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ABSTRACT

I: REACTION OF CH_3Cl WITH H_2 AND CH_4 UNDER OXIDATION AND PYROLYSIS CONDITIONS

II: KINETIC ANALYSIS OF C_2H_6, C_2H_4, AND C_2H_2 REACTIONS WITH OH, O, H, AND Cl

by
Qing-Rui Yu

Experimental and detailed modeling are presented for the high temperature combustion systems involving $CH_3Cl/CH_4/O_2$ and $CH_3Cl/H_2/O_2$ reactions. More important C_2 species reaction rate constant are created. A mechanism incorporating 263 step elementary reactions and 76 stable compounds and active radicals is developed based on (1) fundamental thermochemical and Kinetic principles (2) Quantum Rice-Ramsperger-Kassel (QRRK) theory analysis (3) accurate thermodynamic Properties and thermochemical analysis (4) reliable experimental data to validate our model.

The study of Part II evaluates and analyzes theoretically the rate constants of C_2H_6, C_2H_4, and C_2H_2 reactions with OH, O, H, and Cl important to incineration based on detailed selection of accurate experimental data and QRRK analysis. Recommended rate constants can be applied to model research.

I: REACTION OF CH_3Cl WITH H_2 AND CH_4 UNDER OXIDATION AND PYRLYSIS CONDITIONS

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by
Qing-Rui Yu

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of Master of Science
Department of Chemical Engineering, Chemistry,
and Environmental Science
May 1992

APPROVAL PAGE

I Reaction of CH_3Cl with H_2 and CH_4 under Oxidation and Pyrolysis Conditions

II Kinetic Analysis of C_2H_6, C_2H_4, and C_2H_2 Reactions with OH, O, H, and Cl

by

Qing-Rui Yu

Dr. Joseph W. Bozzelli, Thesis Adviser
Distinguished Professor of
Chemical Engineering, Chemistry,
and Environmental Science, NJIT

Dr. L. Dauerman, Committee Member
Associated Professor of Chemical Engineering,
Chemistry, and Environmental Science, NJIT

Dr. John W. Liskowitz, Committee Member
Distinguished Professor of Civil and
Environmental Engineering, NJIT

BIOGRAPHICAL SKETCH

Author: Qing-Rui Yu

Degree: Master of Science in Environmental Science

Date: May, 1992

Undergraduate and Graduate Education:

- Master of Science in Environmental Science, New Jersey Institute of Technology, Newark, NJ, 1992
- Master of Science in Chemistry, Hangzhou University Hangzhou, P. R. China, 1991
- Bachelor of Science in Chemistry, Peking University Peking, P. R. China, 1965

Major: Environmental Science

Presentations and Publications:

Wenpin Ho, Qing-Rui Yu, and J. W. Bozzelli "Kinetic Study on Pyrolysis and Oxidation of CH_3Cl in $Ar/H_2/O_2$ Mixture" Combustion Science and Technology 1992 England Publishing.

This Thesis is dedicated to NJIT and Dr. Bozzelli

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CHAPTER 1
INTRODUCTION

1.1 Review of Previous Research

Earlier kinetic studies on methyl chloride pyrolysis were reported in 1959 by Shilov and Sabirova [1]. Measurements were made at initial CH_3Cl pressures of 10.1-34.3 torr, temperatures of 1062K-1147K, and at contact times of 0.4-5.0 seconds; They found HCl, CH_4, and C_2H_2 in the ratios of 3:1:0.6. These yields were reported to be consistent with the following proposed mechanism:

$CH_3Cl = CH_3 + Cl$

$CH_3 + CH_3Cl = CH_4 + CH_2Cl$

$Cl + CH_3Cl = CH_2Cl + HCl$

$2CH_2Cl = CH_2ClCH_2Cl$

$CH_2ClCH_2Cl = C_2H_3Cl + HCl$

$C_2H_3Cl = C_2H_2 + HCl$

They also reported that the measured apparent first-order rate constants increased with increasing pressure.

Slater's theory was used by Holbrook [2] to calculate the rate constant for the decomposition of CH_3Cl in the fall-off region. The value obtained was by 5-6 orders of magnitude lower than the reported experimental values above. Frost and Laurent [3] obtained a better fit to this value using RRKM theory, where rotations were considered inactive, and activation energy was taken from the experimental data. With Harmonic energy levels the calculated

rate constant was 32 times smaller than experimental value, and with a correction for an harmonicity the calculated rate constant was only 20 times smaller. These modeling calculation may have indicated that the experimental data was not correctly fit rate constants.

In 1980, Kondo, Saito, Murakami [4] pyrolyzed CH_3Cl in shock tube at temperatures between 1680K and 2430K, at total pressures of 1-5 atm, for reactant mixtures of 0.2%-0.5% methyl chloride in argon. CH_3 concentrations were measured via their absorption band at 216 nm. From the initial rate of CH_3 formation the elementary rate constant for breaking the C-Cl bond was obtained. The reaction [illegible] in the fall-off region even at the highest pressures. For these high temperature shock tube data, the mechanism was considered to include the following likely reactions:

$CH_3Cl + M = CH_3 + Cl + M$ (1)

$CH_3Cl + Cl = CH_2Cl + HCl$ (2)

$CH_3Cl + CH_3 = CH_2Cl + CH_4$ (3)

$CH_3Cl + CH_2Cl = CH_3 + CH_2Cl_2$ (4)

$C_2H_6 + M = 2CH_3 + M$ (5)

$Cl_2 + M = 2Cl + M$ (6)

$2CH_2Cl = C_2H_4Cl_2$ (7)

$C_2H_4Cl_2 = C_2H_3Cl + HCl$ (8)

$C_2H_3Cl + M = C_2H_2 + HCl + M$ (9)

$CH_2Cl + CH_3 = C_2H_5Cl$ (10)

$C_2H_5Cl = C_2H_4 + HCl$ (11)

$C_2H_4 + M = C_2H_2 + H_2 + M$ (12)

Computer simulation of the CH_3 profiles without reaction (4), and with k_7 and k_{10} equal to k_5 fitted the experimental data at high temperatures exactly and were higher by a factor of 2 at low temperatures. Low- and High-pressure rate constants (k_o [Ar] and k_∞) were obtained from the experimental data applying a refined RRKM theory which involved a weak collision effect: $\log k_o/[Ar] = 12.56-59/\theta$ L/mol.s $\log k_\infty = 13.86-91.0/\theta s^{-1}$. The low-pressure rate constant is in agreement with the value derived by Holbrook [2] from the data reported in [1].

