249 | 124.517 | 122.574 |
| A(4,1,5) | 117.778 | 110.625 | 112.845 |
| D(3,2,1,4) | -0.130 | 0.706 | -0.815 |
| D(3,2,1,5) | 179.833 | -179.300 | -180.817 |

^a The geometries are optimized in HF/6-31G* in reference [18, 71]. ^b The geometries are optimized in B3LYP/6-31G(d,p) in this work.

4.3 Results and Discussion

4.3.1 Vibrational frequencies and geometry

Harmonic vibrational frequencies are calculated for the methoxy, chlorinated methoxy, formaldehyde-Cl atom complex, chlorinated formaldehyde-Cl atom complex radicals at the B3LYP/6-31G(d, p) level of theory on the basis of optimized geometry at the same level of theory in Table 4.1. The vibrational frequencies and rotational constants for the methoxy radicals are given in Table 4.1-a. They are in good agreement with other reported calculations^{18,71} and experimental reports.^{72,73,74} The CO stretching frequency mode of CH₃O• shows 737 cm⁻¹ in this work, 728 cm⁻¹ in HF/6-31G*^{18,71} of 662 cm⁻¹ in the laser-excited fluorescence spectra of Powers et al.⁷², 657 cm⁻¹ in the laser-excited fluorescence spectra of Chiang et al.⁷³ and 630 cm⁻¹ in the photoelectron spectra of Ramond et al.⁷⁴ In this work, The CH₂ scissoring frequency mode of CH₃O• shows 1382 cm⁻¹ in this work, 1423 cm⁻¹ in HF/6-31G*,^{18,71} 1403 cm⁻¹ in the laser-excited fluorescence spectra of Powers et al., 1410 cm⁻¹ in the laser-excited fluorescence spectra of Chiang et al.⁷³ and 1465 cm⁻¹ in the photoelectron spectra of Ramond et al.⁷⁴ The CH₃ stretching frequency mode of CH₃O• shows 2978 cm⁻¹ in this work, 2901 cm⁻¹ in HF/6-31G*,^{18,71} 2948 cm⁻¹ in the laser-excited fluorescence spectra of Powers⁷² et al., 3077 cm⁻¹ in the laser-excited fluorescence spectra of Chiang⁷³ et al. and 2895 cm⁻¹ in the photoelectron spectra of Ramond et al.⁷⁴ The vibrational frequencies and rotational constants for multiple chloro-methyl hypochlorites are given in Table 4.1.

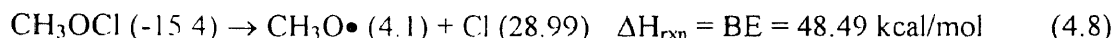
The optimized B3LYP/6-31G(d, p) geometries for radicals are illustrated in Table 4.2. Methoxy and chloro methoxy radicals are tetrahedral structures. HF/6-31G* study by Melius^{18,71} et al. shows similar structure with this study in Table 3.2 The

geometry parameters of Melius were obtained by conversion of his cartesian coordinates; angles $A(2,1,3)$, $A(2,1,4)$ between O-C-H are 116.5, 108.5 degree in HF/6-31G* and 113.7, 110.9 degree in B3LYP/6-31G+(d,p), respectively; angles $A(3,1,4)$, $A(4,1,5)$ between H-C-H are same as 101.6 degree in HF/6-31G* but are different with 106.2, 101.6 degree in B3LYP/6-31G+(d,p), respectively. We think the lone electron pair of oxygen effects the difference with geometry of angle, $A(3,1,4)$ and $A(4,1,5)$. The C-O bond is 1.311 Å in HF/6-31G* and 1.368 Å in this study. Numerical values of the structural parameters including carbon-hydrogen, carbon-chlorine, carbon-oxygen, oxygen-hydrogen bond distances along with bond angles are also listed in Table 4.2. The C-O bond length $R(2,1)$ decreases in this series at 1.369, 1.315, 1.302 Å in methoxy radicals, $\text{CH}_3\text{O}\bullet$, $\text{CH}_2\text{ClO}\bullet$, $\text{CHCl}_2\text{O}\bullet$ and $\text{CCl}_3\text{O}\bullet$ suggesting an increase of C-O bond strength's. It is determined that the radical complex ($\text{CH}_2\text{O}\cdots\text{Cl}$) is a weakly bond (5kcal/mol) in formaldehyde (CH_2O) and Cl atom complex radical in Table 4.2.b. The C-H and O-Cl bond lengths in the equilibrium conformations of three radicals, $\text{CH}_2\text{O}\cdots\text{Cl}$, $\text{CHClO}\cdots\text{Cl}$, and $\text{CCl}_2\text{O}\cdots\text{Cl}$ optimized at the B3LYP/6-31G(d, p) are similar, while the C-O bond lengths $R(2,1)$ also decrease 1.213, 1.195, 1.189 Å in Table 4.2-b. The Cl-O bond length ($R5$) increases in this series at 2.479, 2.612, 2.693 Å in $\text{CH}_2\text{O}\cdots\text{Cl}$, $\text{CHClO}\cdots\text{Cl}$, and $\text{CCl}_2\text{O}\cdots\text{Cl}$ in Table 4.2-b. The calculation indicate that the formation of the C=O double bond in $\text{CH}_2\text{O}\cdots\text{Cl}$, $\text{CHClO}\cdots\text{Cl}$, and $\text{CCl}_2\text{O}\cdots\text{Cl}$ results in gaining more energy in the π bond of the carbonyl more than cleavage of the Cl-O bond (48.49 kcal/mol).

TABLE 4.3. Total Energies vs Different Level of Theory and Composite CBS-Q
Zero Point Vibrational Energies and Thermal Corrections (in Hartree)

| | B3LYP/ 6-31G(d,p) | B3LYP/6- 311G+(d,p) | QCISD(T) 6-31G(d,p) | CBS-Q// B3** ^d | ZPVE ^c | Thermal Correctio |
|-------------------------------------|----------------------|------------------------|------------------------|------------------------------|-------------------|----------------------|
| CH ₃ O• | -115.054 | -115.0992 | -114.746 | -114.872 | 0.0365 | 0.0040 |
| CH ₂ ClO• | -574.656 | -574.7344 | -573.781 | -574.032 | 0.0277 | 0.0044 |
| CHCl ₂ O• | -1034.24 | -1034.353 | -1032.805 | -1033.18 | 0.0189 | 0.0053 |
| CCl ₃ O• | -1493.82 | -1493.971 | -1491.827 | -1492.33 | 0.0099 | 0.0065 |
| CH ₂ O--Cl ^f | -574.653 | -574.7295 | -573.783 | -574.027 | 0.0279 | 0.0054 |
| CHClO--Cl ^f | -1034.26 | -1034.373 | -1032.831 | -1033.20 | 0.0196 | 0.0064 |
| CCl ₂ O--Cl ^f | -1493.85 | -1494.001 | -1491.864 | -1492.36 | 0.0107 | 0.0073 |
| CH ₃ OCl | -575.259 | -575.3390 | -574.384 | -574.629 | 0.0411 | 0.0048 |
| CH ₂ ClOCl | -1034.85 | -1034.968 | -1033.417 | -1033.79 | 0.0327 | 0.0055 |
| CHCl ₂ OCl | -1494.44 | -1494.589 | -1492.443 | -1492.95 | 0.0232 | 0.0064 |
| CH ₄ | -40.524 | -40.5368 | -40.3896 | -40.405 | 0.0441 | 0.0038 |
| CH ₃ | -39.842 | -39.8578 | -39.7162 | -39.740 | 0.0292 | 0.0040 |
| CH ₃ Cl | -500.112 | -500.1589 | -499.414 | -499.556 | 0.0372 | 0.0040 |
| CH ₂ Cl | -499.441 | -499.4900 | -498.749 | -498.901 | 0.0221 | 0.0046 |
| C ₂ H ₆ | -79.838 | -79.8615 | -79.5855 | -79.624 | 0.0735 | 0.0044 |
| C ₂ H ₅ | -79.165 | -79.1900 | -78.9169 | -78.965 | 0.0583 | 0.0049 |
| CH ₃ OH | -115.724 | -115.7729 | -115.412 | -115.534 | 0.0504 | 0.0042 |
| C ₂ H ₅ OH | -155.962 | -155.0210 | -154.532 | -154.762 | 0.0787 | 0.0052 |
| C ₂ H ₅ O | -154.377 | -154.4316 | -153.950 | -154.097 | 0.0636 | 0.0052 |
| CH ₂ ClOH | -575.326 | -575.4077 | -574.450 | -574.698 | 0.0427 | 0.0046 |
| CHCl ₂ OH | -1034.91 | -1035.034 | -1033.481 | -1033.86 | 0.0334 | 0.0054 |
| CCl ₃ OH | -1494.49 | -1494.647 | -1492.501 | -1493.01 | 0.0229 | 0.0066 |

^{a b c} Total energies are in Hartree at 0 K, all molecular geometries are optimized in B3LYP/6-31G(d,p). ^a B3LYP/6-31G(d,p), ^b B3LYP/6-311+G(3df,2p), ^c QCISD(T)/6-31G(d,p). ^d CBS-Q//B3LYP/6-31G(d,p) enthalpies are in Hartree, which include thermal correction and zero-point energy at 298 K. ^e ZPVE is in Hartree and scaled by 0.9806. ^f Thermal corrections are in Hartree. ^f a weak bond (5kcal/mol), formaldehyde-Cl atom couple.



Where the gain in energy from forming the R₂C=O from R₂C•–O• is about 80 kcal/mol.

TABLE 4.4. Reaction Enthalpies (in kcal/mol) at 298 K^a

| | B3LYP/ 6-31G(d,p) | B3LYP/6-3 11+G(3df,2p) | QCISD(T)/ 6-31G(d, p) | CBS-Q// 133** |
|--|----------------------|---------------------------|--------------------------|------------------|
| 1 $\text{CH}_2\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{Cl}$ | -1.42 | 2.74 | 0.49 | 6.43 |
| $\text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{C}_2\text{H}_5\text{OH}$ | 0.19 | 0.4 | -0.92 | -0.14 |
| $\text{C}\cdot\text{H}_2\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{OH}$ | 3.12 | 6.26 | 3.72 | 8.43 |
| $\text{CH}_2\text{ClO} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{CH}_2\text{ClOH}$ | -0.24 | 0.44 | -1.3 | -0.72 |
| $\text{CHCl}_2\text{O} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{CHCl}_2\text{OH}$ | -5.61 | -4.6 | -6.43 | -6.09 |
| $\text{CCl}_3\text{O} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{CCl}_3\text{OH}$ | -3.96 | -2.95 | -5.7 | -4.75 |
| $\text{CH}_2\text{O}-\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{OC}$ | 38.77 | 38.93 | 39.68 | 39.5 |
| $\text{CHClO}-\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{CH}_2\text{ClOCl}$ | 46.57 | 47.62 | 48.81 | 48.22 |
| $\text{CCl}_2\text{O}-\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{CHCl}_2\text{OCl}$ | 49.76 | 51.27 | 53.19 | 51.31 |
| 2 $\text{CH}_2\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{CH}_3\text{Cl}$ | -4.54 | -3.52 | -3.22 | -1.99 |
| $\text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{C}_2\text{H}_5\text{OH}$ | -2.92 | -5.86 | -3.81 | -8.56 |
| $\text{CH}_3\text{O} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{CH}_3\text{OH}$ | -3.12 | -6.26 | -3.72 | -8.43 |
| $\text{CH}_2\text{ClO} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{CH}_2\text{ClOH}$ | -3.36 | -5.81 | -5.02 | -9.14 |
| $\text{CHCl}_2\text{O} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{CHCl}_2\text{OH}$ | -8.72 | -10.86 | -10.15 | -14.52 |
| $\text{CCl}_3\text{O} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{CCl}_3\text{OH}$ | -7.08 | -9.2 | -9.42 | -13.18 |
| $\text{CH}_2\text{O}-\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{CH}_3\text{OCl}$ | 35.65 | 32.67 | 35.97 | 31.04 |
| $\text{CHClO}-\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{CH}_2\text{ClOCl}$ | 43.46 | 41.36 | 45.09 | 39.8 |
| $\text{CCl}_2\text{O}-\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{CHCl}_2\text{OCl}$ | 46.65 | 45 | 49.47 | 42.88 |
| 3 $\text{CH}_2\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_3\text{Cl}$ | 6.04 | 6.13 | 5.05 | 6.16 |
| $\text{C}_2\text{H}_5\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5\text{OH}$ | 7.66 | 3.8 | 4.47 | -0.4 |
| $\text{C}\cdot\text{H}_2\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_3\text{OH}$ | 10.58 | 9.66 | 8.28 | 8.16 |
| $\text{CH}_3\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_3\text{OH}$ | 7.46 | 3.39 | 4.56 | -0.26 |
| $\text{CH}_2\text{ClO} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_2\text{ClOH}$ | 7.22 | 3.84 | 3.26 | -0.98 |
| $\text{CHCl}_2\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CHCl}_2\text{OH}$ | 1.86 | -1.21 | -1.87 | -6.36 |
| $\text{CCl}_3\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CCl}_3\text{OH}$ | 3.5 | 0.45 | -1.14 | -5.02 |
| $\text{CH}_2\text{O}-\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_3\text{OCl}$ | 46.23 | 42.32 | 44.25 | 39.21 |
| $\text{CHClO}-\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_2\text{ClOCl}$ | 54.04 | 51.02 | 53.37 | 47.96 |
| $\text{CCl}_2\text{O}-\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CHCl}_2\text{OCl}$ | 57.23 | 54.67 | 57.75 | 51.04 |
| 4 $\text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{C}_2\text{H}_5\text{OH}$ | 1.62 | -2.33 | -0.59 | -6.57 |
| $\text{C}\cdot\text{H}_2\text{OH} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{CH}_3\text{OH}$ | 4.54 | 3.52 | 3.22 | 2 |
| $\text{CH}_3\text{O} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{CH}_3\text{OH}$ | 1.42 | -2.73 | -0.49 | -6.43 |
| $\text{CH}_2\text{ClO} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{CH}_2\text{ClOH}$ | 1.18 | -2.29 | -1.8 | -7.15 |
| $\text{CHCl}_2\text{O} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{CHCl}_2\text{OH}$ | -4.18 | -7.34 | -6.92 | -12.52 |
| $\text{CCl}_3\text{O} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{CCl}_3\text{OH}$ | -2.54 | -5.68 | -6.2 | -11.18 |
| $\text{CH}_2\text{O}-\text{Cl} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{CH}_3\text{OCl}$ | 40.19 | 36.19 | 39.19 | 33.04 |
| $\text{CHClO}-\text{Cl} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{CH}_2\text{ClOCl}$ | 48 | 44.88 | 48.31 | 41.8 |

TABLE 4.4. Reaction Enthalpies (in kcal/mol) at 298 K^a (cont'd)

| | B3LYP/ 6-31G(d,p) | B3LYP/6-3 11+G(3df,2p) | QCISD(T)/ 6-31G(d, p) | CBS-Q// B3** |
|--|----------------------|---------------------------|--------------------------|-----------------|
| 4 $\text{CCl}_2\text{O--Cl} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{CHCl}_2\text{OCl}$ | 51.19 | 48.53 | 52.70 | 44.88 |
| 5 $\text{CH}_2\text{Cl} + \text{CH}_3\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_3\text{Cl}$ | 1.28 | 1.44 | 2.07 | 2.92 |
| $\text{C}_2\text{H}_5\text{O} \cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$ | 2.90 | -0.89 | 1.49 | -3.64 |
| $\text{C}\cdot\text{H}_2\text{OH} + \text{CH}_3\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_3\text{OH}$ | 5.82 | 4.96 | 5.30 | 4.92 |
| $\text{CH}_3\text{O} \cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_3\text{OH}$ | 2.70 | -1.30 | 1.58 | -3.51 |
| $\text{CH}_2\text{ClO} \cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{ClOH}$ | 2.46 | -0.85 | 0.27 | -4.22 |
| $\text{CHCl}_2\text{O} \cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CHCl}_2\text{OH}$ | -2.90 | -5.90 | -4.84 | -9.60 |
| $\text{CCl}_3\text{O} \cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CCl}_3\text{OH}$ | -1.26 | -4.24 | -4.12 | -8.26 |
| $\text{CH}_2\text{O--Cl} + \text{CH}_3\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_3\text{OCl}$ | 41.47 | 37.63 | 41.26 | 35.96 |
| $\text{CHClO--Cl} + \text{CH}_3\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{ClOCl}$ | 49.28 | 46.32 | 50.39 | 44.72 |
| $\text{CCl}_2\text{O--Cl} + \text{CH}_3\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CHCl}_2\text{OCl}$ | 52.47 | 49.97 | 54.77 | 47.80 |
| 6 $\text{CH}_2\text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{Cl}$ | -1.62 | 2.33 | 0.59 | 6.51 |
| $\text{C}\cdot\text{H}_2\text{OH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{OH}$ | 2.92 | 5.86 | 3.81 | 8.56 |
| $\text{CH}_3\text{O} \cdot + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{OH}$ | -0.20 | -0.40 | 0.09 | 0.14 |
| $\text{CH}_2\text{ClO} \cdot + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{CH}_2\text{ClOH}$ | -0.44 | 0.04 | -1.21 | -0.57 |
| $\text{CHCl}_2\text{O} \cdot + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{CHCl}_2\text{OH}$ | -5.80 | -5.01 | -6.34 | -5.96 |
| $\text{CCl}_3\text{O} \cdot + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{CCl}_3\text{OH}$ | -4.16 | -3.35 | -5.61 | -4.61 |
| $\text{CH}_2\text{O--Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{OCl}$ | 38.57 | 38.52 | 39.78 | 39.54 |
| $\text{CHClO--Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{CH}_2\text{ClOCl}$ | 46.38 | 47.21 | 48.90 | 48.30 |
| $\text{CCl}_2\text{O--Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{CHCl}_2\text{OCl}$ | 49.57 | 50.87 | 53.28 | 51.39 |

^a Reaction enthalpies include thermal correction and zero-point energy correction at 298 K. ^b See foot notes of Table 3 for the explanation of theory levels.