Data on the pyrolysis of CH_3Cl at a high degree of conversion were reported by LeMoan [5]. The reaction was run at 993K in 30 hours in batch reactor at conversion larger than 95%. The gas phase contained HCl, CH_4, and small quantities of H2, benzene, and toluene. At the beginning of the pyrolysis low transient concentrations of CH_2Cl, C_2H_6, and C_2H_5Cl were detected at 993K. In the liquid phase benzene (72%), toluene (11%), xylene (1%), and monochlorobenzene (12%) were identified. There were two distinct solid phases: carbon in the reactor and naphthalene and soot at the exit from the reactor. The reaction mechanism, despite the large number of products identified, was considered to be schematically simple. It was proposed that, initially, CH_3Cl would decompose into

HCl and CH_2, which would dimerize into C_2H_4 or decompose into CH + H or C + H_2. The combination of two CH radicals would form acetylene, which could cyclize to form benzene, from which the identified higher molecular weight compounds would be formed. The hydrogenation of CH_2 radicals would lead to methane. As we shall see later, this mechanism is not plausible.

M. Weissman, and S. W. Benson [6] presented results obtained in batch laboratory experiments and detailed modeling of the chlorine-catalyzed polymerization of methane at 1260-1310K. The reaction can be separated into two stages, the chlorination of methane and pyrolysis of CH_3Cl. The pyrolysis of CH_3Cl formed C_2H_4 and C_2H_2 in increasing yields as the degree of conversion decreased and the excess of methane increased. In the absence of CH_4 C_2H_4 and C_2H_2 are formed by the recombination of CH_3 and CH_2Cl radicals. With added CH_4 recombination of CH_3 forms C_2H_6, which dehydrogenates to C_2H_4 + H_2. C_2H_4 in turn dehydrogenates to C_2H_2 + H_2. They thought that HCl, C, CH_4 and H_2 were the ultimate stable products, C_2H_6, C_2H_4, and C_2H_2 are produced as intermediates and appear to approach stationary concentrations in their reaction system. The secondary reactions can be described by radical reactions. CH_3-initiated polymerization of C_2H_4 was negligible relative to the C_2H_3 formation through H abstraction by Cl. The fastest reaction of C_2H_3 is its

decomposition to C_2H_2. About 20% of the consumption of C_2H_2 can be accounted for by the addition of C_2H_3 to C_2H_2 with formation of the butadienyl radical (C_4H_5 or C*CC*C.); About 10% of C_4H_5 was indicated to abstract H from HCl and form butadiene (C_4H_6 or C*CC*C). Successive additions of C_2H_3 to butadiene and the respective products of addition were reported to form benzene, styrene, naphthalene, and higher polyaromatics under the condition of pyrolysis of CH_3Cl.

A mechanism was written to describe the early stages (10% conversion) of CH_3Cl decomposition in CH_3Cl/CH_4 system:

$CH_3Cl = CH_3 + Cl$ (1)

$Cl + CH_3Cl = CH_2Cl + HCl$ (2)

$Cl + CH_4 = CH_3 + HCl$ (3)

$2\ CH_3 = C_2H_6$ (4)

$2\ CH_2Cl = ClCH_2CH_2Cl$ (5)

$CH_3 + CH_2Cl = CH_3CH_2Cl$ (6)

$CH_3CH_2Cl = C_2H_4 + HCl$ (7)

$ClCH_2CH_2Cl = HCl + C_2H_3Cl$ (8)

$C_2H_3Cl = C_2H_2 + HCl$ (9)

$C_2H_6 + Cl = HCl + C_2H_5$ (10)

$C_2H_5 = C_2H_4 + H$ (11)

$H + HCl = H_2 + Cl$ (12)

$Cl + C_2H_2 = C_2H + HCl$ (13)

$Cl + C_2H_4 = C_2H_3 + HCl$ (14)

$CH_3 + C_2H_4 = CH_3CH_2CH_2$ (15)

$CH_3CH_2CH_2 = CC*C + H$ (16)

$CH_3 + CC*C = C_2CC.$ (17)

$C_2CC. = C_2C*C + H$ (18)

$C_2H_3 + C_2H_4 = C*CCC.$ (19)

$C*CCC. = C*CC*C + H$ (20)

$C_2H_3 + C_2H_2 = C*CC*C.$ (21)

$C*CC*C. = C\#CC*C + H$ (22)

$C*CC*C. + HCl = C*CC*C + Cl$ (23)

Benson postulated that once formed, butadiene can add rapidly to C_2H_3 and through subsequent cyclizations and dehydrogenations, which are very fast processes, lead to benzene:

$C_2H_3 + C*CC*C = C*CCC.C*C$ (24)

$C*CCC.C*C = C*CC*CC*C + H$ (25)

$C*CC*CC*C = C_6H_6 + H_2$ (26)

Other pathways for C_6H_6 formation were reported through the additions of C_4 radicals to C_2H_2 and C_2H_4. The pathways leading to polyaromatics and soot are through reactions of C2H3 radical addition to multiple bonds as, for example,

$C_2H_3 + C_6H_6 = C_6H_6C_2H_3 = C_6H_5C_2H_3 + H$

$C_6H_5C_2H_3 + C_2H_3 = C_6H_5C_4H_6 = C_{10}H_{10} + H$

Benson's modeling did not consider CH_3 addition to C_2H_2 to form C_3 species followed by reactions between C_3 to lead to C_6H_6.

Westbrook C. K. [7] reported his studies on inhibition and extinction of hydrocarbon oxidation by halogen acids and halogenated hydrocarbons formed by combining Cl, Br, or I atoms with methyl, ethyl or vinyl radicals in both laminar flame and detonations both in experiment and theory. In all of cases examined, halogenated species act by catalyzing the recombination of H atoms into relatively non-reactive H_2 molecules reducing the available radical pools and lowing the overall rate of chain breaching. In agreement with experimental observations, his modeling study indicated I atoms are the most effective. Br atoms are slingtly less effective than I atoms and Cl atoms are very much less effective as kinetic inhibitor. The additional fuel content of halogenated hydrocarbons makes their inhibition efficiency vary with equivalence ratio, and for all of the inhibitors increased pressure also increases the inhibition efficiency. The reported inhibition mechanism for HI, HBr, and HCl can be summarized in cycle I of reactions.

$H + X_2 = HX + X$

$H + HX = H_2 + X$

$X + X + M = X_2 + M$

$H + X + M = HX + M$

In cycle I X refers to the halogen atom. The first three reactions in cycle I about constitute a catalyzed recombination of H atoms which are the unavailable for chain

breaching through reaction with O_2 molecules or reactions fuel molecules in the pre-flame pyrolysis region. For the halogenated hydrocarbons C-X bond energies are much less than the C-H bond energies (ie. CH_3-H 104 Kcal/mole; CH_3-Cl 83.5; CH_3-Br 70; CH_3-I 56 [8]) so halogen atom abstraction have a much larger rate than H atom abstraction for these inhibitors. For the halogenated hydrocarbon species the reported inhibition pattern is dominated by cycle II of reactions:

$H + RX = HX + R$

$R + X_2 = RX + X$

$H + HX = H_2 + X$

$X + X + M = X_2 + M$

Like the earlier cycle I, the net result of these reactions is $H + H = H_2$ a catalyzed recombination of H atoms and a reduction in chain breaching.

In 1988, Senkan et al. [9] constructed the CH_3Cl combustion mechanism by combining a mechanism describing CH_4 combustion together with sub-mechanism describing the chlorine inhibition of CO oxidation. This mechanism was used to calculate the stable species concentration profiles in atmospheric pressure sooting $CH_3Cl/CH_4/O_2/Ar$ premixed flat flames [10]. Their studies concluded that CH_3Cl promotes not only the decay of CH_4 to CO_2 and H_2O but also soot formation by simultaneously increasing the rates of C_2H_3 and C_2H_2 formation. However a number of their

rate constants were from estimation techniques and their mechanism extended only up to C_2-species. C_1 reaction mechanism involving unimolecular decomposition, abstraction, and oxidation is reasonably well understood in describing CH_4 combustion at present. The C_2 chemistry, however, is in need of improvement and specially reactions of chlorinated C_2 radicals. CH_3 and C_2 radical reactions: thermal decomposition, oxidation by O and O_2, recombination and addition are four competitive reactions because Cl abstracts H rapidly (high Arrhenius A factor and low energy of activation), which produces and active hydrocarbon or H radical pool early in the reaction. These hydrocarbon radicals combine to C_2 radical more in presence of Cl. Therefore, the C_2 chemistry is important here even though the amount of C^+_2 species account under 15% of carbon in the $CH_3Cl/CH_4/O_2$ system.

1.2. The Objectives of Research

In view of above review, the objectives of this thesis are as follow:

(1). Analysis of selected C_2-species reactions with OH, O, H, and Cl important to incineration and creation of reasonable reaction rate constants of important C_2 species.

(2). Clarifying the important species reaction behavior and their effects on other reations in the studied systems.

(3). Developing a detail model describing CH_3Cl combustion to shed some light on these issues discussed in review.

CHAPTER 2
EXPERIMENTAL METHOD

2.1. The Basis on Use of Tubular Flow Reactor

Isothermal tubular reactors are commonly used for fundamental reaction rate studies. The encountered problem of relating axial distance along the reactor with residence time has been resolved well by Chang and Bozzelli [11]. They have solved the continuity equation for laminar flow in a tubular reactor considering a parabolic velocity profile with radial dispersion, parallel bulk and wall reactions with coupled first order rate constants. They show a method to determine homogeneous and heterogeneous rate parameters simultaneously from their optimum values. The plug flow model is a good approximation for our present reactors.

2.2. Experimental Method

The thermal reaction of CH_3Cl in H_2/O_2 or CH_4/O_2 mixtures in an Ar bath gas was studied at 1 atmosphere total pressure in a 10.5/16.0 mm ID tubular flow reactors. The reaction systems were analyzed systematically over a temperature range from 1098K to 1173/1223K, with average residence times ranging from 0.2/0.4 to 2.0 secands.

A schematic of the apparatus is shown in Chart 1. The feed gases CH_3Cl, O_2, and H_2 were added into the argon flow stream as required and flow rate is measured with calibrated rotameter. Make-up Ar was also introduced after

the mixture to adjust to the total concentration. A small computer code is used to calculate the flow of each reagent for the desired residence times at each temperatures. Complete feed gas mixing occurred in 38 cm of the flow tube located upstream of the furnace and held at 423K.

The high temperature quartz, tubular flow reactors were heated in a three zone electric tube furnace. Temperature profiles were obtained using a type K thermocouple probe moved axially within the reactor under representative flow conditions. Tight control resulted in temperature profiles isothermal to within ± 5K over the central 80% of the furnace length throughout the temperature range studied.

The reactor effluent was monitored by an on-line Perkin Elmer 900 Gas Chromatograph (GC) equipped with dual Flame Ionization Detector (FID). A methanizer catalyst is used to convert CO and CO2 to CH4 so that they can be detected by the FID. The GC peak areas corresponding to the inlet concentrations were determined by sampling a reactor bypass stream. All connecting lines from reactor to the GC (ca 1 meter in length) were heated to 373K to limit condensation. Two VALCO 6 port gas sampling valves were used to direct the reactor effluent to the GC columns. A 1% ALLTECH AT-1000 on Graphpac-GB 60/80 column 3.175 mm x 2.43 m length was used to separate C_2 through

C_6 compounds (acetylene through chlorobenzene). A GCA-013 SPHEROCARB 100/120 column 3.175 mm x 1.8 m length was used to separate CO, CO_2, CH_4, and CH_3Cl before the methanizer and second FID.

A series of seven to eight residence times were run for each given inlet concentration matrix by systematic variation in the methyl chloride, hydrogen, oxygen, and make-up argon flowrates. Every third run was repeated to ensure reproducibility of results. The relative deviation on GC results is less than $\pm$15%.

Quantitative analysis of product HCl was performed for all cases. The samples for HCl analysis were collected independently from GC sampling as illustrated in Chart 1. In this analysis, the effluent was passed through a two stage bubbler containing 0.01 M NaOH before being exhausted to the hood. The effluent HCl concentration was then calculated based upon titration of the solution with 0.01 M HCl to its phenolphthalein end point. Several titrations were performed using buffered solution (pH 4.7) to discern if CO_2 was effecting the quantitative measurement of HCl. No significant effect was observed due to the relatively low levels of CO_2. The relative deviation on HCl analysis is less than $\pm$5%.

Positive identifications of all reactor effluent species were made by GC/Mass Spectrometer applied to batch samples drawn from the reactor exit into previously evacu-

ated 25 ml stainless steel or Pyrex glass sample cylinders. A Finnigan 4000 series GC/MS, with a 0.22 mm x 50 m methyl silicone stationary phase column was used. Gas samples were inlet by cryofocussing (ie 77K) on a 12 cm length of the capillary column.