TABLE 4.5. Enthalpy Data Used in Reactions to Determine $\Delta H_f^{\circ}_{298}$ of Target Radicals

| Compound | | source |
|--------------------------------------|--------|------------|
| CH_3 | -17.89 | Ref.32 |
| CH_3 | 4.10 | Ref. 71 |
| CH_3Cl | -19.60 | Ref.33 |
| CH_2Cl | 26.75 | This Study |
| C_2H_5 | -20.24 | Ref.34 |
| C_2H_5 | 29.30 | Ref.77 |
| CH_3OH | -48.08 | Ref.34 |
| CH_2ClOH | -58.00 | Ref.38 |
| CHCl_2OH | -64.42 | Ref.38 |
| CCl_3OH | -65.01 | Ref.38 |
| CH_3OCl | -15.41 | This Study |
| CH_2ClOCl | -22.05 | This Study |
| CCl_3OCl | -26.14 | This Study |
| $\text{C}_2\text{H}_5\text{OH}$ | -56.12 | This Study |
| $\text{C}_2\text{H}_5\text{O} \cdot$ | -3.30 | Ref.75 |

TABLE 4.6. Enthalpies of Formation^a for Standard Radicals at 298 K (kcal/mol)^a

| Rxn | Level | CH ₂ Cl | C ₂ H ₅ O• | C•H ₂ OH | CH ₃ O• |
|----------------|-------------------------|--------------------|----------------------------------|---------------------|--------------------|
| 1 ^b | B3LYP/ 6-31+G (d,p) | 34.00 | -4.14 | 0.98 | |
| | B3LYP/ 6-311+G (3df,2p) | 29.84 | -4.35 | -2.16 | |
| | QCISD(T)/6-31G(d,p) | 32.09 | -3.85 | 0.38 | |
| | CBSQ//B3** | 26.15 | -3.80 | -4.33 | |
| 2 | B3LYP/ 6-31+G (d,p) | 29.51 | -8.63 | | -0.39 |
| | B3LYP/ 6-311+G (3df,2p) | 28.49 | -5.69 | | 2.75 |
| | QCISD(T)/6-31G(d,p) | 28.19 | -7.74 | | 0.21 |
| | CBSQ//B3** | 26.97 | -2.99 | | 4.92 |
| 3 | B3LYP/ 6-31+G (d,p) | 27.07 | -11.39 | -5.95 | -2.83 |
| | B3LYP/ 6-311+G (3df,2p) | 26.98 | -7.44 | -5.03 | 1.23 |
| | QCISD(T)/6-31G(d,p) | 28.06 | -9.18 | -3.65 | 0.07 |
| | CBSQ//B3** | 26.95 | -3.20 | -3.53 | 4.89 |
| 4 | B3LYP/ 6-31+G (d,p) | | -9.52 | -6.27 | -3.15 |
| | B3LYP/ 6-311+G (3df,2p) | | -5.73 | -5.25 | 1.01 |
| | QCISD(T)/6-31G(d,p) | | -8.11 | -4.95 | -1.24 |
| | CBSQ//B3** | | -2.98 | -3.73 | 4.70 |
| 5 | B3LYP/ 6-31+G (d,p) | 28.62 | -9.52 | -6.95 | -1.28 |
| | B3LYP/ 6-311+G (3df,2p) | 28.46 | -5.73 | -3.54 | 2.72 |
| | QCISD(T)/6-31G(d,p) | 27.83 | -8.11 | -3.88 | -0.16 |
| | CBSQ//B3** | 26.98 | -2.98 | -3.50 | 4.93 |
| 6 | B3LYP/ 6-31+G (d,p) | 34.84 | | 1.82 | 4.93 |
| | B3LYP/ 6-311+G (3df,2p) | 30.89 | | -1.12 | 5.15 |
| | QCISD(T)/6-31G(d,p) | 32.63 | | 0.93 | 4.65 |
| | CBSQ//B3** | 26.71 | | -3.82 | 4.60 |
| Avg | B3LYP/ 6-31+G (d,p) | 30.81 | -8.95 | -3.27 | -0.54 |
| | B3LYP/ 6-311+G (3df,2p) | 28.93 | -6.08 | -3.42 | 2.57 |
| | QCISD(T)/6-31G(d,p) | 29.76 | -7.35 | -2.23 | 0.71 |
| | CBSQ//B3** | 26.75 | -3.19 | -3.78 | 4.81 |
| | CBSQ//B3** STDV | 0.35 | 0.35 | 0.38 | 0.15 |

^a The enthalpies of formation include thermal correction and zero-point energy correction at 298 K. ^b See reaction schemes of Table 4 for the explanation of reactions

TABLE 4.7. Comparison of Enthalpies of Formation^a for Standard Radicals
298 K (kcal/mol)

| | CH ₂ Cl | C ₂ H ₅ O• | C•H ₂ OH | CH ₃ O• |
|--------------|--------------------|----------------------------------|---------------------|--------------------|
| CBS-Q//B3* | 26.75 | -3.19 | -3.78 | 4.81 |
| Reported Dat | 27.10 | -3.30 | -3.51 | 4.10 |
| Reference | 18 | 75 | 76 | 71 |

TABLE 4.8. Comparison of Enthalpies of Formation^a for Target Radicals

298 K (kcal/mol)

| Rxn | Level | CH ₂ Cl | CHCl ₂ O | CCl ₃ O | CH ₂ O-Cl | CHClO-Cl | CCl ₂ O-Cl |
|-----|-------------------------|--------------------|---------------------|--------------------|----------------------|----------|-----------------------|
| 1 | B3LYP/ 6-31+G (d,p) | -5.58 | -6.63 | -8.87 | -2.00 | -16.44 | -23.72 |
| | B3LYP/ 6-311+G (3df,2p) | -6.27 | -7.64 | -9.88 | -2.15 | -17.49 | -25.23 |
| | QCISD(T)/6-31G(d,p) | -4.51 | -5.81 | -7.13 | -2.91 | -18.68 | -27.15 |
| | CBSQ//B3** | -5.10 | -6.15 | -8.08 | -2.70 | -18.10 | -25.27 |
| | | | | | | | |
| 2 | B3LYP/ 6-31+G (d,p) | -10.07 | -11.13 | -13.36 | -6.49 | -20.94 | -28.22 |
| | B3LYP/ 6-311+G (3df,2p) | -7.62 | -8.99 | -11.23 | -3.51 | -18.84 | -26.58 |
| | QCISD(T)/6-31G(d,p) | -8.41 | -9.70 | -11.02 | -6.81 | -22.57 | -31.04 |
| | CBSQ//B3** | -4.29 | -5.33 | -7.26 | -1.88 | -17.28 | -24.45 |
| | | | | | | | |
| 3 | B3LYP/ 6-31+G (d,p) | -12.51 | -13.57 | -13.56 | -8.93 | -23.38 | -30.66 |
| | B3LYP/ 6-311+G (3df,2p) | -9.13 | -10.50 | -11.23 | -5.02 | -20.36 | -28.10 |
| | QCISD(T)/6-31G(d,p) | -8.55 | -9.84 | -11.02 | -6.95 | -22.71 | -31.18 |
| | CBSQ//B3** | -4.31 | -5.35 | -7.26 | -1.91 | -17.30 | -24.47 |
| | | | | | | | |
| 4 | B3LYP/ 6-31+G (d,p) | -12.82 | -13.89 | -16.12 | -9.26 | -23.70 | -30.98 |
| | B3LYP/ 6-311+G (3df,2p) | -9.36 | -10.73 | -12.98 | -5.25 | -20.58 | -28.32 |
| | QCISD(T)/6-31G(d,p) | -9.85 | -11.15 | -12.46 | -8.25 | -24.01 | -32.49 |
| | CBSQ//B3** | -4.50 | -5.55 | -7.48 | -2.10 | -17.50 | -24.67 |
| | | | | | | | |
| 5 | B3LYP/ 6-31+G (d,p) | -10.96 | -12.02 | -14.25 | -7.38 | -21.83 | -29.11 |
| | B3LYP/ 6-311+G (3df,2p) | -7.65 | -9.02 | -11.26 | -3.54 | -18.87 | -26.61 |
| | QCISD(T)/6-31G(d,p) | -8.78 | -10.07 | -11.39 | -7.18 | -22.94 | -31.41 |
| | CBSQ//B3** | -4.28 | -5.32 | -7.25 | -1.87 | -17.27 | -24.44 |
| | | | | | | | |
| 6 | B3LYP/ 6-31+G (d,p) | -4.74 | -5.80 | -8.03 | -1.16 | -15.61 | -22.89 |
| | B3LYP/ 6-311+G (3df,2p) | -5.22 | -6.59 | -8.84 | -1.11 | -16.44 | -24.19 |
| | QCISD(T)/6-31G(d,p) | -3.97 | -5.26 | -6.58 | -2.37 | -18.13 | -26.60 |
| | CBSQ//B3** | -4.60 | -5.64 | -7.58 | -2.14 | -17.53 | -24.71 |
| | | | | | | | |
| Avg | B3LYP/ 6-31+G (d,p) | -9.45 | -10.51 | -12.37 | -5.87 | -20.32 | -27.60 |
| | B3LYP/ 6-311+G (3df,2p) | -7.54 | -8.91 | -10.90 | -3.43 | -18.76 | -26.51 |
| | QCISD(T)/6-31G(d,p) | -7.35 | -8.64 | -9.93 | -5.75 | -21.51 | -29.98 |
| | CBSQ//B3** | -4.51 | -5.56 | -7.49 | -2.10 | -17.50 | -24.67 |
| | CBSQ//B3** STDV | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 |

4.3.2 Enthalpies of Formation ($\Delta H_f^\circ_{298}$)

Enthalpies of formation ($\Delta H_f^\circ_{298}$) for the target radicals are estimated using total energies obtained by the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) calculation methods and up to six reaction schemes in Table 4.4. Total energies are corrected by zero-point vibration energies (ZPVE) which are scaled by 0.9806 as recommended by Scott et al.³¹ Thermal correction, 0 K to 298.15 K, is calculated to estimate $\Delta H_f^\circ_{298}$ at 298.15 K.²⁵

Density functional and ab initio calculations with ZPVE and thermal correction are performed for all radicals in each reaction, and enthalpy of reaction $\Delta H_{rxn}^\circ_{298}$ is calculated. Enthalpy of formation for the target radical in the reaction is determined from value of the 3 known values and ΔH_{rxn} calculation since enthalpies of formation of three compounds have been experimentally determined or theoretically calculated. The unknown enthalpies of formation for $\text{CH}_2\text{ClO}\bullet$, $\text{CHCl}_2\text{O}\bullet$, $\text{CCl}_3\text{O}\bullet$, $\text{CH}_2\text{O--Cl}$, CHClO--Cl , and $\text{CCl}_2\text{O--Cl}$ are estimated in this calculations.

As example, $\Delta H_f^\circ_{298}$ ($\text{CH}_2\text{ClO}\bullet$) is calculated from reaction scheme 1 in Table 4.4.

$$\Delta H_{rxn, 298} = \Delta H_f^\circ_{298} \{ (\text{CH}_3\text{O}\bullet) + (\text{CH}_2\text{ClOH}) - (\text{CH}_2\text{ClO}\bullet) - (\text{CH}_3\text{OH}) \} \quad (4.9)$$

and the listed known enthalpies of $\text{CH}_3\text{O}\bullet$, CH_2ClOH and CH_3OH . The enthalpies of reaction are obtained by the reaction schemes tabulated in Tables 4.4. The $\Delta H_f^\circ_{298}$ on the standard compounds in reaction sets are from literature in Table 4.5 and are used to determine $\Delta H_f^\circ_{298}$ values in Table 4.6.

The enthalpy of formation for radicals at the CBS-Q calculation level in all reaction schemes is consistent in Table 3.6. The $\Delta H_f^\circ_{298}$ for $\text{CH}_3\text{O}\bullet$ is -4.8 kcal/mol,

using the CBS-Q//B3** method through all reaction schemes in Table 3.6, Tsang et al.¹⁵ report enthalpy of formation for -4.1 ± 1 kcal/mol at 298 K. Melius et al.¹⁶ report $\Delta H_f^\circ_{298}$ of $\text{CH}_3\text{O}\bullet$ at -3.9 kcal/mol from BAC/MP4 analysis. The $\Delta H_f^\circ_{298}$ for CH_2Cl , $\text{C}_2\text{H}_5\text{O}$, and $\text{C}\bullet\text{H}_2\text{OH}$ are 26.8, -3.2, -3.8 kcal/mol, respectively, using the CBS-Q//B3** method and all reaction schemes in Table 3.6. Melius calculated enthalpy of formation 27.1 kcal/mol for CH_2Cl . Yamada reported $\Delta H_f^\circ_{298}$ for $\text{C}_2\text{H}_5\text{O}$ of -3.3 kcal/mol. Traeher evaluated $\Delta H_f^\circ_{298}$ for $\text{C}\bullet\text{H}_2\text{OH}$ to be -3.5 kcal/mol.

The accuracy of the enthalpies of formation obtained by our theoretical calculation methods is controlled by several factors; the level of sophistication (method + basis set) applied to calculate the electronic energy, the reliability of the enthalpies of formation of the reference compounds, the uncertainty in the thermal corrections, and the extent to which error cancellation occurs in the working chemical reaction used in the evaluation. The results for the B3LYP/6-31G(d, p), B3LYP/6-311+G(3df, 2p), and QCISD(T)/6-31G(d, p) calculation analysis show relatively uniform $\Delta H_f^\circ_{298}$ values and CBS-Q//B3** shows consistency through the all reaction schemes.

The method of isodesmic reactions relies on the similarity of bonding environment in the reactants and products that leads to cancellation of systematic errors in the density functional and ab initio molecular orbital calculations. In the radical systems, we try to calculate $\Delta H_f^\circ_{298}$ for our target molecule using bond cleavage reaction with a known molecules and radicals with the same bond cleavage. We are not always able to do this. For $\text{C}\bullet\text{H}_2\text{OH}$, there is resonance stabilization between the radical p orbital (on the carbon) and the p orbitals of the oxygen. This resonance does not exist in $\text{CH}_3\text{O}\bullet$, $\text{CH}_2\text{ClO}\bullet$, $\text{CHCl}_2\text{O}\bullet$ and $\text{CCl}_3\text{O}\bullet$ because the C atom is fully

saturated and has no empty or partially empty p orbitals available for resonance. The enthalpy of formation for chloro-methoxy radicals and other radicals show good consistency in all 6 reaction schemes in Table 4.8. The $\Delta H_f^\circ_{298}$ of $\text{CH}_2\text{ClO}\bullet$, $\text{CHCl}_2\text{O}\bullet$, and $\text{CCl}_3\text{O}\bullet$ are -4.5 ± 0.3 kcal/mol, -5.6 ± 0.3 kcal/mol, and -7.5 ± 0.3 kcal/mol, respectively.

The $\Delta H_f^\circ_{298}$ of $\text{CH}_2\text{O--Cl}$, CHClO--Cl , and $\text{CCl}_2\text{O--Cl}$ are -2.1 ± 0.3 kcal/mol, -17.5 ± 0.3 kcal/mol, and -24.7 ± 0.3 kcal/mol, respectively. The $\Delta H_f^\circ_{298}$ of CHClO--Cl does not include statistical analysis of conformers; There are two conformers, which show different enthalpies in CHClO--Cl as shown in Figures 4.2. We calculate the correction to enthalpy of formation using statistical analysis of the conformer values listed in Table 4.11. The $\Delta H_f^\circ_{298}$ of CHClO--Cl , is -17.4 kcal/mol in Table 4.10.

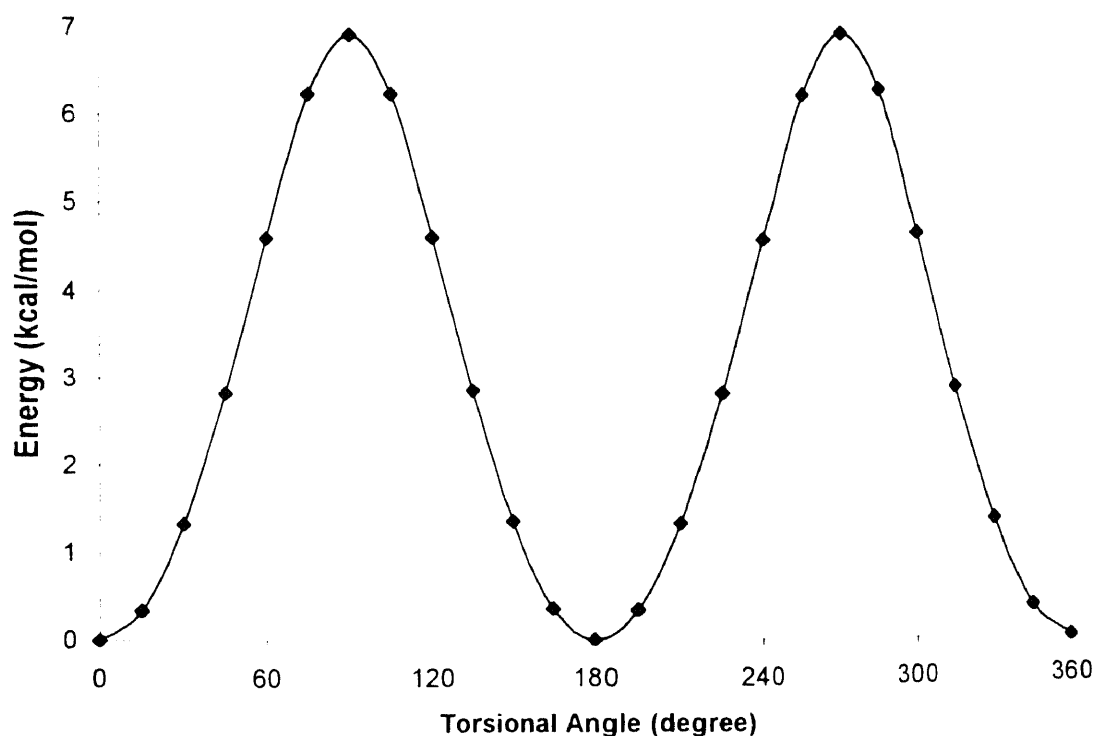


Figure 4.1. Potential energy for internal rotation about C-O bond of $\text{CH}_2\text{O--Cl}$ versus torsion angle (0=Optimized Geometry)

Table 4.9. Total Energy^a (Hartrees) of Molecules by Torsion angle

| Angle(gree) | CH ₂ O--Cl | CHClO--Cl | CCl ₂ O--Cl |
|-----------------|-----------------------|-------------|------------------------|
| 0 | -574.65382 | -1034.26023 | -1493.85431 |
| 15 | -574.65327 | -1034.26005 | -1493.85423 |
| 30 | -574.65169 | -1034.25953 | -1493.85397 |
| 45 | -574.64930 | -1034.25868 | -1493.85350 |
| 60 | -574.64649 | -1034.25776 | -1493.85300 |
| 75 | -574.64388 | -1034.25715 | -1493.85268 |
| 90 | -574.64280 | -1034.25691 | -1493.85256 |
| 105 | -574.64388 | -1034.25716 | -1493.85266 |
| 120 | -574.64648 | -1034.25814 | -1493.85296 |
| 135 | -574.64927 | -1034.25950 | -1493.85346 |
| 150 | -574.65165 | -1034.26088 | -1493.85394 |
| 165 | -574.65325 | -1034.26190 | -1493.85422 |
| 180 | -574.65382 | -1034.26223 | -1493.85431 |
| 195 | -574.65328 | -1034.26183 | -1493.85424 |
| 210 | -574.65170 | -1034.26076 | -1493.85398 |
| 225 | -574.64933 | -1034.25936 | -1493.85352 |
| 240 | -574.64654 | -1034.25802 | -1493.85302 |
| 255 | -574.64393 | -1034.25711 | -1493.85260 |
| 270 | -574.64280 | -1034.25691 | -1493.85256 |
| 285 | -574.64383 | -1034.25719 | -1493.85265 |
| 300 | -574.64642 | -1034.25784 | -1493.85295 |
| 315 | -574.64924 | -1034.25877 | -1493.85344 |
| 330 | -574.65165 | -1034.25959 | -1493.85393 |
| 345 | -574.65325 | -1034.26009 | -1493.85422 |
| 360 | -574.65382 | -1034.26023 | -1493.85431 |

^a Total energies are in Hartree in B3LYP/6-31G(d,p) theory. ^b The torsion angle in degree.

Table 4.10. $\Delta H_{f,298}^{\circ}$ for Rotational Conformers, Relative fraction, and Overall $\Delta H_{f,298}^{\circ}$ Values

| Compound | energy(kcal/mol) ^c | relative (%) ^d | final value(kcal/mol) ^e |
|------------------------|-------------------------------|---------------------------|------------------------------------|
| C•H ₂ OC1 | -2.10 | 100.00 | -2.10 |
| CHClO--Cl ^a | -17.50 | 94.40 | -17.43 |
| CHClO--Cl ^b | -16.24 | 5.60 | |
| CCl ₂ O--Cl | -24.67 | 100.00 | -24.07 |

^a H-Cl anti staggered. ^b Cl-Cl anti staggered. ^c Energy of conformer = overall value in Table 6 + energy barrier; Energy barrier = energy of conformer- energy of most stable conformer ^d Relative (%) = conformer fraction ÷ total fraction; Conformer fraction = $e^{(-B/R^T)}$; B = Energy difference, R = 1.987 (cal/mol-K), T = 298 K. ^e Final value = $\Sigma(\text{Energy} \times \text{relative fraction})$

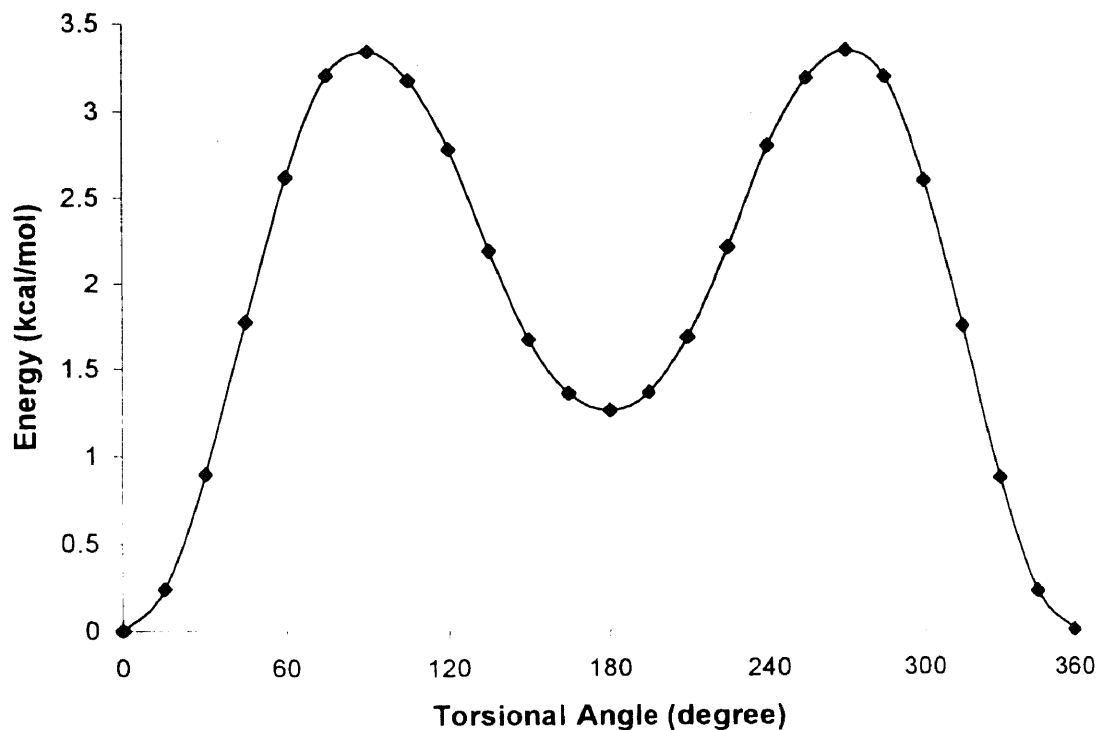


Figure 4.2. Potential energy for internal rotation about C-O bond of CHClO--Cl versus torsion angle (0=Optimized Geometry)

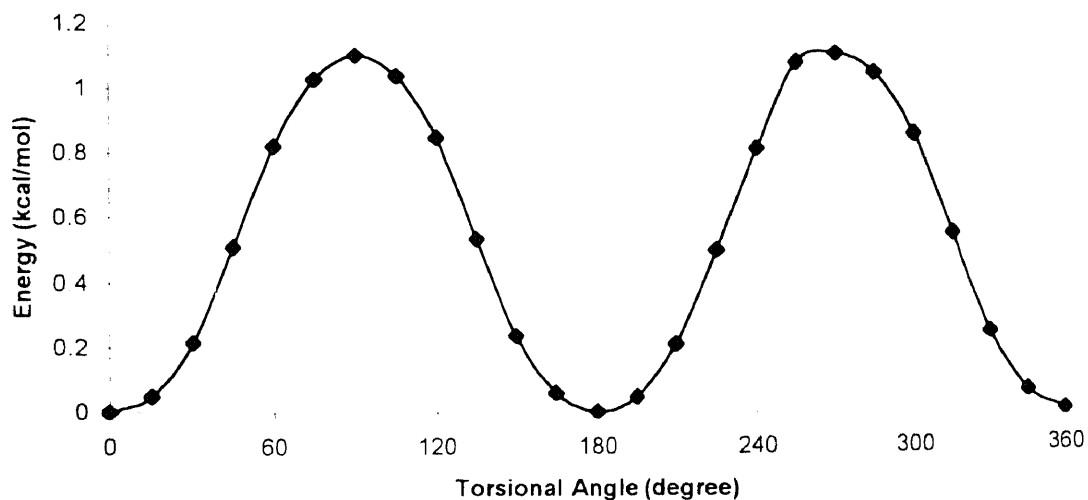


Figure 4.3. Potential energy for internal rotation about C-O bond of CCl₂O--Cl versus torsion angle (0=Optimized Geometry)

TABLE 4.11: Coefficients^a (kcal/mol) of Truncated Fourier Series Representation

Expansion for Internal Rotation Potentials

| Coefficients | CH ₂ O--Cl | CHClO--Cl | CCl ₂ O--Cl |
|----------------|-----------------------|-----------|------------------------|
| a ₀ | 3.148 | 1.989 | 0.538 |
| a ₁ | 0.023 | -0.466 | 0.005 |
| a ₂ | -3.379 | -1.377 | -0.566 |
| a ₃ | 0.006 | -0.158 | 0.000 |
| b ₁ | 0.000 | 0.002 | 0.000 |
| b ₂ | -0.020 | 0.012 | -0.017 |
| b ₃ | 0.000 | 0.002 | 0.000 |

^a Unit in kcal/mol. Values of rotational barriers computed using the B3LYP/6-31G(d,p) theory. Coefficients are calculated as follows: $V(\theta) = a_0 + a_1 \cos(\theta) + a_2 \cos(2\theta) + a_3 \cos(3\theta) + b_1 \sin(\theta) + b_2 \sin(2\theta) + b_3 \sin(3\theta)$.

TABLE 4.12. Ideal Gas Phase Thermodynamic Properties^a

| | | $11\Delta_f^\circ_{892}^b$ | $^\circ\Sigma_{892}^\circ$ | C_{p300} | C_{p400} | C_{p500} | C_{p600} | C_{p800} | C_{p1000} | C_{p1500} |
|-------------------------------------|-------------------|----------------------------|----------------------------|------------|------------|------------|------------|------------|-------------|-------------|
| CH ₂ Cl (2) ^e | TVR ^c | 26.75 | 58.61 | 10.08 | 11.45 | 12.53 | 13.38 | 14.66 | 15.64 | 17.3 |
| CH ₃ O- (3) | TVR | 4.10 ^c | 54.41 | 9.61 | 11.26 | 12.92 | 14.42 | 16.88 | 18.77 | 21.73 |
| CH ₂ ClO- | TVR | -4.51 | 64.68 | 12.18 | 14.27 | 15.99 | 17.38 | 19.42 | 20.86 | 23 |
| CHCl ₂ O- | TVR | -5.56 | 72.17 | 15.58 | 17.71 | 19.27 | 20.4 | 21.93 | 22.9 | 24.23 |
| CCl ₃ O- (3) | TVR | -7.49 | 76.85 | 19.8 | 21.65 | 22.8 | 23.56 | 24.44 | 24.9 | 25.4 |
| C-H ₂ O-Cl | TVR | | 65.37 | 11.93 | 13.01 | 14.15 | 15.23 | 17.07 | 18.5 | 20.75 |
| (2) | Int. ^f | | 2.9 | 1.82 | 2.02 | 2.16 | 2.25 | 2.27 | 2.17 | 1.81 |
| | Tot. | -2.1 | 68.27 | 13.75 | 15.03 | 16.31 | 17.48 | 19.34 | 20.67 | 22.56 |
| CHClO--Cl | TVR | | 74.74 | 14.41 | 15.82 | 16.99 | 17.95 | 19.4 | 20.42 | 21.91 |
| | Int. | | 6.48 | 3.2 | 2.67 | 2.11 | 1.65 | 1.05 | 0.7 | 0.33 |
| | Tot. | -17.5 | 81.22 ^h | 17.61 | 18.49 | 19.1 | 19.6 | 20.45 | 21.12 | 22.24 |
| C-Cl ₂ O--Cl | TVR | | 81.12 | 17.67 | 19.17 | 20.18 | 20.91 | 21.86 | 22.44 | 23.15 |
| (2) | Int. | | 8.42 | 1.2 | 0.8 | 0.56 | 0.41 | 0.25 | 0.16 | 0.08 |
| | Tot. | -24.67 | 89.54 | 18.87 | 19.97 | 20.74 | 21.32 | 22.11 | 22.6 | 23.23 |

^a Thermodynamic properties are referred to standard state of an ideal gas of pure enantiomer at 1atm. Units enthalpy in kcal/mol; entropy and heat capacity in cal/mol·K. ^b $\Delta H_f^\circ_{298}$ is the average value of CBS-Q level considering the statistical contribution of rotational conformers in kcal/mol excluding reaction scheme 4. (see footnote e in Table 6 and final value in Table 8) ^c Reference 32. ^d Units in cal/mol K. ^e The sum of contributions from translations, external rotations, and vibrations. ^f Contributions from internal rotation about C-O bond ^g Symmetry number is taken into account for S°_{298} . ^h Entropy corrections for C•HClO-Cl mixing of 0.43 are not included above.

4.3.3 Rotational Barriers

Potential barriers for internal rotations of $\text{CH}_2\text{O--Cl}$, CHClO--Cl , and $\text{CCl}_2\text{O--Cl}$ are calculated at the B3LYP/6-31G(d, p) level. Potential energy as function of torsion angle, by varying the torsion angle at 15° intervals and allowing the remaining molecular structural parameters to be optimized. The geometry and harmonic vibrational frequencies are calculated for all rotational conformers at the B3LYP/6-31G(d, p) level. The barriers for internal rotations are calculated from the differences between the total energy of each conformer as a function of torsion angle. Potential energy vs. torsion angle diagrams for internal rotations about C-O bond of the formaldehyde and Cl atom complex radicals are shown in Figures 4.1, 4.2, and 4.3. The values of the coefficients of the Fourier expansion, a_i and b_i in equation 1 are listed in Table 4.11.

The calculated symmetric rotational barrier for $\text{CH}_2\text{O--Cl}$ is shown in Figure 4.1. The calculation shows a rotational barrier of 0.01 kcal/mol and that the barrier is uniform for the two hydrogens. Figure 4.2 shows calculated rotational barriers for CHClO--Cl . The H-Cl eclipsed planar is 2.08 kcal/mol higher in energy than the Cl-Cl planar conformer. The non planar rotational barrier is 3.34 kcal/mol. Calculated rotational barriers and conformer energies in $\text{CCl}_2\text{O--Cl}$ are shown in figure 4.3. The non planar rotational barrier is 0.002 kcal/mol.

4.3.4 Entropy, S°_{298} and Heat Capacity, $C_p(T)$ from 300 to 1500 K

S°_{298} and $C_p(T)$ calculations use the B3LYP/6-31g(d, p) determined geometry and frequencies with values summarized in Table 3.13. TVR represents the sum of the

contributions from translations, external rotations and vibrations for S_{298}° and $C_p(T)$. The torsion frequency corresponding to the internal rotor is not included in TVR. Instead, a more exact contribution from the hindered rotation is calculated and listed under I.R. in Table 4.12. I.R. represents the contributions from internal rotation about C-O bond for S_{298}° and $C_p(T)$'s for formaldehyde (CH_2O)~Cl complex or chloro-formaldehyde (CHClO)~Cl, (CHCl_2O)~Cl complex radicals. $R = 1.987$ cal/mol K, and σ is symmetry number, Entropy of mixing = $-R \sum \{(n_i) \times \ln(n_i)\}$; where n_i is fraction of conformer i. Mixing entropy is included in CHClO--Cl , chloro-formaldehyde~Cl atom complex radical as $-R\{0.944 \times \ln(0.056) + 0.056 \times \ln(0.056)\} = 0.43$. There is no published data on entropy and heat capacity values for $\text{CH}_2\text{ClO}\bullet$, $\text{CHCl}_2\text{O}\bullet$, $\text{CCl}_3\text{O}\bullet$, $\text{CH}_2\text{O--Cl}$, CHClO--Cl , or $\text{CCl}_2\text{O--Cl}$.

4.4 Summary

Thermochemical Properties of methoxy and formaldehyde-Cl atom complex radicals are calculated using density functional and *ab initio calculations*. Enthalpies, $\Delta H_f^\circ_{298}$ are presented as average data from the selected reaction schemes (up to seven) based on the composite CBS-Q calculation level results considering statistical distribution of rotational conformers. CBS-Q calculation values of $\Delta H_f^\circ_{298}$ show consistency for all reaction schemes, which is not observed in the B3LYP/6-31G(d, p), B3LYP/6-311+G(3df, 2p), QCISD(T)/6-31G(d, p) calculations. Entropies, S°_{298} and heat capacities, $C_p(T)$ from 300 K to 1500 K are reported. Torsion potentials are presented for intramolecular rotations. The hypochlorite – methyl radicals ($C\bullet H_2OCl$, $C\bullet HClOCl$, $C\bullet Cl_2OCl$) does not exist, instead, form formaldehyde and Cl atom complex radicals ($CH_2O\cdots Cl$, $CHClO\cdots Cl$, $CCl_2\cdots OCl$).

CHAPTER 5

KINETIC STUDY FOR THE REACTION OF METHYL RADICAL AND CHLORINE MONOXIDE

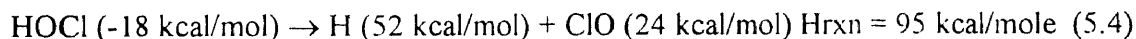
5.1 Overview

Thermochemical properties and thermochemistry of the reaction path are reported by CBS-Q//B3LYP/6-31g(d,p) calculations and methods fully described in chapters 1 to 3. Stable molecule and radical structures are optimized in B3LYP/6-31G(d,p) for the geometries, vibrational frequencies and rotational constants. The total energies are calculated using B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q methods with single point calculation. The reaction system ($\text{CH}_3 + \text{ClO} \leftrightarrow \text{CH}_3\text{OCl}^* \leftrightarrow \text{Products}$) is important because monochlorine monoxide radical (ClO)¹⁻⁴ is a known chemical that strongly effects ozone depletion in the Antarctic and Arctic polar regions after nocturnal winters. There is a significant amount of literature data on methyl and methyl halide radicals and chlorine oxide radical. However, chlorinated radicals are relatively unstable and some of the kinetics have been not studied. Atomic chlorine reacts with ozone to form the chlorine oxide radical plus O_2 . The chlorine oxide radical (ClO) is not as active as hydroxyl radical (OH), hydrogen atom (H), or oxygen atom (O) and is not rapidly converted at low temperature,

Chlorine Oxide Catalytic Destruction of Ozone Cycle



Because the H-OCl bond formed in ClO abstraction of H is only 94 kcal/mol.



This chlorine oxide radical (ClO) is known to be important in destruction of the ozone layer. Because of its low reactivity it also reacts to form alkyl hypochlorite with alkyl radical.^{3,4}



In the case of the reaction system, ($\text{CH}_2\text{Cl} + \text{ClO} \leftrightarrow \text{CH}_2\text{ClOCl} \leftrightarrow \text{Products}$) and ($\text{CHCl}_2 + \text{ClO} \leftrightarrow \text{CHCl}_2\text{OCl} \leftrightarrow \text{Products}$), there is no experimental data. In this study, kinetics for the reactions of monochlorine monoxide radical (ClO) with methyl and chloro methyl radicals are analyzed by using Quantum Rice-Ramsperger-Kassel (QRRK) theory for $k(T)$ and a modified strong collision approach for falloff. The reaction paths that have transition state (TS) are studied using the canonical Transition State Theory (TST);



5.2. RRK Theory

Most modern theories of unimolecular reaction rates, including the Slater theory, the RRK (Rice and Ramsperger and Kassel) theory and the RRKM (Marcus Rice) theory, are based on the fundamental Lindemann mechanism involving collision energization of the reactant molecules.

The Slater theory⁸¹ is a dynamical theory concerned with the detailed treatment of molecular vibrations and the behavior of particular molecular coordinates as a function of time. A reaction is postulated to occur in Slater theory when a chosen coordinate achieves a critical extension by the phase-coincidence of certain modes of vibration. The rate

constant of an energized molecule dissociation to product(s) (k_a) is related to a “specific dissociation probability” L ; this is the probability that a frequency or vibration mode with which a chosen coordinate in the molecule reaches a critical value, and can be calculated for the case in which the vibrations of the molecule are assumed to be harmonic. The specific dissociation probability (L) is a function of the energies in the individual oscillators and not simply of the total energy E of the molecule.

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

The Marcus Rice theory, is known as RRKM theory since its basic model is RRK model.⁹² The main developments are the calculation of the rate constant of energization by quantum-statistical mechanisms and the application of ideas related to the Absolute Rate Theory for the calculation of the rate of conversion of energized molecules into products.

5.2.1 Lindemann-Hinshelwood Mechanism for Unimolecular Reactions

The theory known as Lindemann theory, which forms the basis for all modern theories of unimolecular reactions, has been developed from ideas published almost simultaneously by Lindemann⁸² and Christiansen⁸³. The concept is that: (a) By collision, a certain fraction of the molecules become energized, i.e., the molecule gains energy in excess of a critical quantity E_0 . The rate of the energization process depends upon the rate of

bimolecular collision. (b) This energized molecule terms A^* . 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_2 by assuming that every collision of A^* leads to a de-energized start. (c) There is a time-lag between the energization and unimolecular dissociation or isomerization of the energized molecules.