Tubular Flow Reactor
Temp. Constant ± 5 Degree
GC and GC/Mass Spec Analysis

VARIABLES
Residence Time (0.2 to 2.0 sec)
Temperature 1098-1223 K

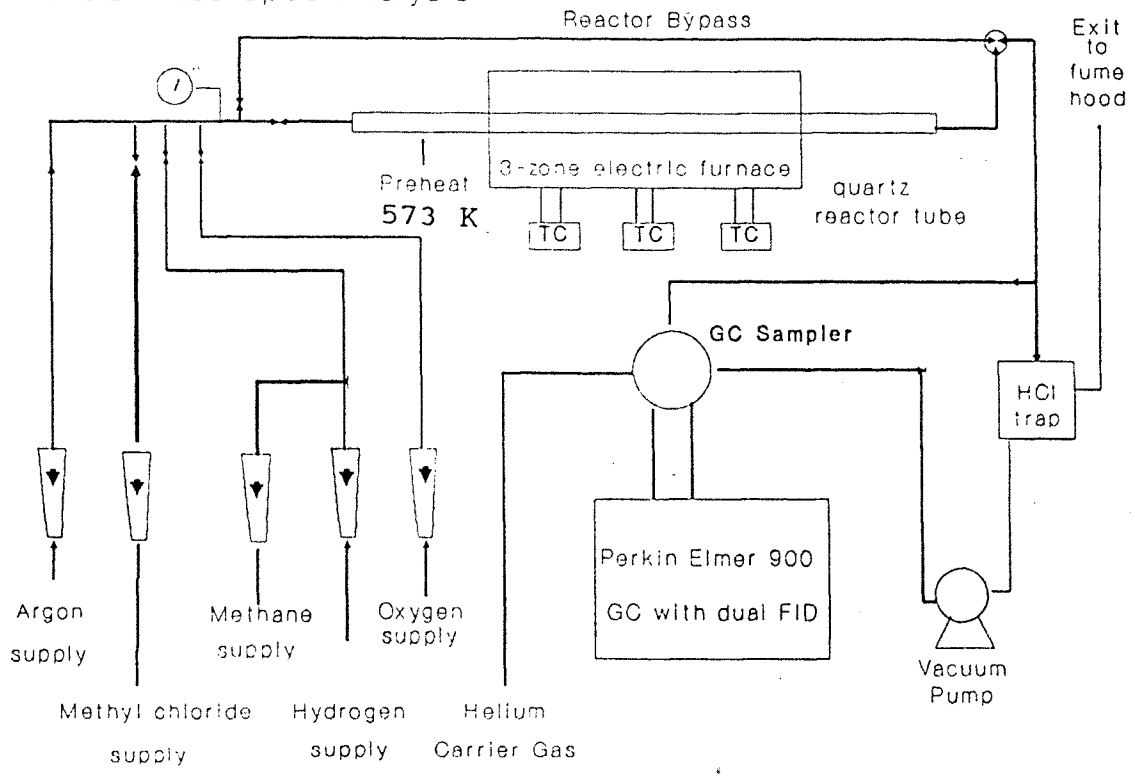


Chart 1 SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS

Table 1. Average Retention Time of Products

Compound	Average Retention Time (min.) Column A	Column B
CH_4	6.82	1.73
CO_2	9.63	
C_2H_2	12.48	2.39
C_2H_4	14.44	2.66
C_2H_6	16.87	
CH_3Cl	30.64	4.43
C_2H_3Cl		7.42
C_2Cl_2*		9.97
$C_2H_2Cl_2$		12.78
C_6H_6		17.97

* Estimated compound based on its retention time and reaction mechanism of CH3Cl.

** A column, GCA-OB SPHERO CARB 100/120 3.175 mm * 18 m. B column, 1% ALLTECH AT-1000 on GRAPHPAC-GB 60/80, 3.18 mm * 2.43 m (the below is same).

Table 2. Relative Response Factors of Several Compounds

Compound	Relative Response Factors (RRF) Column A	Column B
CO	1.082	
CH_4	1.00	1.00
CO_2	1.19	
C_2H_2	1.14	
C_2H_4	1.972	2.00
C_2H_6	2.036	
CH_3Cl	1.00	1.00
C_2H_3Cl		1.67
C_2Cl_2*		2.00
$C_2H_2Cl_2$*		2.00
C_6H_6*		6.00

* Estimated on Carbon Number Contribution to Response Values

** Corrected area = Measured area/RRF

2.3 Kinetic Model Computer Integration — A Thinking Experimental Tool

The CHEMKIN computer program package is used in interpreting and integrating the detailed reaction mechanism (model) of the reaction system. The CHEMKIN program [12], Chart 2, reads the user's symbolic description of the reaction mechanism. The thermodynamic data base, which has the appropriate thermodynamic information and mass for all species present in mechanism. The information on the elements, species, and reactions in the mechanism; and finally the CHEMKIN gas phase subroutines, which can be called to return information on the elements, species, reactions equations of state, thermodynamic properties, chemical production rates, and derivatives of thermodynamic properties relative to any time in the integration. The input to these subroutines are usually the state variables of gas pressure or density, temperature and species composition at initial time of reaction. The routines can be called with the species composition defined in terms of either mass fraction or molar concentration. Numerical calculations were carried out using the CHEMKIN computer code coupled to LSODE a linear solver of ordinary differential calculations.

The input data requirement to run CHEMKIN program include:

. Detailed reaction mechanism

Mole fraction of all gases present in the reaction system

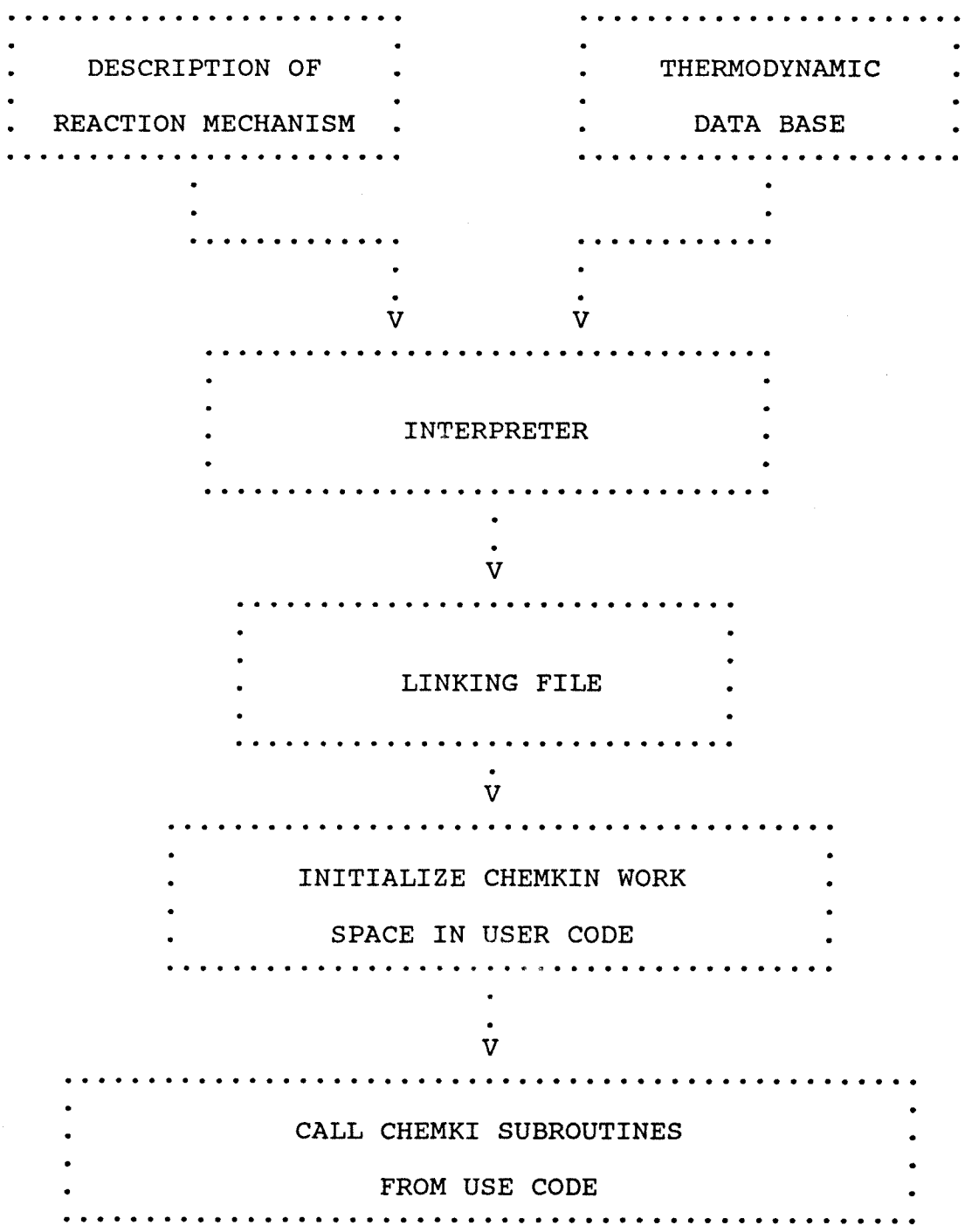


Chart 2. Structure of the **CHEMKIN** Package

. Pressure and temperature at which the reaction system being studied

. Time increament at which the concentration of species present in the system be reported

A thermodynamic data base for species with C/H/Cl/O elements is developed at NJIT and used for modeling the kinetic scheme of elementary reactions input to the program. For those species where thermodynamic information was not available in the data base, thermo data was generated utilizing **Thermfit** program. This program requires heat of formation and entropies, as well as heat capacities, from 298 to 1000K as input. These parameters were calculated by group additivity method of Benson [8] when not available in literature and computer code **THERM** [13].

CHAPTER 3
RESULTS and DISCUSSION

The experimental conditions of the reaction of $CH_3Cl/H_2/O_2$ and $CH_3Cl/CH_4/O_2$ mixtures with argon are listed below:

Reactant molar ratios:

(I). $Ar:CH_3Cl:H_2:O_2 = 97:1:1:1$

(II). $Ar:CH_3Cl:H_2:O_2 = 96:2:1:1$

(III). $Ar:CH_3Cl:CH_4:O_2 = 96:1:1:2$

(IV). $Ar:CH_3Cl:CH_4:O_2 = 95:2:1:2$

Reactor Internal Diameter (ID) is 10.5 mm.

Reaction Temperature (^oK): 1098, 1123, 1148, 1173, 1198, 1223.

For the 16.0 mm ID reactor,

Reactant molar ratios:

(I). $Ar:CH_3Cl:H_2:O_2 = 97:1:1:1$

(V). $Ar:CH_3Cl:H_2:O_2 = 95.5:1:1:2.5$

(III). $Ar:CH_3Cl:CH_4:O_2 = 96:1:1:2$

(VI). $Ar:CH_3Cl:CH_4:O_2 = 94:1:1:4$

Reaction Temperature (^oK): 1098, 1123, 1148, 1173.

Residence Time (second=sec):

0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0 (ID=10.5 mm)

0.4, 1.0, 1.2, 1.4, 1.8, 2.0 (ID=16.0 mm)

Operation Pressure: 1 atm.

Effective Reactor Length: 38.0 cm.

3.1 Thermal Reaction of $CH_3Cl/H_2/O_2/Ar$ Systems

In the thermal reaction systems of $CH_3Cl/H_2/O_2/Ar$ of this study, CH_3Cl, CH_4, C_2H_4, C_2H_2, C_2H_3Cl, CO, CO_2, and HCl were major products. small amounts of C_2H_6, $C_2H_2Cl_2$, C_2Cl_2, and C_6H_6 were sometimes measured depending on residence time, temperature. Experimental results on product distribution of thermal reaction of methyl chloride are in Figure 1 to 36 (ID=10.5 mm) and 78 to 101 (ID=16.0 mm). These Figures show normalized concentration (Cx/Co) as a function of the average residence time for several temperatures.

3.1.1 Initial Conversion and Complete Conversion Temperatures

The temperature of initial conversion (around 5%) for methyl chloride at 0.4 s is 1098K and the temperature of complete conversion (around 99%) is 1173K at less than 1.0 second reaction time for the ratio of $Ar:CH_3Cl:H_2:O_2$ = 95.5:1:1:2.5 (close to stoichiometric ratio). The ratios of CH_3Cl and H_2 to O_2 (mole) and of reactor surface (S) to volume (V) influence the conversion of CH_3Cl and product distribution.

3.1.2 Residence Time and Temperature Effects

The figures 1 to 36 and 78 to 101 show the effects of time and temperature on the reaction system. Methyl chloride decay, and the formation of CO_2, and HCl increase with time and temperature. CH_4, CO, C_2H_2, C_2H_4, C_2H_3Cl, C_2H_6,

$C_2H_2Cl_2$, C_2Cl_2, C_6H_6 increases with time at lower temperature. Their maxima were present with time increase. These maxima shift to lower times with increasing temperature.