The Lindemann theory suggests the unimolecular dissociation also occurs with a rate constant k_3 independent of the energy content of A^* . The whole idea can be expressed by the following equations.



where M can represent a product molecule, an added “inert” gas molecule, or a second molecule of reactant. 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. By application of the steady-state hypothesis to the concentration of A^* , the unimolecular rate constant and high pressure limit and low pressure limit rate and rate constants are then given as follows.

$$\text{High pressure limit rate} \quad v_\infty = (k_1 k_3 / k_2) [A] = k_\infty [A] \quad (5.9)$$

$$\text{Low pressure limit rate} \quad v_0 = v_{\text{bim}} = k_1 [A] [M] = k_{\text{bim}} [A] [M] \quad (5.10)$$

$$\text{Unimolecular rate constant} \quad k_{\text{uni}} = (k_1 k_3 / k_2) / (1 + k_3 / k_2 [M]) = k_\infty / (1 + k_\infty / k_1 p) \quad (5.11)$$

$$\text{Fall-off} \quad k_{\text{uni}} / k_\infty = 1 / (1 + k_\infty / k_1 p) \quad (5.12)$$

The Lindemann theory predicts a change on the order of the initial rate of a unimolecular reaction with respect to concentration at low pressure. The rate constant, k_1

in the original Lindemann theory is taken from the collision theory expression ($k_1 = Z_1 \exp(-E_0/kT)$ with $Z_1 = (\sigma_d^2 N_A / R)(8\pi N_A k / \mu)^{1/2} (1/T)^{1/2}$, where Z_1 will be in $\text{Torr}^{-1} \text{s}^{-1}$ (consistent with $[M]$ in Torr and k_3 in s^{-1}) when σ_d = collision diameter in cm; μ = reduced molar mass in $\text{g-mol}^{-1} = (1/M_A + 1/M_B)^{-1}$; T = temperature in K; $N_A = 6.0225 \times 10^{23} \text{ mol}^{-1}$; $R = 6.2326 \times 10^4 \text{ cm}^3 \text{-Torr-K}^{-1} \text{-mol}^{-1}$; $k = 1.3805 \times 10^{-16} \text{ erg-K}^{-1}$.

Based on Lindemann's suggestion that k_1 could be increased by assuming that the required energy (energize molecules) could be drawn in part from the internal degrees of freedom (mainly vibration) of the reactant molecule, Hinshelwood⁸⁴ increases k_1 by using a much higher chance of a molecule possessing total energy $\geq E_0$ in s classical degrees of freedom, $k_1 = Z_1 \exp(-E_0/kT) = [Z_1/(s-1)!] (E_0/kT)^{s-1} \exp(-E_0/kT)$, when $\exp(-E_0/kT) = (E_0/kT)^{s-1} \exp(-E_0/kT)/(s-1)!$ and replace k_1 and A^* as $k_1(E \rightarrow E^* + \delta E)$ and $A^*_{(E \rightarrow E^* + \delta E)}$ in mechanism above.

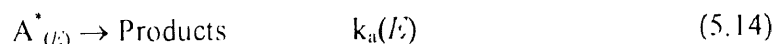
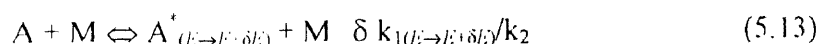
5.2.2 RRK Theory of Unimolecular Reactions

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_a (k_1) for the conversion of energized molecules into activated complexes and hence products. One of accepted theories is the RRK theory, a statistical theory used in this thesis because it is more computable and needed parameters are readily obtained.

The RRK theory was developed virtually simultaneously by Rice and Ramsperger⁸⁵ and Kassel⁸⁶⁻⁸⁸ with very similar approaches. Both consider that for reaction to occur a critical energy E_0 must become concentrated in one part (one vibration mode) of the molecule. They used the basic Lindemann-Hinshelwood mechanism of

collision energization and de-energization, but assume more realistically that the rate constant of conversion of an energized molecule to products is proportional to a specific probability. A finite statistical probability that E_0 is found in the relevant part of the energized molecule which contains E greater than E_0 . E of the molecule under consideration is assumed to be rapidly redistributed around the molecule. Obviously this probability will increase with E and make k_a a function of its energy content.

The difference between these two models is twofold. Firstly, Rice and Ramsperger used classical statistical mechanics throughout, while Kassel used classical method but also developed a quantum treatment; the latter is very much more realistic and accurate. Secondly, different assumptions were made about the part of the molecule into which the critical energy E_0 has to be concentrated. 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 kinetic calculations performed in this thesis. The mechanism of RRK theory is written as:



The quantum version of version of Kassel's theory is based on the calculation of the probability that a system of s quantum oscillators, while the classical version considered s classical oscillators, with total energy E should have energy $\geq E_0$ in one chosen oscillator. In Kassel's version, it assumes that there are s identical quantum oscillators, all having frequency ν and hence energy $h\nu$. The critical energy E_0 is expressed as the critical number of quanta, $m = E_0/h\nu$, and the energy E of energized molecule is expressed as a total of n quanta with $n = E/h\nu$. The probability that one

oscillator contains at least m quanta, probability (energy $\geq m$ quanta in one chosen oscillator) is then equal to:

$$\text{Probability (energy } \geq m \text{ quanta in one chosen oscillator)} = \frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!}$$

Hence,

$$k_n(nh\nu) = A \frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!} \quad (5.15)$$

where A is proportion constant here and actually the same as the classical determination.

A is the Arrhenius factor in his representation of k_{rate} : $k = A \cdot \exp(-E_a/RT)$

Now the $k_1(E)$ in the Hinshelwood expression is derived; it refers to energization into a specific quantum state rather than into an energy range E to $E+\delta E$, as

$$k_1(nh\nu) = k_2 \alpha^{n-m+1} \frac{(n+s-1)!}{n!(s-1)!} \quad (5.16)$$

where $\alpha = \exp(-h\nu/kT)$.

5.2.3 Chemical Activation Reactions

Molecules undergo thermal unimolecular reactions as a result of energization by molecular collision in normal thermal collisional (non chemical) activation reactions.

This molecular collision at a given temperature produces energized molecules with an equilibrium distribution of energy which enables or produces the fraction of molecules energized into a particular energy range or quantum state. Other 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 amount of excess of energy contained in energized

adduct often makes chemical activation reactions much more important in a particular system, and a much different treatment for the rate of conversion decomposition of energized adduct to product (including back to reactant) which is very competing with the rate of its collision stabilization.

A example of chemically activated reaction system is the association of CH_3 with ClO . The methyl radical, CH_3 , reacts with ClO to form a chemically activated, energized adduct $[\text{CH}_3\text{OCl}^*]$. This process of forming this energized (chemically activated) adduct is much more efficient than that by thermal molecular collision, and the adduct contains the excess energy from the chemical reaction. The energized adduct $[\text{CH}_3\text{OCl}^*]$ could react back to reactant $\text{CH}_3 + \text{ClO}$, or could directly go to products $\text{H} + \text{CH}_2=\text{O} + \text{Cl}$ via formaldehyde-Cl atom complete radical and hydrogen. Both are simple dissociation or simple bond cleavage. Other reactions include molecular HCl elimination forming formaldehyde, $\text{CH}_2\text{O} + \text{HCl}$ or Cl elimination (cleavage of the weak $\text{O}-\text{Cl}$ bond).

The basic idea of the treatment of a chemical activation system is that a vibration excited molecule A^* by an association of reactants can reform reactants with a rate constant $k'_{-a}(E)$, form decomposition products with a rate constant $k_a(E)$ or be de-energized to stable molecules A by collisions with bath gas $k_{\text{stab}}(m)$.

On 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

Suppose that the fraction of molecules which are energized per unit time into the energy range between E and $E+\delta E$ is $f(E)\delta E$. To simplify, one can consider only one decomposition path (back to reactant can be considered as one of decomposition path),

then the fraction of A^* decomposing (say path D) compared with those stabilized (say path S) is $k_a(E)/[k_a(E)+\omega]$. The fraction of molecules in the energy range between E and $E+\delta E$ decomposing to products is therefore $\{k_a(E)/[k_a(E)+\omega]\}f(E)\delta E$, and the total number of molecules decomposing per unit time (D), at all energies above the critical energy E_0 , is:

$$D = \int_{E_0}^{\infty} \frac{k_a(E)}{k_a(E) + \omega} f(E) dE \quad (5.17)$$

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

$$S = \int_{E_0}^{\infty} \frac{\omega}{k_a(E) + \omega} f(E) dE \quad (5.18)$$

Considering an average rate constant $\langle k_a \rangle$ for all energies above E_0 , there have:

$$\frac{\langle k_a \rangle}{\omega} = \frac{D}{S} = \frac{\text{No. molecules decomposing per unit time}}{\text{No. of molecules being stabilized per unit time}} \quad (5.19)$$

So,

$$\langle k_a \rangle = \omega \frac{\int_{E_0}^{\infty} \{k_a(E) / [k_a(E) + \omega]\} f(E) dE}{\int_{E_0}^{\infty} \{\omega / [k_a(E) + \omega]\} f(E) dE} \quad (5.20)$$

The $f(E)$ is the distribution function of energized molecules in the energy range between E and $E+\delta E$. In thermal energization systems, this distribution function is simply the thermal quantum Boltzmann distribution $K(E)$ and the rate of energization into the energy range between E and $E+\delta E$ is $K(E)\delta E = \delta k_1/k_2$. For the chemically activated system described here, the distribution function can be derived by applying the principle of detailed balance to the reverse process to reactants. Consider a situation in which the processes D and S can be ignored and equilibrium is established between A^* and reactants, then the fraction of molecules with energy between E and $E+\delta E$ is Boltzmann

distribution $K(E)\delta E$, so the rate of dissociation to reactants is then $k'_a(E)K(E)\delta E$, 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 energization to all levels above the minimum energy E_{\min} (the minimum energy of A^*) is:

$$\text{Total rate of energization} = \int_{E_{\min}}^{\infty} k'_a(E)K(E)dE \quad (5.21)$$

Therefore, the distribution function is given by:

$$f(E)\delta E = \frac{k'_a(E)K(E)\delta E}{\int_{E_{\min}}^{\infty} k'_a(E)K(E)dE} \quad (5.22)$$

The $f(E)\delta E$ can be incorporated into QRRK theory for $k_a(E)$ and $k_i(E)$ serves as a basis for the calculations for chemical activation reaction systems.

5.2.4 QRRK Analysis for Unimolecular and Chemical Activation Reactions

QRRK analysis, as initially presented by Dean⁸⁹⁻⁹¹ combined with the modified strong collision approach of Gilbert et al⁹²⁻⁹⁴, are used 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, (σ (Angstroms) and ϵ/k (Kelvin)), and (4) molecular weight of adduct species. All these

input parameters are readily available or straightforward to estimate, but it is impossible to estimate them accurately.

5.2.5 Input Information Requirements for QRRK Calculation

Pre-exponential factors ($A_{\infty}s$), are calculated using canonical TST⁹⁵ along with CBS-Q//B3LYP/6-31G(d,p), determined entropies of intermediates and TSs for the reactions where thermodynamic properties of TS are available. High-pressure limit pre-exponential factors for combination reactions are obtained from the literature and from trends in homologous series of reactions. Activation energies come from complete basis model calculations CBS-Q plus evaluated thermodynamic properties and literature data.

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.^{96,97} These have been shown by Ritter to accurately reproduce molecular heat capacities, $C_p(T)$, and by Bozzelli et al.⁹⁷ to yield accurate ratios of density of states to partition coefficient, $\rho(E)/Q$.

Lennard-Jones parameters, sigma (Angstroms) and ϵ/k (Kelvins), are obtained from tabulations⁹⁸ and from a calculation method based on molar volumes and compressibility.⁹⁹ 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.

5.2.6 Recent Modifications to the Quantum RRK Calculation Include

(a) Use of a manifold of three frequencies plus incorporation of one external rotation for the density of states, $\rho(E)/Q$ and in calculation of $k(E)$. (b) The Leonard-Jones collision frequency Z_{LJ} is now calculated by $Z_{LJ} = Z \Omega(2,2)$ integral^{98, 99} obtained from fit of Reid et al.⁹⁹.

The QRRK analysis for $k(E)$ with modified strong collision and a constant E_E for falloff has been used previously to analyze a variety of chemical activation reaction systems, Westmoreland et al.^{100,101}, Dean et al.¹⁰², and Bozzelli et al.^{103, 104} There are a number of recent publications by other researchers that utilize the QRRK formalism with a more exact calculation E_E in modified strong collision analysis^{105,110} or utilize just a QRRK formalism.^{111, 112} It is shown to yield reasonable results in these applications, and provides a framework by which the effects of both temperature and pressure can be estimated for complex chemical activation or unimolecular dissociation reaction systems.

5.3. Thermodynamic Properties Using *ab initio* Calculations

Enthalpy, $\Delta H_f^\circ_{298}$, entropy, S°_{298} and heat capacities $C_p(T)$, from 300 to 1500 K are determined for methyl hypochlorites (CH_3OCl), formaldehyde~Cl atom complex radical ($\text{CH}_2=\text{O}--\text{Cl}$) and transition state (TS) using density functional B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p) and *ab initio* QCISD(T)/6-31G(d,p) and CBS-Q calculation methods.²⁵⁻³⁰ Thermodynamic properties of CH_3 ,³² CH_2O ,³² HCl ,³² ClO ,³² Cl ,³² and ClO^\bullet ³² are taken from literature data. Enthalpy, $\Delta H_f^\circ_{298}$, for methoxy radical (CH_3O) is used from literature data,⁷⁸ and its entropy, S°_{298} and heat capacities $C_p(T)$, from 300 to 1500 K used are the values evaluated in this study, in chapter 4.

Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) density functional calculation level, with single point calculations for energy at the B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q levels of calculation. Vibration frequencies are scaled by 0.9806³¹ for zero point energies (ZPVE) and for thermal corrections. Enthalpies of formation ($\Delta H_f^\circ_{298}$) for transition state is calculated in CBS-Q//B3** by the difference of the total energy for CH₃OCl and transition state (TS).

5.4 QRRK Input Parameter

5.4.1 CH₃OCl → CH₂O + HCl

Methyl radical (CH₃) reacts with chlororine monoxide to form methyl hypochlorite. This adduct, methyl hypochlorite goes to formaldehyde and hydrogen chloride through a saddle point transition state (TS). It is the path way, which has transition state (TS) and pre-exponential factors (A_∞ s), calculated using canonical TST¹⁶ along with CBS-Q//B3LYP/6-31G(d,p), determined enthalpies of intermediates and TS for the reaction (CH₃OCl → CH₂O + HCl) system. B3LYP/6-31G(d,p) is used to determine entropies and heat capacities. The thermodynamic properties are listed in Table 5.1. The frequency, moment of inertia, and geometry of transition state is displayed in Table 5.2. We calculate three parameters (A, n, and Ea) for the model equation of $A(T) = A \times T^n \times \exp(-E_a/RT)$; $A = 2.58 \times 10^{10}$ (1/sec), $n = 1.0$, $E_a = 54.2$ (kcal/mol)

TABLE 5.1. Ideal Gas Phase Thermodynamic Properties^a at 298 K

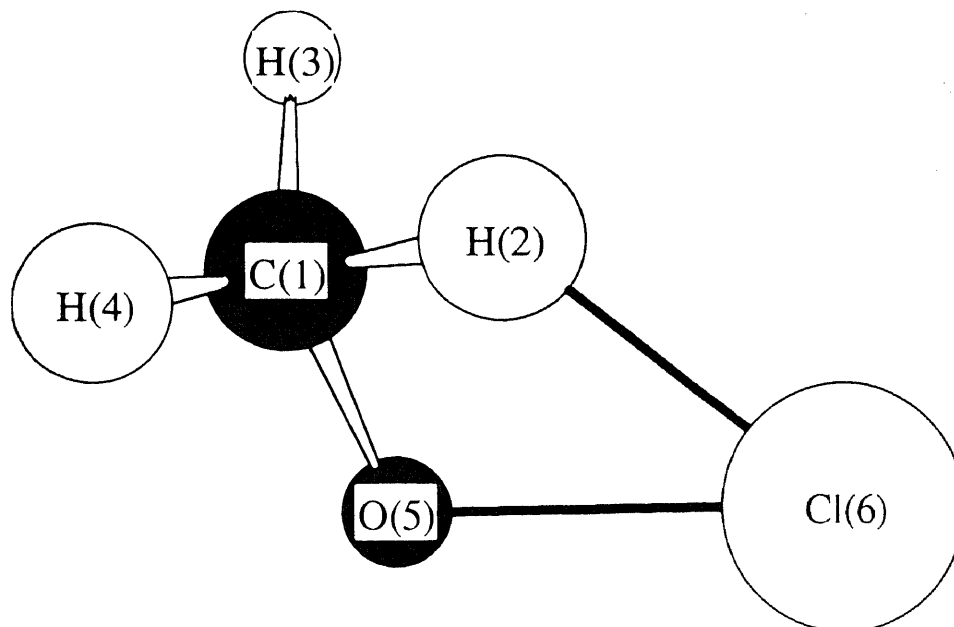
| SPECIES | $H_{\Delta}^{\circ}_{892}^{\beta}$ | $\Delta\Sigma^{\circ}_{892}^{\chi}$ | C_{p300} | C_{p400} | C_{p500} | C_{p600} | C_{p800} | C_{p1000} | C_{p1500} | Ref ^b |
|-----------------------|------------------------------------|-------------------------------------|------------|------------|------------|------------|------------|-------------|-------------|------------------|
| CH ₃ | 34.82 | 46.41 | 9.26 | 10.05 | 10.82 | 11.54 | 12.89 | 14.09 | 16.29 | 32 |
| ClO | 24.29 | 53.79 | 8.24 | 8.44 | 8.58 | 8.69 | 8.83 | 8.92 | 9.05 | 32 |
| CH ₃ OCi | -15.41 | 65.19 | 13.59 | 15.73 | 17.63 | 19.23 | 21.73 | 23.61 | 26.57 | d |
| CH ₂ =O~Cl | -1.97 | 68.27 | 13.75 | 15.03 | 16.31 | 17.48 | 19.34 | 20.67 | 22.56 | d |
| H | 52.1 | 27.42 | 4.97 | 4.97 | 4.97 | 4.97 | 4.97 | 4.97 | 4.97 | 32 |
| CH ₃ O• | 4.1 | 54.41 | 9.61 | 11.26 | 12.92 | 14.42 | 16.88 | 18.77 | 21.73 | c |
| Cl | 28.99 | 39.48 | 5.22 | 5.37 | 5.44 | 5.45 | 5.39 | 5.31 | 5.18 | 32 |
| HCl | -22.06 | 44.67 | 6.96 | 6.97 | 7 | 7.07 | 7.29 | 7.56 | 8.14 | 32 |
| CH ₂ O | -27.7 | 52.33 | 8.47 | 9.38 | 10.45 | 11.52 | 13.37 | 14.81 | 17.01 | 32 |
| TS | 38.8 | 65.47 | 13.52 | 15.69 | 17.63 | 19.3 | 21.86 | 23.69 | 26.36 | d |

^a Thermodynamic properties are referred to standard state of an ideal gas of pure enantiomer at 1atm. Units enthalpy in kcal/mol; entropy and heat capacity in cal/mol·K. ^b $AlI_1^{\circ}_{298}$ is the average value of CBS-Q level in kcal/mol (see footnote e in Table 2.13 and 4.13). ^c Units in cal/mol·K. ^d This study in Table 4.13. ^e $AlI_1^{\circ}_{298}$ is from Reference 78; entropy and heat capacity come from 4.13 in this study.

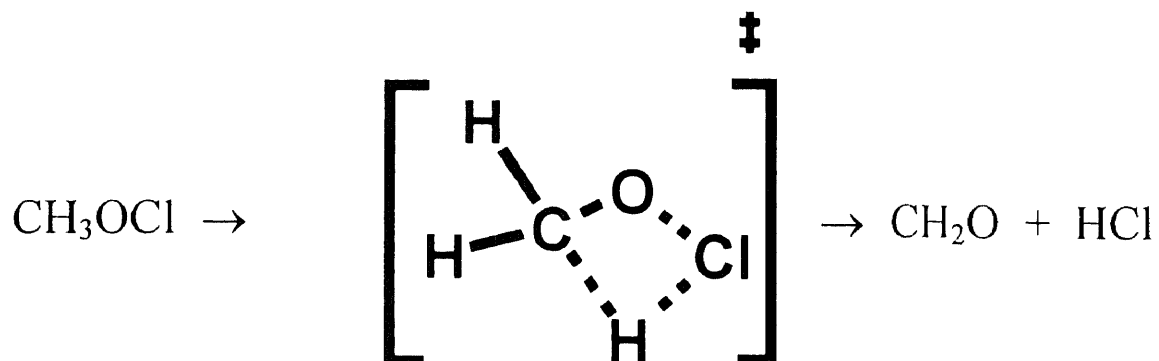
TABLE 5.2-a. Vibrational Frequencies (cm⁻¹) and Rotational constants (Ghz) for TransitionState (CH₃OCi → TS → HCl + CH₂O)

| Frequencies | | TS | |
|-------------|-------|----|------------|
| | v(1) | | -1906.7089 |
| | v(2) | | 307.5896 |
| | v(3) | | 404.7409 |
| | v(4) | | 493.3063 |
| | v(5) | | 932.8767 |
| | v(6) | | 1151.5984 |
| | v(7) | | 1232.5084 |
| | v(8) | | 1258.5843 |
| | v(9) | | 1522.1827 |
| | v(10) | | 1739.9088 |
| | v(11) | | 2946.8725 |
| | v(12) | | 3042.9863 |

| TS | Rotational constants (Ghz) | | |
|--------------------|----------------------------|---------|---------|
| Calculation method | A | B | C |
| B3LYP/6-31G(d,p) | 32.18664 | 4.69024 | 4.21574 |

Table 5.2-b. Geometry of Transition State ($\text{CH}_3\text{OCl} \rightarrow \text{TS} \rightarrow \text{HCl} + \text{CH}_2\text{O}$)

| Name | Definition | Value |
|----------|------------|----------|
| H-C | R(3,1) | 1.103 |
| H-C | R(4,1) | 1.103 |
| O-C | R(5,1) | 1.304 |
| Cl-H | R(6,2) | 1.919 |
| Cl-O | R(6,5) | 2.410 |
| H-C-H | A(3,1,4) | 117.218 |
| H-C-O | A(3,1,5) | 116.889 |
| H-C-O | A(4,1,5) | 116.889 |
| C-O-Cl | A(1,5,6) | 92.131 |
| H-O-Cl | A(2,6,5) | 49.524 |
| Cl-O-C-H | D(6,5,1,3) | 106.842 |
| Cl-O-C-H | D(6,5,1,4) | -106.842 |
| H-Cl-O-C | D(2,6,5,1) | 0.000 |



Transition State

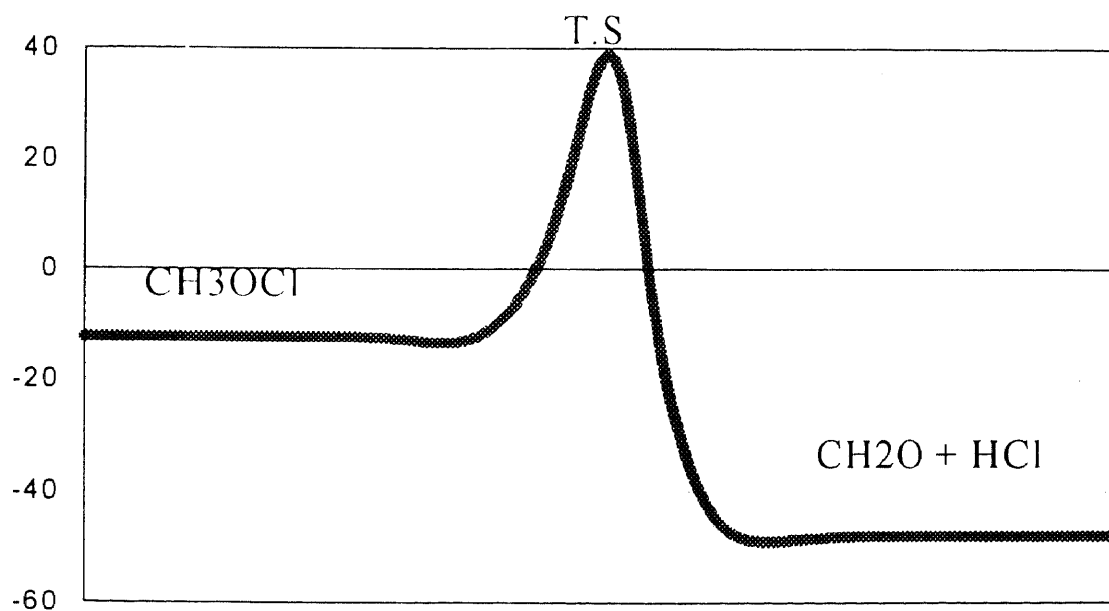


Figure 5.1. Potential energy diagram in the reaction ($\text{CH}_3\text{OCl} \rightarrow \text{TS} \rightarrow \text{CH}_2\text{O} + \text{HCl}$).

TABLE 5.3. Total Energies at Different Levels of Theory, Composite CBS-Q, Zero Point Vibrational Energy and Thermal Correction (in Hartree)

| | Total energies | | | ZPE ^d | Therm.cor ^e |
|----|------------------------|-----------------------|--------------------|------------------|------------------------|
| | B3lyp6-31 ^a | Qcisd(t) ^b | CBS-Q ^c | | |
| TS | -575.17186 | -574.29334 | -574.54311 | 0.07836 | 0.00525 |

^{a,b} Total energies are in Hartree at 0K; ^a B3LYP/6-31G(d,p), ^b QCISD(T)/6-31G(d,p). ^c CBS-Q enthalpies are in Hartree, which include thermal correction and zero-point energy at 298.15 K. ^d ZPE is in Hartree and scaled by 0.9806. ^e Thermal corrections are in Hartree.

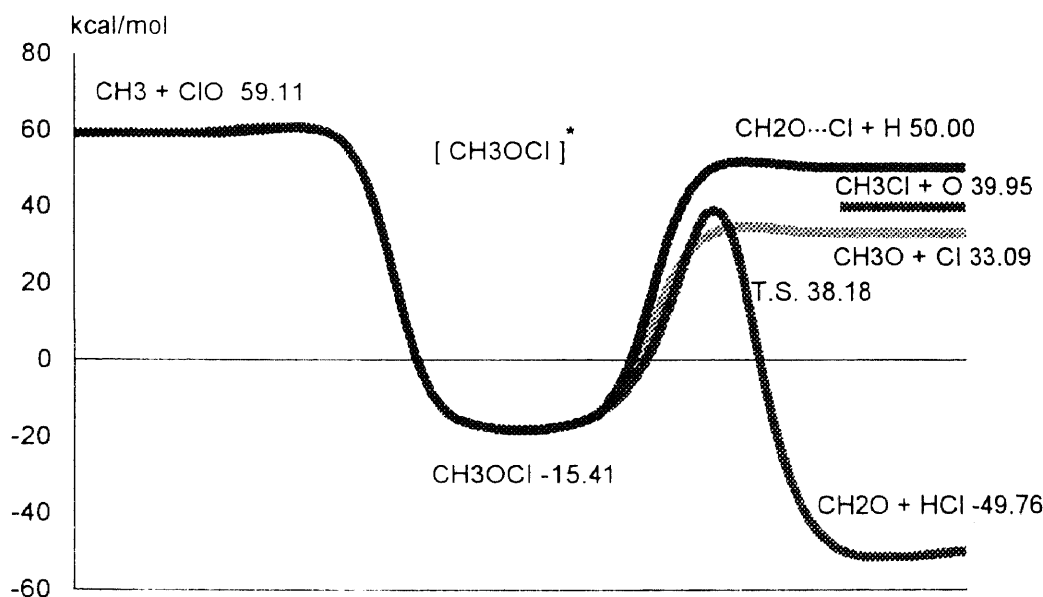


Figure 5.2. Potential energy diagram in the reaction of methyl radical and chloro monoxide ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl} \rightarrow \text{Products}$).

Table 5.4. QRRK Input Parameter^a for the Reaction of Methyl radical and Chlorine Oxide

| | A | n | Ea | Ref |
|---|----------|--------|--------|------------|
| k1 | | | | |
| $\text{CH}_3 + \text{OCl} \rightarrow \text{CH}_3\text{OCl}$ | 7.83E+13 | 0 | 0 | 8 |
| $\text{CH}_3\text{OCl} \rightarrow \text{CH}_3 + \text{OCl}$ | 2.51E+16 | 0 | 74.61 | b |
| k2 | | | | |
| $\text{CH}_3\text{O} + \text{Cl} \rightarrow \text{CH}_3\text{OCl}$ | 6.03E+13 | 0 | 0 | 79 |
| $\text{CH}_3\text{OCl} \rightarrow \text{CH}_3\text{O} + \text{Cl}$ | 7.35E+14 | 0 | 48.84 | b |
| k3 | | | | |
| $\text{CH}_2=\text{OCl} + \text{H} \rightarrow \text{CH}_3\text{OCl}$ | 1.00E+14 | 0 | 0 | 80 |
| $\text{CH}_3\text{OCl} \rightarrow \text{CH}_2=\text{O} + \text{Cl} + \text{H}$ | 6.98E+15 | 0 | 67.03 | b |
| k4 | | | | |
| $\text{CH}_3\text{OCl} \rightarrow \text{HCl} + \text{CH}_2\text{O}$ | 2.59E+10 | 0.9907 | 54.225 | CBSQ//B3** |

^a $k = AT^n \cdot \text{Exp}(-E_a/RT)$ ^b Microscopic reversibility, L.J Parameter of CH_3OCl : $\sigma = 4.63 \text{ \AA}$, $e/k = 380$. Bath gas = N_2 .

5.4.2 $\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl}$

The reaction $\text{CH}_3 + \text{ClO}$ system is a chemically activated reaction system. The methyl radical, CH_3 , associates with ClO to form a chemically activated, energized adduct $[\text{CH}_3\text{OCl}]^*$. The adduct contains excess energy from the chemical reaction equal to the energy of the new bond formed. The energized adduct $[\text{CH}_3\text{OCl}]^*$ could go back to reactants $\text{CH}_3 + \text{ClO}$, or could directly go to products $\text{H} + \text{CH}_2=\text{O} + \text{Cl}$ via formaldehyde~Cl atom complete radical and hydrogen or to $\text{Cl} + \text{CH}_3\text{O}\bullet$ via a Cl elimination. Both are simple dissociation or simple bond cleavage. Other reactions include molecular HCl elimination forming formaldehyde, $\text{CH}_2\text{O} + \text{HCl}$ or Cl elimination (cleavage of the weak O~Cl bond). The energized adduct $[\text{CH}_3\text{OCl}]^*$ can stay as CH_3OCl in the well in the Figure 5.2.

We use the experimental kinetic data for $\text{CH}_3 + \text{ClO} \rightarrow \text{Products}$, $A = 7.83 \times 10^{13}$ ($\text{cm}^3/\text{mol}\cdot\text{sec}$) from Biggs,⁸ et. al.. They used laser induced fluorescence spectroscopy at

298 K from 1 to 3 torr in He bath gas. We calculate A and Ea for the reverse reaction, $\text{CH}_3\text{OCl} \rightarrow \text{CH}_3 + \text{ClO}$; $A = 2.50 \times 10^{16}$ (1/sec) and $E_a = 74.6$ (kcal/mol).

5.4.3 $\text{CH}_3\text{OCl} \rightarrow \text{CH}_3\text{O} + \text{Cl}$

The reaction of methyl radical and chloro monoxide forms methyl hypochlorite (CH_3OCl) and this adduct react further to $\text{Cl} + \text{CH}_3\text{O}\bullet$ via a O-Cl cleavage. We use the experimental kinetic data for the assumed reaction $\text{CH}_3\text{O} + \text{Cl} \rightarrow \text{HCl} + \text{CH}_2\text{O}$ for the reaction, $\text{CH}_3\text{O} + \text{Cl} \rightarrow \text{CH}_3\text{OCl}$; $A = 6.03\text{E}13$ ($\text{cm}^3/\text{mol}\cdot\text{sec}$) from Jungkamp,⁷⁹ et. al.. They used laser induced fluorescence spectroscopy at 300 K from 1.9 to 7.5 torr with He bath gas. We calculate A and Ea for the reverse reaction, $\text{CH}_3\text{OCl} \rightarrow \text{CH}_3\text{O} + \text{Cl}$; $A = 7.35 \times 10^{14}$ (1/sec) and $E_a = 48.8$ (kcal/mol) using microscopic reversibility.

5.4.4 $\text{CH}_3\text{OCl} \rightarrow \text{CH}_2\text{O} + \text{Cl} + \text{H}$

The reaction of methyl radical and chloro monoxide associate methyl hypochlorite (CH_3OCl) and this molecule can go to $\text{H} + \text{CH}_2\text{O} + \text{Cl}$ ($\text{CH}_2=\text{O}$, formaldehyde, and Cl atom complete radical) via a intramolecular H elimination. We use the experimental kinetic data for the assumed reaction $\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6$ for the reaction, $\text{CH}_2\text{O} + \text{Cl} + \text{H} \rightarrow \text{CH}_3\text{OCl}$; $A = 1.00 \times 10^{14}$ ($\text{cm}^3/\text{mol}\cdot\text{sec}$) from Sillesen,⁸⁰ et. al.. They used Infrared (IR) absorption spectroscopy at 298 K at 75 torr with H_2 bath gas. We calculate A and Ea for the reverse reaction, $\text{CH}_3\text{OCl} \rightarrow \text{C}\bullet\text{H}_2\text{O}\cdot\text{Cl} + \text{H}$; $A = 6.98\text{E}15$ (1/sec) and $E_a = 66.9$ (kcal/mol).

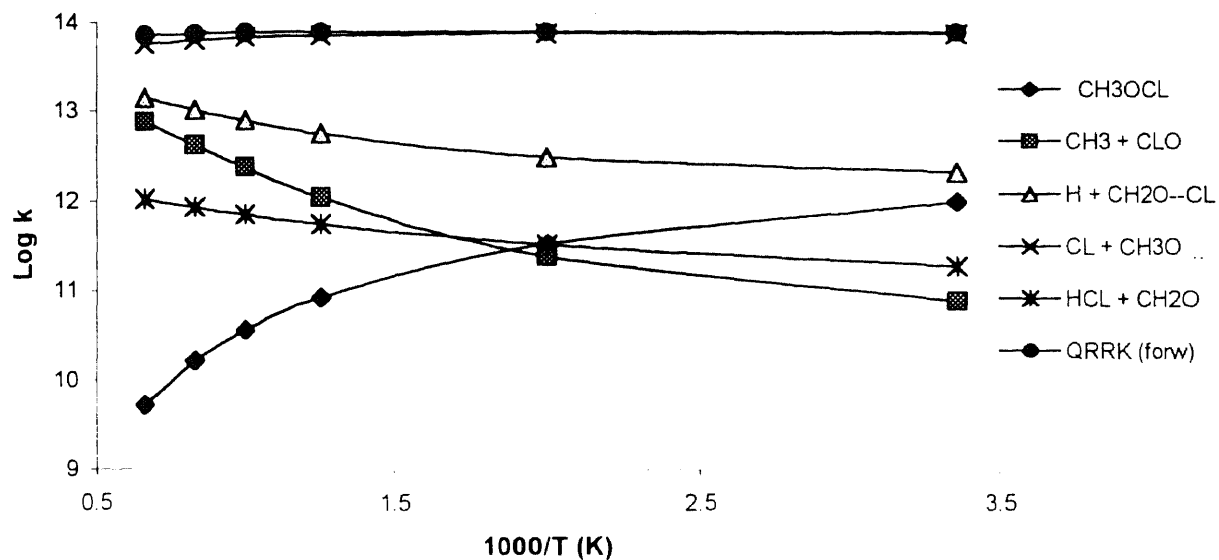


Figure 5.3. QRRK analysis of the reaction in methyl radical and chlorine oxide ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl} \rightarrow \text{Products}$) at 1 atm.

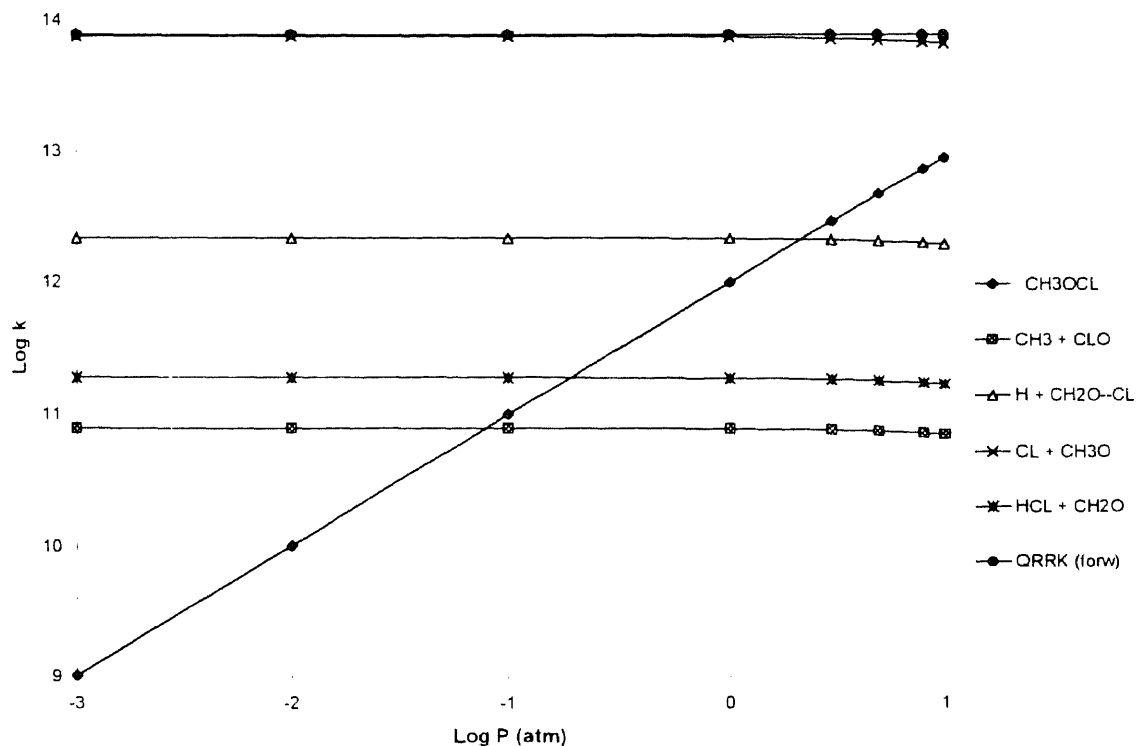


Figure 5.4. QRRK analysis of the reaction in methyl radical and chlorine oxide ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl} \rightarrow \text{Products}$) at 298 K.