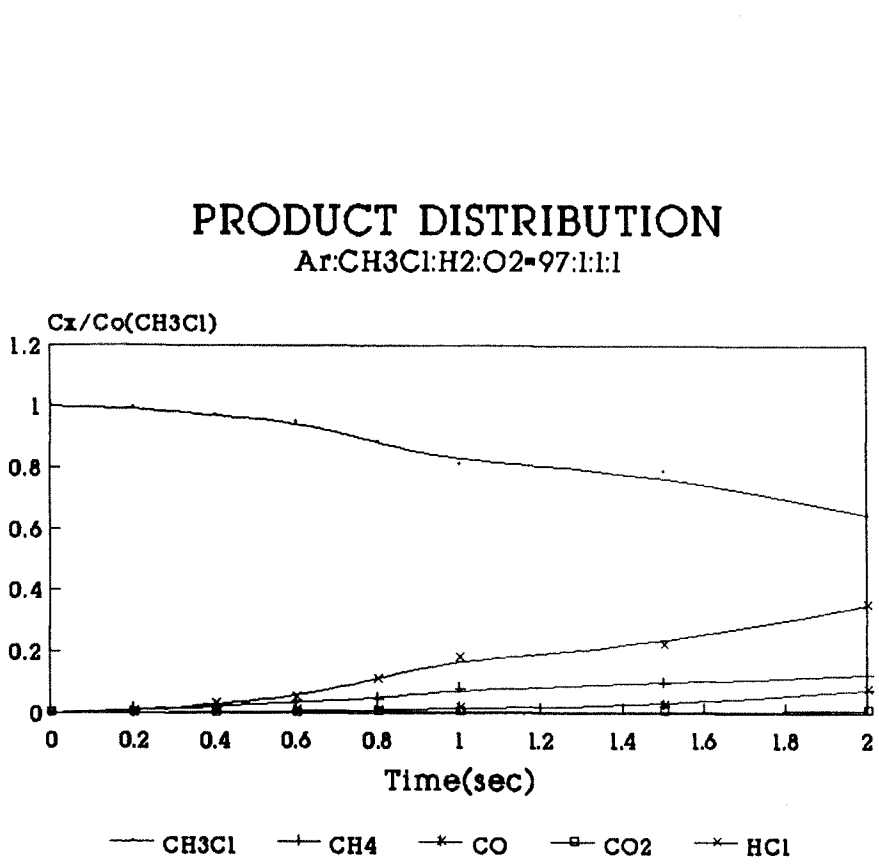


Fig. 1 1098K "10.5" Tube

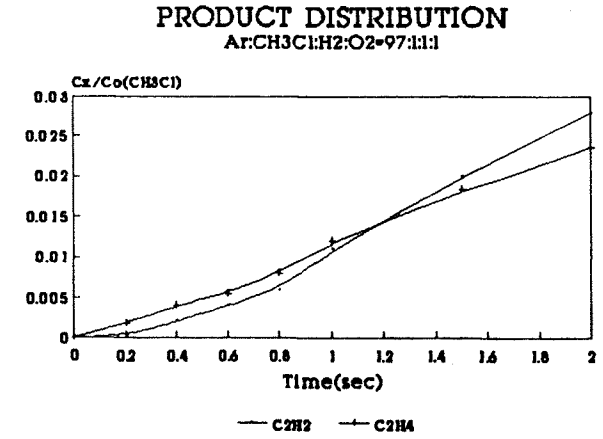


Fig. 2 1098K "10.5" Tube

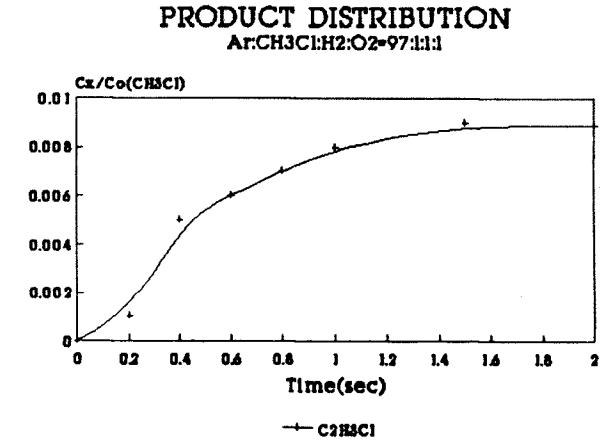


Fig. 3 1098K "10.5" Tube

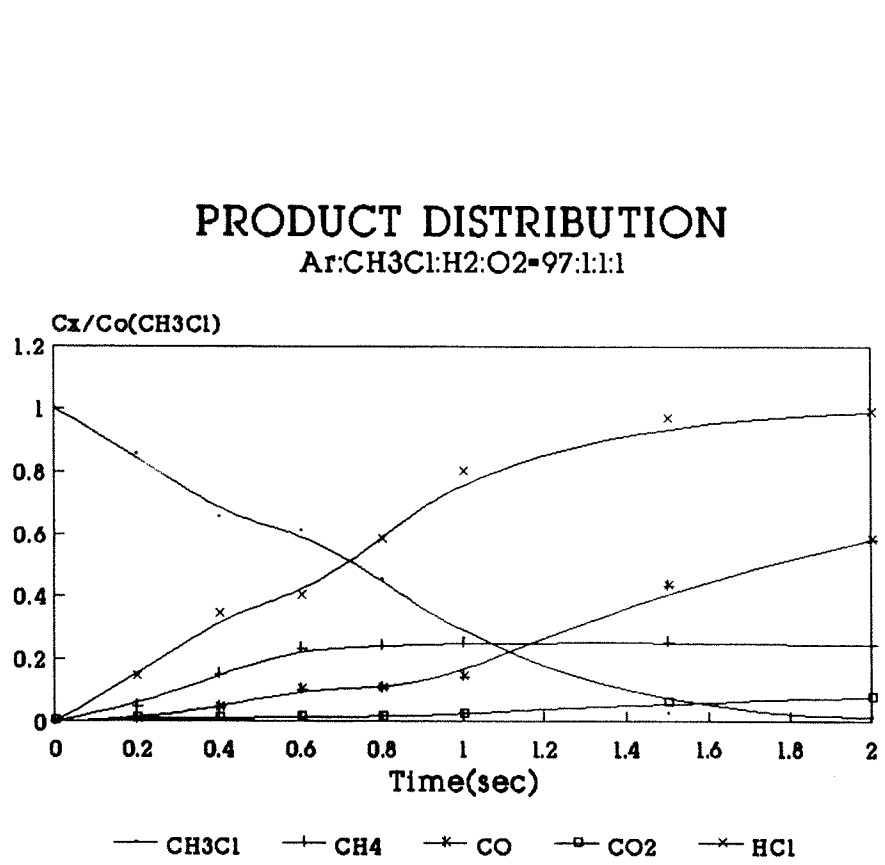


Fig. 4 1123K "10.5" Tube