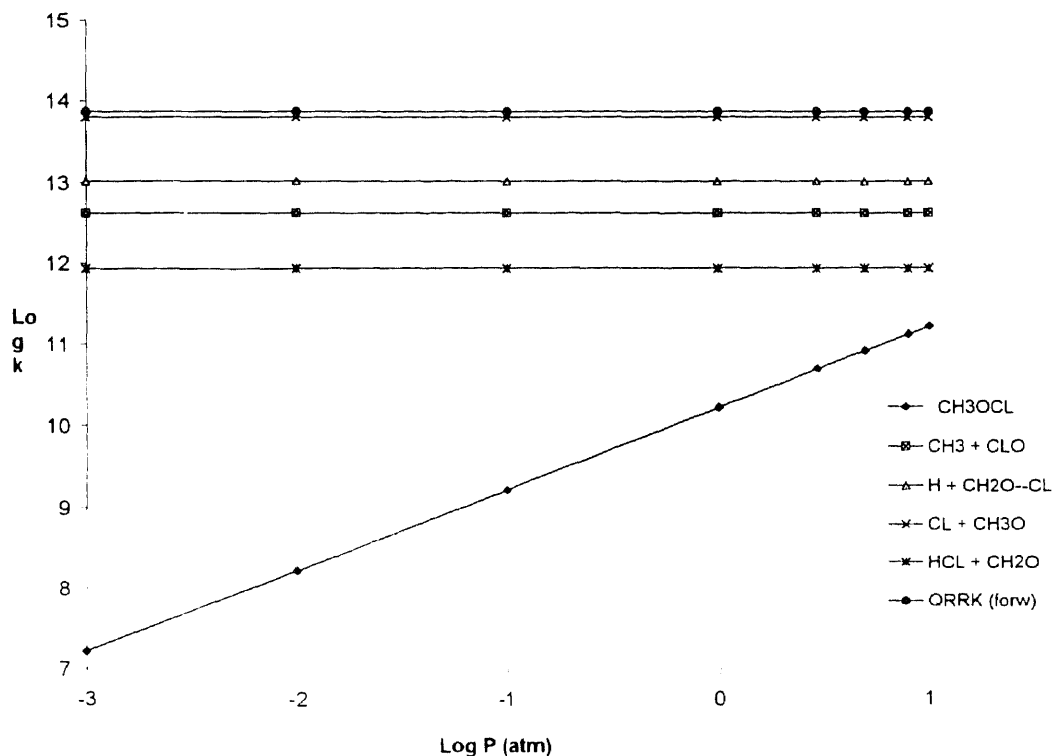


Figure 5.5. QRRK analysis of the reaction in methyl radical and chlorine oxide ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl} \rightarrow \text{Products}$) at 1200 K

5.5 Results and Discussion

Figure 5.3 shows results from the QRRK analysis for the chemical activation reaction of methyl radical with chloro monoxide. The reaction pathway ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl}^* \rightarrow \text{Cl} + \text{CH}_3\text{O}^\bullet$) simple cleavage of the O—Cl bond is the dominant channel over the temperature range of 298 to 1500 K from at 1 atm. The H—C cleavage ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl}^* \rightarrow \text{H} + \text{CH}_2\text{O--Cl}$) shows higher rate constant than the reaction pathway ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl} \rightarrow \text{HCl} + \text{CH}_3\text{O}$) through transition state(TS). I note that the $\text{CH}_2\text{O--Cl}$ product is a weakly bound adduct of chlorine atom with formaldehyde, it is not a $\text{C}^\bullet\text{H}_2\text{OCl}$ molecule.

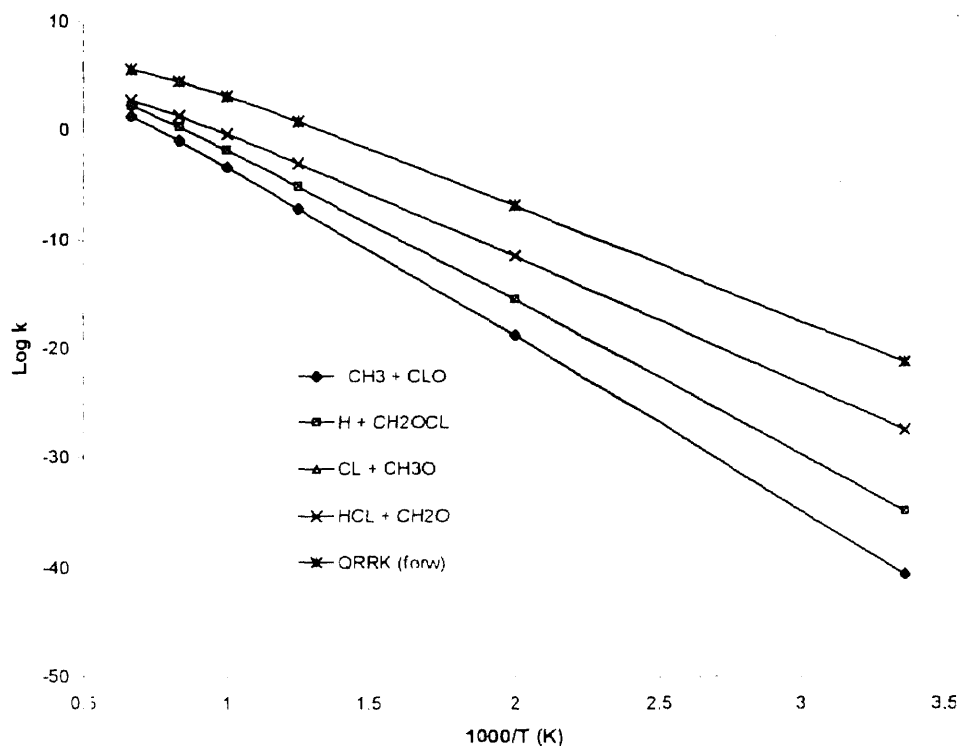


Figure 5.6. QRRK analysis of the dissociation reaction in methyl hypochlorite ($\text{CH}_3\text{OCl} \rightarrow \text{Products}$) at 1atm.

The rate constants for chlorine dissociation ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl}^* \rightarrow \text{Cl} + \text{CH}_3\text{O}\bullet$) are $A = 3.43 \times 10^{15} \text{ (cm}^3/\text{mol}\cdot\text{sec)}$, $n = -0.54$, $E_a = 0.45 \text{ (kcal/mol)}$, for hydrogen dissociation to hydrogen and formaldehyde~Cl complex radical ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl}^* \rightarrow \text{H} + \text{CH}_2=\text{O}\cdots\text{Cl}$) is $A = 1.24 \times 10^7 \text{ (cm}^3/\text{mol}\cdot\text{sec)}$, $n = 1.87$, $E_a = -0.83 \text{ (kcal/mol)}$, for transition reaction pathway ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl}^* \rightarrow \text{HCl} + \text{CH}_3\text{O}$) is $A = 1.03 \times 10^9 \text{ (cm}^3/\text{mol}\cdot\text{sec)}$, $n = 0.95$, $E_a = 0.14 \text{ (kcal/mol)}$, for reaction pathway to methyl hypochlorite ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl}$) is $A = 5.87 \times 10^{27} \text{ (cm}^3/\text{mol}\cdot\text{sec)}$, $n = -5.54$, $E_a = 2.83 \text{ (kcal/mol)}$, for the reverse reaction pathway to reactant ($\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl}^* \rightarrow$

$\text{CH}_3 + \text{ClO}$) is $A = 1.17 \times 10$ ($\text{cm}^3/\text{mol}\cdot\text{sec}$), $n = 3.69$, $E_a = -0.94$ (kcal/mol), when $k = A \times T^n \exp(-E_a/RT)$, $R = 1.987$ ($\text{cal/mol}\cdot\text{K}$).

The QRRK analysis of the reaction, $\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl}^* \rightarrow \text{Products}$ are analyzed by the $\text{Log } k$ ($\text{cm}^3/\text{mol}\cdot\text{sec}$) versus $\text{Log } P$ (atm) at 298 K in Figure 5.4 and at 1200 K in Figure 5.5. The reaction path, $\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl}^* \rightarrow \text{CH}_3\text{O} + \text{Cl}$ is the prevalent channel from 298 to 1200 K in the all pressure ranges (0.001 atm – 10 atm) in this study.

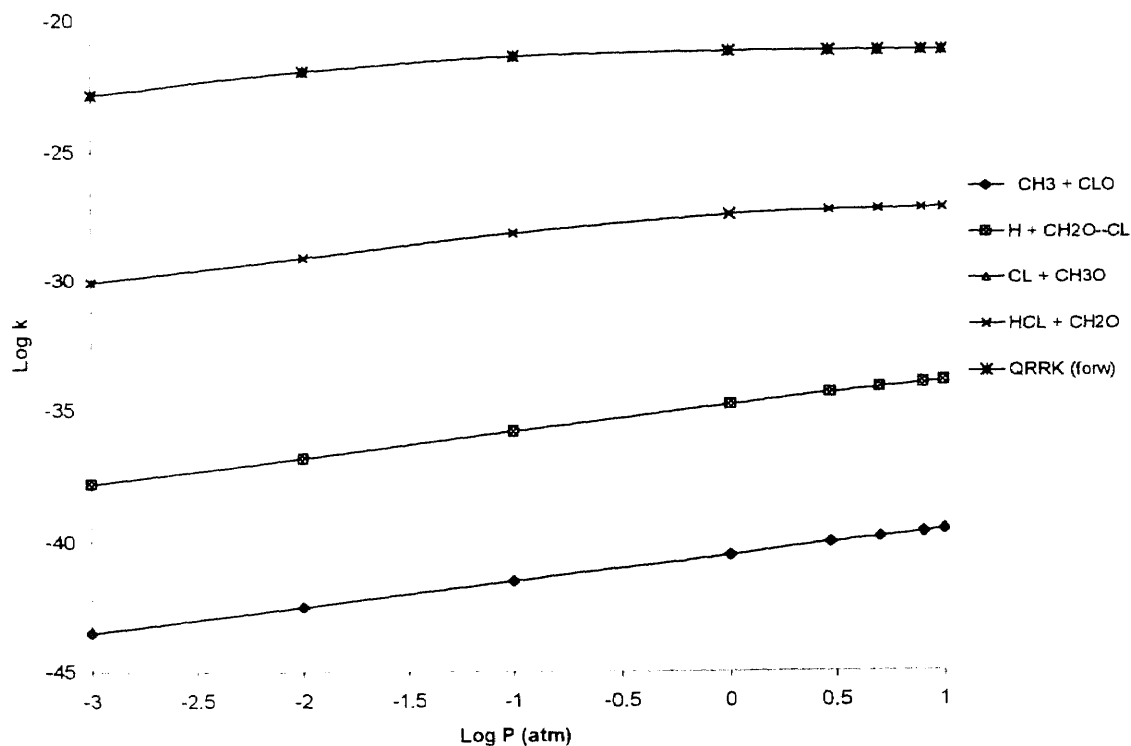
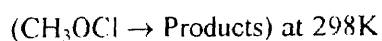


Figure 5.7. QRRK analysis of the dissociation reaction in methyl hypochlorite



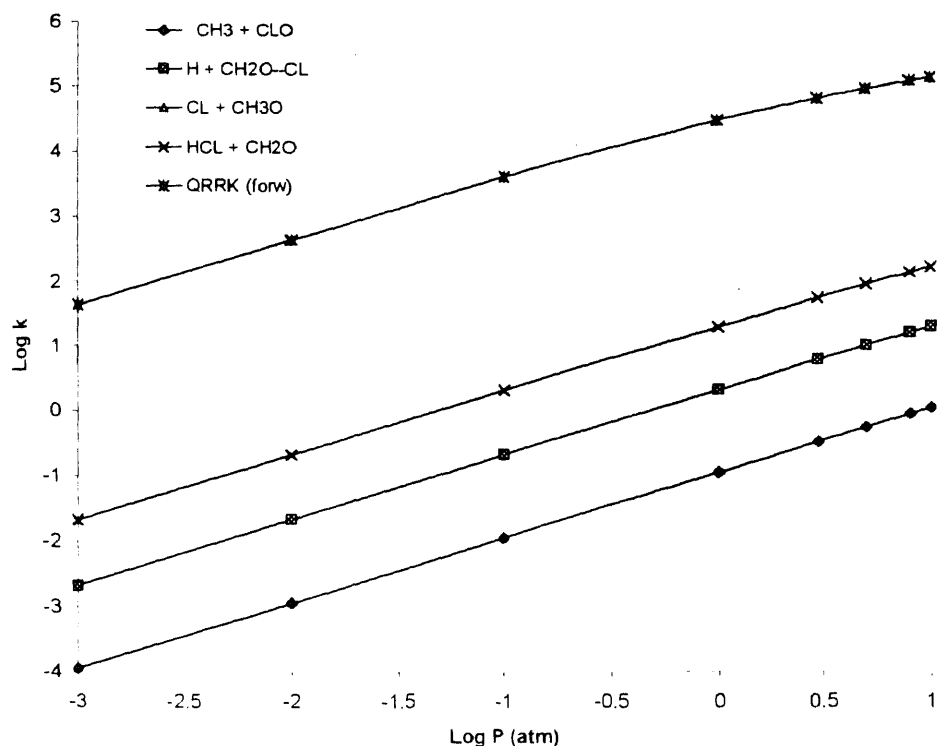


Figure 5.8. QRRK analysis of the dissociation reaction in methyl hypochlorite ($\text{CH}_3\text{OCl} \rightarrow \text{Products}$) at 1200 K.

The rate constants for dissociation ($\text{CH}_3\text{OCl}^* \rightarrow \text{Cl} + \text{CH}_3\text{O}^\bullet$) is $A = 9.69 \times 10^{37}$ (1/sec), $n = -7.64$, $E_a = 54.93$ (kcal/mol), for hydrogen dissociation to hydrogen and formaldehyde-Cl complex radical ($\text{CH}_3\text{OCl}^* \rightarrow \text{H} + \text{CH}_2=\text{O}-\text{Cl}$) is $A = 1.63 \times 10^{31}$ (1/sec), $n = -5.89$, $E_a = 70.15$ (kcal/mol), for transition reaction pathway ($\text{CH}_3\text{OCl}^* \rightarrow \text{HCl} + \text{CH}_3\text{O}$) is $A = 1.45 \times 10^{32}$ (1/sec), $n = -6.52$, $E_a = 59.26$ (kcal/mol), for the reverse reaction pathway to reactant ($\text{CH}_3\text{OCl}^* \rightarrow \text{CH}_3 + \text{ClO}$) is $A = 4.53 \times 10^{30}$ (1/sec), $n = -5.66$, $E_a = 77.94$ (kcal/mol), when $k = A \times T^n \exp(-E_a/RT)$, $R = 1.987$ (cal/mol·K).

The QRRK analysis of the reaction, $\text{CH}_3\text{OCl}^* \rightarrow \text{Products}$ are analyzed by the Log k (1/sec) versus Log P (atm) at 298 K in Figure 5.7. 1200 K in Figure 5.8. The

reaction path, $\text{CH}_3\text{OCl}^* \rightarrow \text{CH}_3\text{O} + \text{Cl}$ is the prevalent dissociation channel from 298 to 1200 K in the all pressure ranges (0.001 atm – 10 atm) in this study.

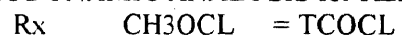
5.6 Summary

Transition state of the reaction ($\text{CH}_3 + \text{ClO} \rightarrow \text{TS} \rightarrow \text{CH}_2\text{O} + \text{HCl}$) is optimized in B3LYP/6-31G(d,p) for the geometry and vibrational frequencies and rotational constants. With single point calculation, the total energies are calculated in B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q methods. kinetics for the reactions of monochlorine monoxide radical (ClO) with methyl and chloro methyl radicals are analyzed by using quantum Rice-Ramsperger-Kassel (QRRK) theory for $k(T)$ and a modified strong collision approach for falloff. The most important path in the reaction of methyl radical and monochloro monoxide radical ($\text{CH}_3\text{Cl} + \text{ClO} \leftrightarrow \text{CH}_3\text{OCl}^* \leftrightarrow$ Products) is the ClO bond cleavage ($\text{CH}_3\text{Cl} + \text{ClO} \rightarrow \text{CH}_3\text{OCl}^* \rightarrow \text{Cl} + \text{CH}_3\text{O}\bullet$).

APPENDIX 5.1

THERMODYNAMIC ANALYSIS FOR CH₃ + CLO REACTION

THERMODYNAMIC ANALYSIS for REACTION



Hf {Kcal/mol} -15.410 38.800

S {cal/mol K} 65.190 65.470

dHr {kcal/mol} (298K) = 54.21 dHr avg (298., 1500. K) = 54.19
dU (dE) {kcal/mol} (") = 54.21 dUr avg (298., 1500. K) = 54.19
dSr {cal/mol K} (") = .28 dSr avg (298., 1500. K) = .27
dGr {kcal/mol} (") = 54.13 dGr avg (298., 1500. K) = 53.94
Af/Ar (") = 1.151E+00 Af/Ar avg (298., 1500. K) = 1.145E+00
Fit Af/Ar : A = 7.763E-01 n = .07 alpha = 1.029E-04 avg error .41 %
Fit Af/Ar w/ddU: A = 5.731E-01 n = .13 alpha = 1.883E-04 avg error .66 %

| T (K) | dH(Kcal/mol) | dU(Kcal/mol) | dS(cal/mol K) | (Af/Ar) | dG(Kcal/mol) |
|---------|--------------|--------------|---------------|-----------|--------------|
| 300.00 | 5.421E+01 | 5.421E+01 | 2.801E-01 | 1.151E+00 | 5.413E+01 |
| 400.00 | 5.421E+01 | 5.421E+01 | 2.850E-01 | 1.154E+00 | 5.410E+01 |
| 500.00 | 5.421E+01 | 5.421E+01 | 2.896E-01 | 1.157E+00 | 5.407E+01 |
| 600.00 | 5.422E+01 | 5.422E+01 | 2.950E-01 | 1.160E+00 | 5.404E+01 |
| 800.00 | 5.422E+01 | 5.422E+01 | 3.054E-01 | 1.166E+00 | 5.398E+01 |
| 1000.00 | 5.423E+01 | 5.423E+01 | 3.084E-01 | 1.168E+00 | 5.392E+01 |
| 1200.00 | 5.421E+01 | 5.421E+01 | 2.979E-01 | 1.162E+00 | 5.386E+01 |
| 1500.00 | 5.416E+01 | 5.416E+01 | 2.584E-01 | 1.139E+00 | 5.377E+01 |
| 2000.00 | 5.404E+01 | 5.404E+01 | 1.886E-01 | 1.100E+00 | 5.366E+01 |

The model fitted is for uni-molecular reaction.

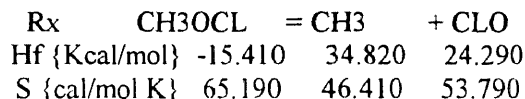
The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$
A_{prime} = 2.5882E+10 n = .99067 E_a = 5.4225E+04

| Temp(K) | AF(T) | T_K^n | k_calc(T) | k_fit |
|---------|-----------|-----------|-----------|-----------|
| 300.00 | 7.197E+12 | 2.845E+02 | 2.301E-27 | 2.296E-27 |
| 400.00 | 9.620E+12 | 3.783E+02 | 2.295E-17 | 2.298E-17 |
| 500.00 | 1.205E+13 | 4.718E+02 | 2.412E-11 | 2.417E-11 |
| 600.00 | 1.450E+13 | 5.653E+02 | 2.579E-07 | 2.584E-07 |
| 800.00 | 1.944E+13 | 7.517E+02 | 2.979E-02 | 2.980E-02 |
| 1000.00 | 2.434E+13 | 9.376E+02 | 3.420E+01 | 3.414E+01 |
| 1200.00 | 2.905E+13 | 1.123E+03 | 3.877E+03 | 3.863E+03 |
| 1500.00 | 3.560E+13 | 1.401E+03 | 4.566E+05 | 4.553E+05 |
| 2000.00 | 4.582E+13 | 1.863E+03 | 5.694E+07 | 5.719E+07 |

APPENDIX 5.1

THERMODYNAMIC ANALYSIS FOR CH₃ + CLO REACTION
(Continued)

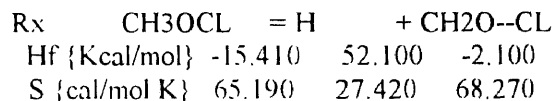
THERMODYNAMIC ANALYSIS for REACTION



$\text{dHr \{kcal/mol\} (298K) = 74.52}$ $\text{dHr avg (298., 1500. K) = 74.61}$
 $\text{dU (dE) \{kcal/mol\} (") = 73.93}$ $\text{dUr avg (298., 1500. K) = 72.83}$
 $\text{dSr \{cal/mol K\} (") = 35.01}$ $\text{dSr avg (298., 1500. K) = 35.72}$
 $\text{dGr \{kcal/mol\} (") = 64.08}$ $\text{dGr avg (298., 1500. K) = 42.50}$
 $\text{Af/Ar (") = 6.749E+02}$ $\text{Af/Ar avg (298., 1500. K) = 3.199E+02}$

| T (K) | dH(Kcal/mol) | dU(Kcal/mol) | dS(cal/mol K) | (Af/Ar) | dG(Kcal/mol) |
|---------|--------------|--------------|---------------|-----------|--------------|
| 300.00 | 7.453E+01 | 7.393E+01 | 3.504E+01 | 6.794E+02 | 6.402E+01 |
| 400.00 | 7.487E+01 | 7.408E+01 | 3.603E+01 | 8.425E+02 | 6.046E+01 |
| 500.00 | 7.511E+01 | 7.411E+01 | 3.656E+01 | 8.775E+02 | 5.683E+01 |
| 600.00 | 7.525E+01 | 7.406E+01 | 3.682E+01 | 8.347E+02 | 5.316E+01 |
| 800.00 | 7.533E+01 | 7.374E+01 | 3.695E+01 | 6.690E+02 | 4.577E+01 |
| 1000.00 | 7.525E+01 | 7.326E+01 | 3.686E+01 | 5.102E+02 | 3.839E+01 |
| 1200.00 | 7.506E+01 | 7.268E+01 | 3.669E+01 | 3.911E+02 | 3.103E+01 |
| 1500.00 | 7.471E+01 | 7.173E+01 | 3.643E+01 | 2.741E+02 | 2.006E+01 |
| 2000.00 | 7.401E+01 | 7.004E+01 | 3.603E+01 | 1.682E+02 | 1.952E+00 |

THERMODYNAMIC ANALYSIS for REACTION



$\text{dHr \{kcal/mol\} (298K) = 65.41}$ $\text{dHr avg (298., 1500. K) = 66.90}$
 $\text{dU (dE) \{kcal/mol\} (") = 64.82}$ $\text{dUr avg (298., 1500. K) = 65.11}$
 $\text{dSr \{cal/mol K\} (") = 30.50}$ $\text{dSr avg (298., 1500. K) = 32.92}$
 $\text{dGr \{kcal/mol\} (") = 56.32}$ $\text{dGr avg (298., 1500. K) = 37.30}$
 $\text{Af/Ar (") = 6.975E+01}$ $\text{Af/Ar avg (298., 1500. K) = 7.832E+01}$

| T (K) | dH(Kcal/mol) | dU(Kcal/mol) | dS(cal/mol K) | (Af/Ar) | dG(Kcal/mol) |
|---------|--------------|--------------|---------------|-----------|--------------|
| 300.00 | 6.542E+01 | 6.482E+01 | 3.053E+01 | 7.043E+01 | 5.626E+01 |
| 400.00 | 6.589E+01 | 6.510E+01 | 3.189E+01 | 1.048E+02 | 5.313E+01 |
| 500.00 | 6.629E+01 | 6.530E+01 | 3.279E+01 | 1.315E+02 | 4.990E+01 |
| 600.00 | 6.663E+01 | 6.544E+01 | 3.342E+01 | 1.503E+02 | 4.658E+01 |
| 800.00 | 6.720E+01 | 6.561E+01 | 3.423E+01 | 1.700E+02 | 3.981E+01 |
| 1000.00 | 6.765E+01 | 6.566E+01 | 3.473E+01 | 1.750E+02 | 3.291E+01 |
| 1200.00 | 6.800E+01 | 6.562E+01 | 3.506E+01 | 1.719E+02 | 2.593E+01 |
| 1500.00 | 6.839E+01 | 6.541E+01 | 3.535E+01 | 1.590E+02 | 1.537E+01 |
| 2000.00 | 6.871E+01 | 6.473E+01 | 3.554E+01 | 1.311E+02 | -2.365E+00 |

APPENDIX 5.2

KINETIC DATA FOR CH₃ + CLO REACTIONS IN ARREHENIUS FORM

$$k = AT^n \exp(-E_a/RT); R = 1.987 \text{ (cal/mol}\cdot\text{K)}$$

| Rxn | A | n | Ea(cal/mol) | P (atm) |
|----------------------------|----------|-------|-------------|----------|
| CH3 + CLO <=> CH3OCL | 5.57E+24 | -5.53 | 2813 | 1.00E-03 |
| CH3 + CLO <=> CH3OCL | 5.57E+25 | -5.53 | 2813 | 1.00E-02 |
| CH3 + CLO <=> CH3OCL | 5.60E+26 | -5.54 | 2815 | 1.00E-01 |
| CH3 + CLO <=> CH3OCL | 5.87E+27 | -5.54 | 2830 | 1.00E+00 |
| CH3 + CLO <=> CH3OCL | 1.94E+28 | -5.55 | 2863 | 3.00E+00 |
| CH3 + CLO <=> CH3OCL | 3.56E+28 | -5.56 | 2895 | 5.00E+00 |
| CH3 + CLO <=> CH3OCL | 6.49E+28 | -5.58 | 2940 | 8.00E+00 |
| CH3 + CLO <=> CH3OCL | 8.81E+28 | -5.59 | 2969 | 1.00E+01 |
| CH3 + CLO <=> CH3 + CLO | 1.10E+01 | 3.7 | -953 | 1.00E-03 |
| CH3 + CLO <=> CH3 + CLO | 1.10E+01 | 3.7 | -953 | 1.00E-02 |
| CH3 + CLO <=> CH3 + CLO | 1.10E+01 | 3.7 | -951 | 1.00E-01 |
| CH3 + CLO <=> CH3 + CLO | 1.17E+01 | 3.69 | -935 | 1.00E+00 |
| CH3 + CLO <=> CH3 + CLO | 1.32E+01 | 3.67 | -901 | 3.00E+00 |
| CH3 + CLO <=> CH3 + CLO | 1.49E+01 | 3.66 | -867 | 5.00E+00 |
| CH3 + CLO <=> CH3 + CLO | 1.77E+01 | 3.64 | -819 | 8.00E+00 |
| CH3 + CLO <=> CH3 + CLO | 1.97E+01 | 3.62 | -788 | 1.00E+01 |
| CH3 + CLO <=> H + CH2O--CL | 1.16E+07 | 1.88 | -845 | 1.00E-03 |
| CH3 + CLO <=> H + CH2O--CL | 1.16E+07 | 1.88 | -845 | 1.00E-02 |
| CH3 + CLO <=> H + CH2O--CL | 1.17E+07 | 1.88 | -843 | 1.00E-01 |
| CH3 + CLO <=> H + CH2O--CL | 1.24E+07 | 1.87 | -827 | 1.00E+00 |
| CH3 + CLO <=> H + CH2O--CL | 1.39E+07 | 1.86 | -793 | 3.00E+00 |
| CH3 + CLO <=> H + CH2O--CL | 1.55E+07 | 1.84 | -759 | 5.00E+00 |
| CH3 + CLO <=> H + CH2O--CL | 1.82E+07 | 1.82 | -711 | 8.00E+00 |
| CH3 + CLO <=> H + CH2O--CL | 2.01E+07 | 1.81 | -680 | 1.00E+01 |
| CH3 + CLO <=> CL+CH3O | 3.25E+15 | -0.53 | 434 | 1.00E-03 |
| CH3 + CLO <=> CL+CH3O | 3.25E+15 | -0.53 | 434 | 1.00E-02 |
| CH3 + CLO <=> CL+CH3O | 3.26E+15 | -0.53 | 435 | 1.00E-01 |
| CH3 + CLO <=> CL+CH3O | 3.43E+15 | -0.54 | 451 | 1.00E+00 |
| CH3 + CLO <=> CL+CH3O | 3.81E+15 | -0.55 | 485 | 3.00E+00 |
| CH3 + CLO <=> CL+CH3O | 4.21E+15 | -0.56 | 517 | 5.00E+00 |
| CH3 + CLO <=> CL+CH3O | 4.85E+15 | -0.58 | 564 | 8.00E+00 |
| CH3 + CLO <=> CL+CH3O | 5.30E+15 | -0.59 | 593 | 1.00E+01 |
| CH3 + CLO <=> HCl + CH2O | 9.75E+08 | 0.96 | 119 | 1.00E-03 |
| CH3 + CLO <=> HCl + CH2O | 9.75E+08 | 0.96 | 119 | 1.00E-02 |
| CH3 + CLO <=> HCl + CH2O | 9.80E+08 | 0.96 | 121 | 1.00E-01 |
| CH3 + CLO <=> HCl + CH2O | 1.03E+09 | 0.95 | 136 | 1.00E+00 |
| CH3 + CLO <=> HCl + CH2O | 1.15E+09 | 0.94 | 170 | 3.00E+00 |
| CH3 + CLO <=> HCl + CH2O | 1.27E+09 | 0.93 | 203 | 5.00E+00 |
| CH3 + CLO <=> HCl + CH2O | 1.47E+09 | 0.91 | 250 | 8.00E+00 |
| CH3 + CLO <=> HCl + CH2O | 1.61E+09 | 0.9 | 280 | 1.00E+01 |

APPENDIX 5.2

KINETIC DATA FOR CH₃ + CLO REACTIONS IN ARREHENIUS FORM
(Continued)
 $k = AT^n \exp(-E_a/RT)$; R = 1.987 (cal/mol-K)

| Rxn | | | | A | n | Ea(cal/mol) | P(atm) |
|---------------------|-----|-----------------|-------------------------|----------|-------|-------------|----------|
| CH ₃ OCL | <=> | CH ₃ | + CLO | 4.31E+27 | -5.65 | 77923 | 1.00E-03 |
| CH ₃ OCL | <=> | CH ₃ | + CLO | 4.31E+28 | -5.65 | 77923 | 1.00E-02 |
| CH ₃ OCL | <=> | CH ₃ | + CLO | 4.33E+29 | -5.65 | 77925 | 1.00E-01 |
| CH ₃ OCL | <=> | CH ₃ | + CLO | 4.53E+30 | -5.66 | 77939 | 1.00E+00 |
| CH ₃ OCL | <=> | CH ₃ | + CLO | 1.50E+31 | -5.67 | 77971 | 3.00E+00 |
| CH ₃ OCL | <=> | CH ₃ | + CLO | 2.73E+31 | -5.68 | 78002 | 5.00E+00 |
| CH ₃ OCL | <=> | CH ₃ | + CLO | 4.97E+31 | -5.7 | 78047 | 8.00E+00 |
| CH ₃ OCL | <=> | CH ₃ | + CLO | 6.73E+31 | -5.71 | 78075 | 1.00E+01 |
| CH ₃ OCL | <=> | H | + CH ₂ O--CL | 1.38E+28 | -5.87 | 70092 | 1.00E-03 |
| CH ₃ OCL | <=> | H | + CH ₂ O--CL | 1.38E+29 | -5.87 | 70092 | 1.00E-02 |
| CH ₃ OCL | <=> | H | + CH ₂ O--CL | 1.40E+30 | -5.87 | 70098 | 1.00E-01 |
| CH ₃ OCL | <=> | H | + CH ₂ O--CL | 1.63E+31 | -5.89 | 70148 | 1.00E+00 |
| CH ₃ OCL | <=> | H | + CH ₂ O--CL | 6.63E+31 | -5.93 | 70249 | 3.00E+00 |
| CH ₃ OCL | <=> | H | + CH ₂ O--CL | 1.43E+32 | -5.96 | 70339 | 5.00E+00 |
| CH ₃ OCL | <=> | H | + CH ₂ O--CL | 3.12E+32 | -5.99 | 70458 | 8.00E+00 |
| CH ₃ OCL | <=> | H | + CH ₂ O--CL | 4.63E+32 | -6.01 | 70527 | 1.00E+01 |
| CH ₃ OCL | <=> | CL | + CH ₃ O | 1.54E+37 | -8.38 | 53538 | 1.00E-03 |
| CH ₃ OCL | <=> | CL | + CH ₃ O | 3.56E+38 | -8.49 | 53816 | 1.00E-02 |
| CH ₃ OCL | <=> | CL | + CH ₃ O | 1.22E+40 | -8.61 | 54717 | 1.00E-01 |
| CH ₃ OCL | <=> | CL | + CH ₃ O | 9.69E+37 | -7.64 | 54927 | 1.00E+00 |
| CH ₃ OCL | <=> | CL | + CH ₃ O | 2.72E+35 | -6.73 | 54507 | 3.00E+00 |
| CH ₃ OCL | <=> | CL | + CH ₃ O | 1.05E+34 | -6.24 | 54219 | 5.00E+00 |
| CH ₃ OCL | <=> | CL | + CH ₃ O | 4.26E+32 | -5.77 | 53911 | 8.00E+00 |
| CH ₃ OCL | <=> | CL | + CH ₃ O | 8.83E+31 | -5.54 | 53753 | 1.00E+01 |
| CH ₃ OCL | <=> | HCL | + CH ₂ O | 1.58E+28 | -6.26 | 58367 | 1.00E-03 |
| CH ₃ OCL | <=> | HCL | + CH ₂ O | 1.67E+29 | -6.26 | 58382 | 1.00E-02 |
| CH ₃ OCL | <=> | HCL | + CH ₂ O | 2.59E+30 | -6.32 | 58522 | 1.00E-01 |
| CH ₃ OCL | <=> | HCL | + CH ₂ O | 1.45E+32 | -6.52 | 59260 | 1.00E+00 |
| CH ₃ OCL | <=> | HCL | + CH ₂ O | 3.06E+32 | -6.45 | 59720 | 3.00E+00 |
| CH ₃ OCL | <=> | HCL | + CH ₂ O | 1.57E+32 | -6.28 | 59831 | 5.00E+00 |
| CH ₃ OCL | <=> | HCL | + CH ₂ O | 4.15E+31 | -6.04 | 59840 | 8.00E+00 |
| CH ₃ OCL | <=> | HCL | + CH ₂ O | 1.73E+31 | -5.89 | 59811 | 1.00E+01 |

APPENDIX 5.3

LOG RATE CONSTANTS VS PRESSURE AND TEMPERATURE
FOR $\text{CH}_3 + \text{CLO}$ REACTIONChemact reactants $\text{CH}_3 + \text{CLO}$ Rate constants in log form

| P (ATM) | T (K) | 1000/T | CH_3OCL | $\text{CH}_3 + \text{CLO}$ | $\text{H} + \text{CH}_2\text{O}-\text{CL}$ | $\text{CL} + \text{CH}_3\text{O}$ | $\text{HCL} + \text{CH}_2\text{O}$ | QRRK |
|---------|---------|--------|-------------------------|----------------------------|--|-----------------------------------|------------------------------------|-------|
| 0.00 | 298.00 | 3.36 | 9.01 | 10.90 | 12.34 | 13.88 | 11.28 | 13.89 |
| 0.00 | 500.00 | 2.00 | 8.53 | 11.39 | 12.49 | 13.87 | 11.52 | 13.89 |
| 0.00 | 800.00 | 1.25 | 7.93 | 12.05 | 12.75 | 13.85 | 11.75 | 13.89 |
| 0.00 | 1000.00 | 1.00 | 7.56 | 12.37 | 12.90 | 13.83 | 11.85 | 13.88 |
| 0.00 | 1200.00 | 0.83 | 7.21 | 12.62 | 13.01 | 13.80 | 11.93 | 13.87 |
| 0.00 | 1500.00 | 0.67 | 6.72 | 12.88 | 13.14 | 13.75 | 12.01 | 13.85 |

| P (ATM) | T (K) | 1000/T | CH_3OCL | $\text{CH}_3 + \text{CLO}$ | $\text{H} + \text{CH}_2\text{O}-\text{CL}$ | $\text{CL} + \text{CH}_3\text{O}$ | $\text{HCL} + \text{CH}_2\text{O}$ | QRRK |
|---------|---------|--------|-------------------------|----------------------------|--|-----------------------------------|------------------------------------|-------|
| 0.01 | 298.00 | 3.36 | 10.01 | 10.90 | 12.34 | 13.88 | 11.28 | 13.89 |
| 0.01 | 500.00 | 2.00 | 9.53 | 11.39 | 12.49 | 13.87 | 11.52 | 13.89 |
| 0.01 | 800.00 | 1.25 | 8.93 | 12.05 | 12.75 | 13.85 | 11.75 | 13.89 |
| 0.01 | 1000.00 | 1.00 | 8.56 | 12.37 | 12.90 | 13.83 | 11.85 | 13.88 |
| 0.01 | 1200.00 | 0.83 | 8.21 | 12.62 | 13.01 | 13.80 | 11.93 | 13.87 |
| 0.01 | 1500.00 | 0.67 | 7.72 | 12.88 | 13.14 | 13.75 | 12.01 | 13.85 |

| P (ATM) | T (K) | 1000/T | CH_3OCL | $\text{CH}_3 + \text{CLO}$ | $\text{H} + \text{CH}_2\text{O}-\text{CL}$ | $\text{CL} + \text{CH}_3\text{O}$ | $\text{HCL} + \text{CH}_2\text{O}$ | QRRK |
|---------|---------|--------|-------------------------|----------------------------|--|-----------------------------------|------------------------------------|-------|
| 0.10 | 298.00 | 3.36 | 11.00 | 10.90 | 12.34 | 13.88 | 11.28 | 13.89 |
| 0.10 | 500.00 | 2.00 | 10.53 | 11.39 | 12.49 | 13.87 | 11.52 | 13.89 |
| 0.10 | 800.00 | 1.25 | 9.93 | 12.05 | 12.75 | 13.85 | 11.75 | 13.89 |
| 0.10 | 1000.00 | 1.00 | 9.56 | 12.37 | 12.90 | 13.83 | 11.85 | 13.88 |
| 0.10 | 1200.00 | 0.83 | 9.21 | 12.62 | 13.01 | 13.80 | 11.93 | 13.87 |
| 0.10 | 1500.00 | 0.67 | 8.72 | 12.88 | 13.14 | 13.75 | 12.01 | 13.85 |

| P (ATM) | T (K) | 1000/T | CH_3OCL | $\text{CH}_3 + \text{CLO}$ | $\text{H} + \text{CH}_2\text{O}-\text{CL}$ | $\text{CL} + \text{CH}_3\text{O}$ | $\text{HCL} + \text{CH}_2\text{O}$ | QRRK |
|---------|---------|--------|-------------------------|----------------------------|--|-----------------------------------|------------------------------------|-------|
| 1.00 | 298.00 | 3.36 | 12.00 | 10.89 | 12.33 | 13.87 | 11.27 | 13.89 |
| 1.00 | 500.00 | 2.00 | 11.53 | 11.38 | 12.49 | 13.87 | 11.52 | 13.89 |
| 1.00 | 800.00 | 1.25 | 10.93 | 12.05 | 12.75 | 13.85 | 11.75 | 13.89 |
| 1.00 | 1000.00 | 1.00 | 10.56 | 12.37 | 12.90 | 13.83 | 11.85 | 13.88 |
| 1.00 | 1200.00 | 0.83 | 10.21 | 12.62 | 13.01 | 13.80 | 11.93 | 13.87 |
| 1.00 | 1500.00 | 0.67 | 9.72 | 12.88 | 13.14 | 13.75 | 12.01 | 13.85 |

| P (ATM) | T (K) | 1000/T | CH_3OCL | $\text{CH}_3 + \text{CLO}$ | $\text{H} + \text{CH}_2\text{O}-\text{CL}$ | $\text{CL} + \text{CH}_3\text{O}$ | $\text{HCL} + \text{CH}_2\text{O}$ | QRRK |
|---------|---------|--------|-------------------------|----------------------------|--|-----------------------------------|------------------------------------|-------|
| 3.00 | 298.00 | 3.36 | 12.47 | 10.88 | 12.32 | 13.86 | 11.26 | 13.89 |
| 3.00 | 500.00 | 2.00 | 12.00 | 11.38 | 12.49 | 13.87 | 11.51 | 13.89 |
| 3.00 | 800.00 | 1.25 | 11.41 | 12.05 | 12.75 | 13.85 | 11.74 | 13.89 |
| 3.00 | 1000.00 | 1.00 | 11.04 | 12.37 | 12.90 | 13.83 | 11.85 | 13.88 |
| 3.00 | 1200.00 | 0.83 | 10.69 | 12.62 | 13.01 | 13.80 | 11.93 | 13.87 |
| 3.00 | 1500.00 | 0.67 | 10.20 | 12.88 | 13.14 | 13.75 | 12.01 | 13.85 |