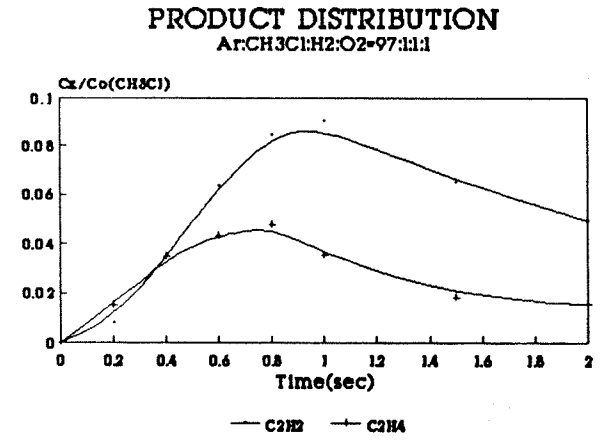


Fig. 4 1123K "10.5" Tube

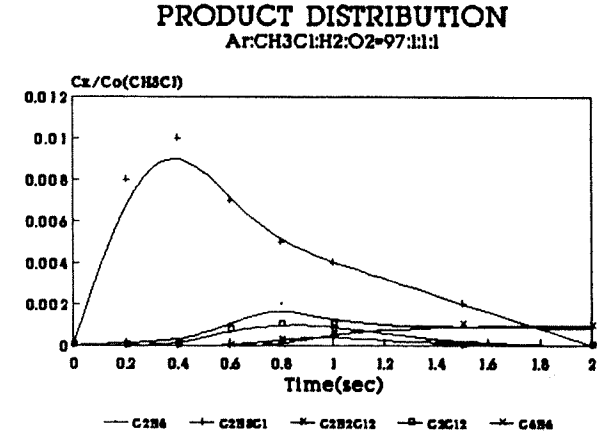
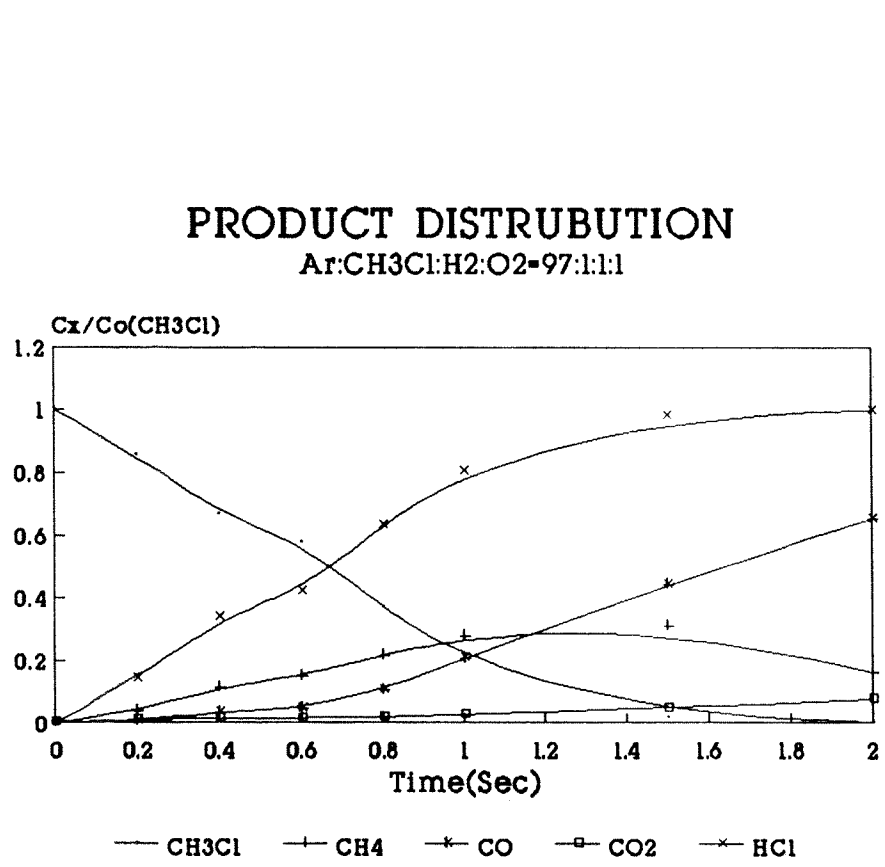


Fig. 4 1123K "10.5" Tube



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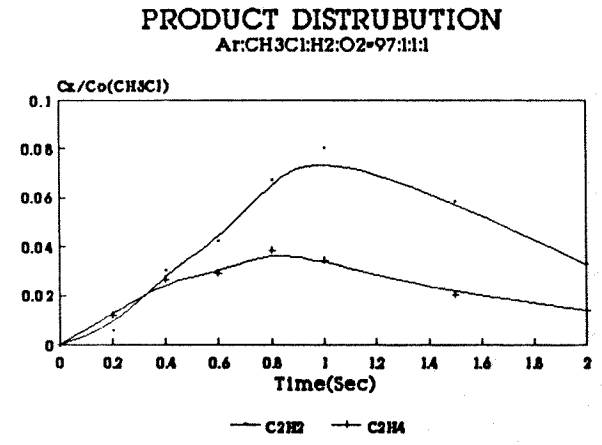