APPENDIX 5.3

**LOG RATE CONSTANTS VS PRESSURE AND TEMPERATURE
FOR CH₃ + CLO REACTION
(Continued)**

| P (ATM) | T (K) | 1000/T | CH ₃ OCL | CH ₃ + CLO | H + CH ₂ O-CL | CL + CH ₃ O | HCL + CH ₂ O | QRRK |
|---------|---------|--------|---------------------|-----------------------|--------------------------|------------------------|-------------------------|-------|
| 5.00 | 298.00 | 3.36 | 12.68 | 10.88 | 12.31 | 13.85 | 11.25 | 13.89 |
| 5.00 | 500.00 | 2.00 | 12.22 | 11.38 | 12.48 | 13.86 | 11.51 | 13.89 |
| 5.00 | 800.00 | 1.25 | 11.63 | 12.05 | 12.75 | 13.85 | 11.74 | 13.89 |
| 5.00 | 1000.00 | 1.00 | 11.26 | 12.37 | 12.90 | 13.83 | 11.85 | 13.88 |
| 5.00 | 1200.00 | 0.83 | 10.91 | 12.62 | 13.01 | 13.80 | 11.93 | 13.87 |
| 5.00 | 1500.00 | 0.67 | 10.42 | 12.88 | 13.14 | 13.75 | 12.01 | 13.85 |

| P (ATM) | T (K) | 1000/T | CH ₃ OCL | CH ₃ + CLO | H + CH ₂ O-CL | CL + CH ₃ O | HCL + CH ₂ O | QRRK |
|---------|---------|--------|---------------------|-----------------------|--------------------------|------------------------|-------------------------|-------|
| 8.00 | 298.00 | 3.36 | 12.87 | 10.86 | 12.30 | 13.84 | 11.24 | 13.89 |
| 8.00 | 500.00 | 2.00 | 12.41 | 11.37 | 12.48 | 13.86 | 11.50 | 13.89 |
| 8.00 | 800.00 | 1.25 | 11.83 | 12.05 | 12.75 | 13.85 | 11.74 | 13.89 |
| 8.00 | 1000.00 | 1.00 | 11.46 | 12.37 | 12.90 | 13.83 | 11.85 | 13.88 |
| 8.00 | 1200.00 | 0.83 | 11.12 | 12.62 | 13.01 | 13.80 | 11.93 | 13.87 |
| 8.00 | 1500.00 | 0.67 | 10.62 | 12.88 | 13.14 | 13.75 | 12.01 | 13.85 |

| P (ATM) | T (K) | 1000/T | CH ₃ OCL | CH ₃ + CLO | H + CH ₂ O-CL | CL + CH ₃ O | HCL + CH ₂ O | QRRK |
|---------|---------|--------|---------------------|-----------------------|--------------------------|------------------------|-------------------------|-------|
| 10.00 | 298.00 | 3.36 | 12.95 | 10.85 | 12.29 | 13.83 | 11.23 | 13.89 |
| 10.00 | 500.00 | 2.00 | 12.51 | 11.37 | 12.48 | 13.86 | 11.50 | 13.89 |
| 10.00 | 800.00 | 1.25 | 11.93 | 12.05 | 12.75 | 13.85 | 11.74 | 13.89 |
| 10.00 | 1000.00 | 1.00 | 11.56 | 12.37 | 12.90 | 13.83 | 11.85 | 13.88 |
| 10.00 | 1200.00 | 0.83 | 11.21 | 12.62 | 13.01 | 13.80 | 11.93 | 13.87 |
| 10.00 | 1500.00 | 0.67 | 10.72 | 12.88 | 13.14 | 13.75 | 12.01 | 13.85 |

REFERENCES

- (1) Abbatt, J.P.D.; Molina, M.J. *Geophys. Res. Lett.* **1992**, *19*, 461.
- (2) Farman, J. G.; Gardiner, B.G.; Shanklin, J. D. *Nature* **1985**, *315*, 207.
- (3) Solomon, S. *Nature*. **1990**, *347*, 347.
- (4) Helleis, F.; Crowley, J. N.; Moortgat, G. K. *J. Phys. Chem.* **1993**, *97*, 11464.
- (5) Markert, F.; Nielsen, O.J. *Chem. Phys. Lett.* **1992**, *194*, 123.
- (6) Ennis, C.A.; Birks, J.W. *J. Phys. Chem.* **1988**, *92*, 1119.
- (7) Hatakeyama, S.; Leu, M-T. *J. Phys. Chem.* **1989**, *93*, 5784.
- (8) Biggs, P.; Canosa-Mas, C. E.; Fracheboud, J-M.; Marston, G.; Shallcross, D. E.; Wayne, R. P. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 3045.
- (9) Carol, S.A.; Müller, R.; Moortgat, G. K.; Crowley, J. N. *J. Phys. Chem.* **1996**, *100*, 17191.
- (10) Crowley, J. N.; Helleis, F.; Müller, R.; Moortgat, G. K.; Crutzen, P. J. *Geophys. Res. Lett.* **1994**, *99*, 20683.
- (11) Markert, F.; Nielsen, O. J. *Chem. Phys. Lett.* **1992**, *189*, 171.
- (12) Bozzelli, J.W.; Dean, A.M. *J. Phys. Chem.* **1993**, *97*, 4427.
- (13) Kaiser, E. W. *Int. J. Chem. Kinet.* **1992**, *24*, 179.
- (14) Li, Y.; Francisco, J. S. *J. Chem. Phys.* **1999**, *111*, 8384.
- (15) Francisco, Joseph S. *Int. J. Quantum Chem.* **1999**, *73*, 29.
- (16) Messer, B. M.; Elrod, M. J. *Chem. Phys. Lett.* **1999**, *301*, 10.
- (17) Grela, M.A.; Colussi, A. J. *J. Phys. Chem.* **1996**, *100*, 10150.
- (18) Melius, C. Web site: (a) <http://z.ca.sandia.gov/~melius/> Feb., 2000.

- (b) <http://www.nist.gov/cstl/div836/ckmech/SpeciesData.html>. May, 2000.
- (19) Carl, S. A.; Miller, R.; Moortgat, G. K.; Crowley, J. N. *J. Phys. Chem.* **1996**, *100*, 17191.
- (20) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience, New York. 1976.
- (21) Durant, J. L. *Chem. Phys. Lett.* **1996**, *256*, 595
- (22) Andino, J. M.; Smith, J. N.; Flagan, R. C.; Goddard, W. A.; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 10967.
- (23) Mayer, P. M.; Parkinson, O. J.; Smith, D. M.; Radom, L.; *J. Chem. Phys.* **1998**, *108*, 604.
- (24) Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Phys. Chem.* **1998**, *102*, 9965.
- (25) Hehre, W.; Radom, L.; Schleyer, P. R.; Pople, J. A. *Ab-Initio Molecular Orbital Theory*; John Wiley & Sons: New York, NJ, 1986.
- (26) Seminario, P., Ed. *Modern density Functionl Theory*; Elsevier, New York, 1995.
- (27) Chong, D.P., Ed. *Recent Advances in Density Functional Methods*; World scientific: Singapore, 1996.
- (28) Nyden, N. R.; Peterson, G. A. *J. Chem. Phys.* **1981**, *75*, 1843.
- (29) Peterson, G. A.; Al-Laharm, M. A. *J. Chem. Phys.* **1991**, *94*, 6081.
- (30) Montgomery, J. A.; Ochterski, J. W.; Peterson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.
- (31) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
- (32) Chase, M. W. *NIST-JANAF Thermochemical Tables; Fourth Edition*, J. Phys. Chem. Ref. Data, Monograph 9, New York, 1998.

- (33) Frenkel M.; Kabo, G. J.; Marsh, K. N.; Roganov, G. N.; Wilhoit, R. C. *Thermodynamics of Organic Compounds in the Gas State*; volume 1, Thermodynamic Research Center, Texas A&M University System, College Station, Texas, 1994.
- (34) Stull, D. R.; Westrum, E. F. Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Robert E. Krieger Publishing, Malabar, Florida, 1987.
- (35) Lay, H. T.; Bozzelli, J. W. *J. Phys. Chem.* **1997**, *101*, 9505.
- (36) McQuarrie, D. A. *Statistical Mechanics*; Harper & Row, New York, 1976.
- (37) Lay, H. T.; Krasnoperov, L. N.; Venanzi, C. A.; Bozzelli, J. W. *J. Phys. Chem.* **1996**, *100*, 8240.
- (38) Sun, H.; Chen C.; Bozzelli, J. W. Submitted for publication, J. Phys and Chemical Reference Data.
- (39) Chen, C. J.; Wong, D.; Bozzelli, J. W. *J. Phys. Chem.* **1998**, *102*, 4551.
- (40) Zhu, L.; Bozzelli, J. W.; Lay T. *Ind. Chem. Res.* **1998**, *37*, 3497.
- (41) Yamada, T.; Lay, T.; Bozzelli J. W. *J. Phys. Chem.* **1998**, *102*, 7286.
- (42) Yamada, T.; Bozzelli J. W.; Berry, R. J. *J. Phys. Chem.* **1999**, *103*, 5602.
- (43) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds* 2nd ed.; Chapman and Hall, London, New York, 1986.
- (44) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press, New York, 1970.
- (45) We note that OCl/Cl₃ is a unique group, but we list it here for illustration of trend in the interaction terms with increased number of chlorines.
- (46) Jungkamp, Tim P. W.; Kirchner, Ulf; Schmidt, Mark; Schindler, Ralph N. *J. Photochem. Photobiol.* **1995**, *91*, 1.

- (47) Rigden, J. S.; Butcher, S. S. *J. Chem. Phys.* **1964**, *40*, 2109.
- (48) Prosen, E.J.; Rossini, F.D. *J. Res. NBS.*, **1945**, 263.
- (49) Fletcher, R.A.; Pilcher, G. *Trans. Faraday. Soc.* **1971**, *67*, 3191.
- (50) Mansson, M.; Ringner, B.; Sunner, S. *J. Chem. Thermodyn.* **1971**, *3*, 547.
- (51) Kirkbride, F.W. *J. Appl. Chem.*, **1956**, *6*, 11.
- (52) Green, J. H. S. *Chem. Ind. (London)*, **1960**, 121.
- (53) Wong, M. W.; Radom, L. *J. Phys. Chem.* **1998**, *102*, 2237
- (54) Espinosa-Garcia, J. *Chem. Phys. Lett.* **1999**, *301*, 10.
- (55) MOPAC: *A General Molecular Orbital Package* (QCPE 445). QCPE Bull. 1983, *3*, 43. MOPAC 6.0; Frank J. Seiler Research Lab., US Air Force Academy: CO, 1990.
- (56) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
- (57) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
- (58) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Ibid. *10*, 221.
- (59) Cohen, N. *J. Phys. Chem. Ref. Data.* **1996**, *25*, 1411.
- (60) Personnel communication, Jung, D.; Chen, C.; Bozzelli, J. W., Department of Chemistry, New Jersey Institute of Technology, Manuscript on thermodynamic properties of chlorinated methyl ethers in preparation.
- (61) Donaghy, T.; Snanahan, I.; Hande, M.; Fitzpatrick, S. *Int. J. Chem Kinet.* **1993**, *25*, 273.
- (62) Ragains, M. L.; Finlayson-Pitts, B. J. *J. Phys. Chem.* 1997, *101*, 1509.
- (63) Pilcher, G.; Pell, A.S.; Coleman, D. J., *Trans. Faraday Soc.*, 1964, *60*, 499.

- (64) Frisch, M.J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, R. J.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; and Pople, J. A. *Gaussian 94*, Gaussian, Inc., Pittsburgh, 1995.
- (65) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B41*, 785.
- (66) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
- (67) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.
- (68) Durant, J. L.; Rohlfing, C. M. *J. Chem. Phys.* **1993**, *98*, 8031.
- (69) Petersson, G. A.; Malick, D. K.; Wilson, W. G. *J. Chem. Phys.* **1998**, *109*, 10570.
- (70) Ochterski, J. W.; Petersson, G. A. Montgomery *J. Chem. Phys.* **1996**, *104*, 2598.
- (71) Zachariah, M.R.; Westmoreland, P.R.; Burgess Jr, D, R.; Tsang, W.;Melius, C. F. *J. Phys. Chem* **1996**, *100*, 8737.
- (72) Powers, D E.; Pushkarsky, M.B.; Miller, T.A. *J. Chem. Phys.*, **1997**, *106*, 6863.
- (73) Chiang, S.-Y.; Hsu, Y.-C.; Lee, Y.-P. *J. Chem. Phys.*, **1989**, *90*, 81.
- (74) Ramond, T. M.; Davico, G. E.; Schwartz, R. L.; Lineberger, W. C. *J. Chem. Phys.*, **2000**, *112*, 1158.
- (75) Yamada, T.; Bozzelli J. W.; Berry, R. J. *J. Phys. Chem.* **1999**, *103*, 5602.
- (76) Traher, J.; Holmes, J. *J. Phys. Chem.* **1993**, *97*, 3453.
- (77) Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Am. Chem Soc.* **1997**, *119*, 11452.

- (78) Tsang, W., Heats of Formation of Organic Free Radicals by Kinetic Methods in *Energetics of Organic Free Radicals*, Martinho Simoes, J.A.; Greenberg, A.; Liebman, J.F., eds., Blackie Academic and Professional, London, 1996, 22.
- (78) Jungkamp, T.P.W.; Kukui, A.; Schindler, R.N. *Ber. Bunsenges. Phys. Chem.* **1995**, *99*, 1057.
- (79) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (80) Slater, N. B. *Theory of Unimolecular Reactions*, Methuen, London, 1959
- (81) Lindemann, F. A. *Trans. Faraday Soc.* **1922**, *17*, 598.
- (82) Christiansen, J. A. Ph.D. Thesis, Dept. of Chemistry, Copenhagen, 1921.
- (84) Hinshelwood, C. N. *Proc. Roy. Soc. A* **1927**, *113*, 230.
- (85) Rice, O. K.; Ramsperger, H. C. *J. Am. Chem. Soc.* **1927**, *49*, 1617.
- (86) Kassel, L. S. *J. Phys. Chem.* **1928**, *32*, 225.
- (87) Kassel, L. S. *J. Phys. Chem.* **1928**, *32*, 1065.
- (88) Kassel, L. S. Kinetics of Homogenous Gas Reaction, Chemical Catalog Co., NY, 1932.
- (89) Chang, A. Y.; Bozzelli, J. W.; Dean, A. M. submitted to *J. Phys. Chem.* **2000**.
- (90) Dean, A. M. *J. Phys. Chem.* **1985**, *89*, 4600.
- (91) Dean, A. M.; Bozzelli, J. W.; Ritter, E. R. *Combust. Sci. and Tech.* **1991**, *80*, 63.
- (92) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*, Black Scientific Publications, Mass, 1990.
- (93) Gilbert, R. G.; Smith, S. C.; Jordan, M. J. T., UNIMOL program suite (calculation of falloff curves for unimolecular and recombination reactions) (1993). Available from

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(94) Personal communication Dean, A. M.; Chang, A. Y., Exxon Corp. Res., Annandale NJ.

(95) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*, Prentice Hall, NJ, 1989.

(96) Ritter, E. R. *J. Chem. Info. Comput. Sci.* **1991**, *31*, 400.

(97) Bozzelli J. W.; Chang, A. Y.; Dean, A. M. *Int. J. Chem. Kinet.* **1997**, *29*, (3), 161.

(98) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*, 2nd Ed., Wiley, London, 1963.

(99) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *Properties of Gases and Liquids*, 2nd Ed., McGraw Hill, NY, 1997.

(100) Westmoreland, P. R.; Howard, J.B.; Longwell, J. P.; Dean, A.M., AIChE Annual meeting, 1986, 32.

(101) Westmoreland, P. R. *Combust. Sci. and Tech.* **1992**, *82*, 1515.

(102) Dean, A. M.; Westmoreland, P. R. *Int. J. Chem. Kinet.* **1987**, *19*, 207.

(103) Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem.* **1990**, *94*, 3313.

(104) Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem.* **1993**, *97*, 4427.

(105) Sengupta, D.; Chandra, A. K. *J. Chem. Phys.* **1994**, *101*, 3906.

(106) Nguyen, M. T.; Sengupta, D.; Vanquickenborne, J. *J. Phys. Chem.* **1996**, *100*, 10956.

(107) Nguyen, M. T.; Sengupta, D.; Vanquickenborne, J. *J. Phys. Chem.* **1996**, *100*, 9730.

- (108) Wooldridge, P.; Hanson, R. 25th Symposium (Intern'l) on Combustion, The Combustion Inst., Pittsburgh, PA, 1994, 983.
- (109) Nguyen, M. T.; Sengupta, D. *J. Chem. Phys.* **1997**, *106*, 9703.
- (110) Biggs, P.; C.; Mas, C. E.; Frachebourg, J. M.; Pan, A.; Shallcross, D. E.; Wayne, R. P. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 4163.
- (111) Craig, S. L.; Zhong, M.; Choo, B.; Brauman, J. L. *J. Phys. Chem.* **1997**, *101*, 19.
- (112) Zhong, M.; Brauman, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 636.