Fig. 8 1148K "10.5" Tube

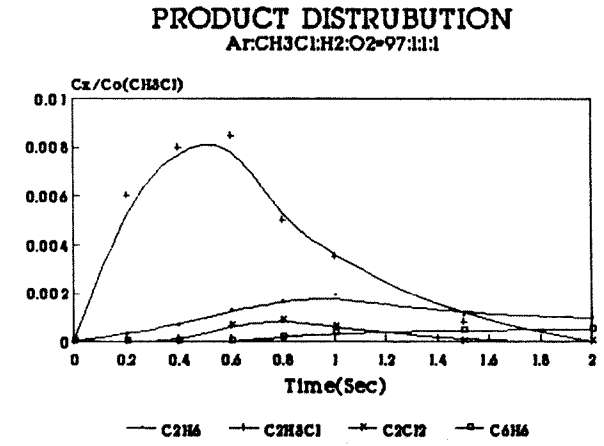


Fig. 9 1148K "10.5" Tube

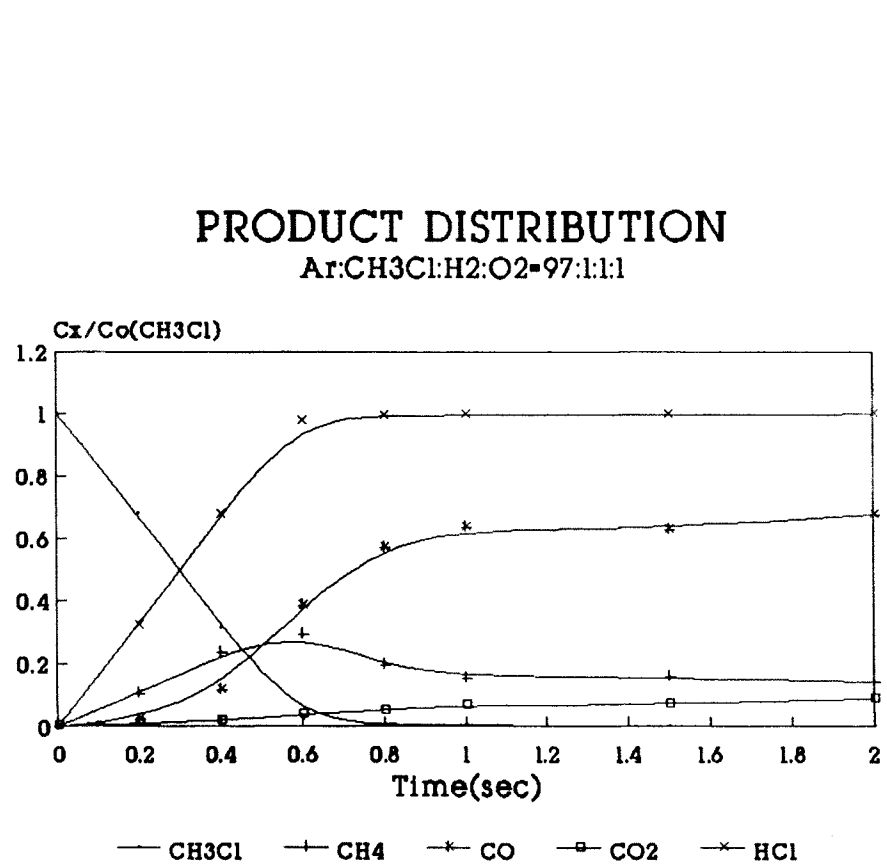


FIG. 10 1173K "10.5" Tube

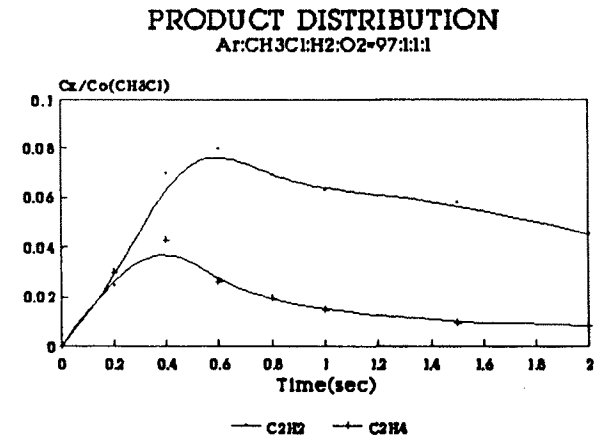


Fig. 11 1173K "10.5" Tube

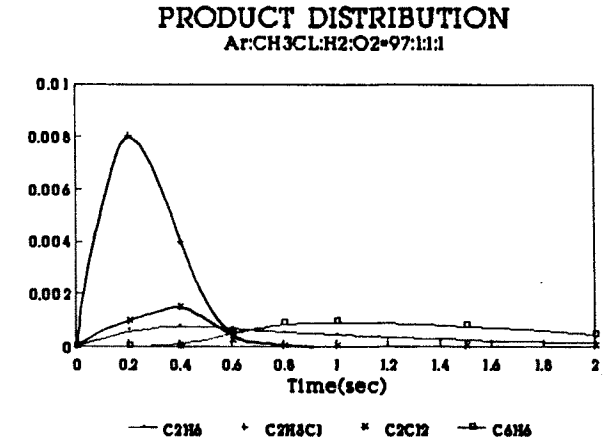


Fig. 12 1173K "10.5" Tube

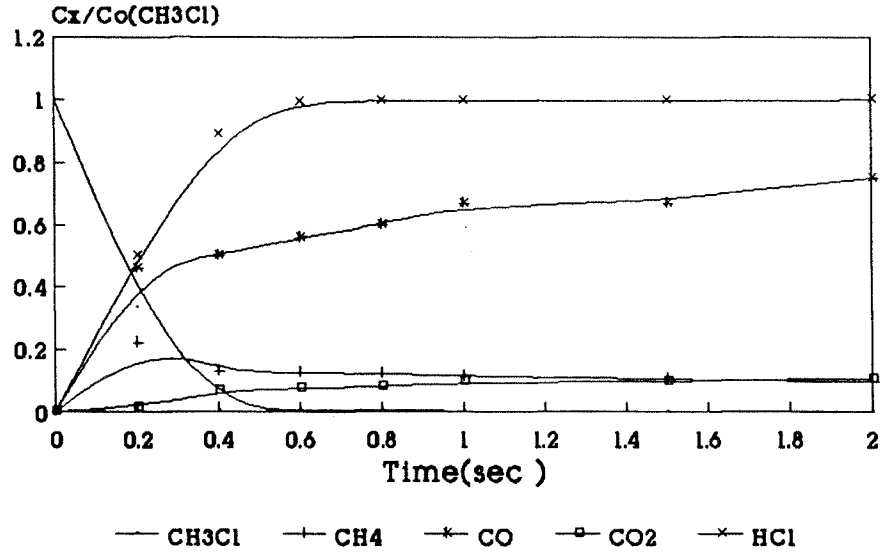


Fig. 13 1198K "10.5" Tube

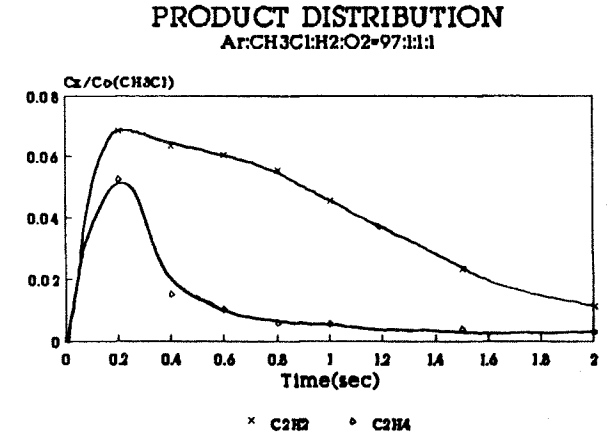


Fig. 14 1198K "10.5" Tube

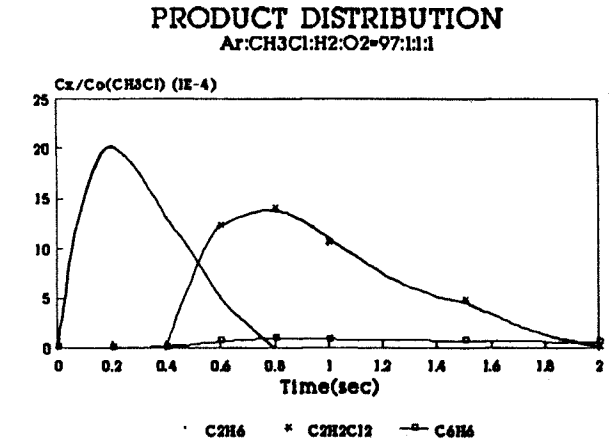


Fig. 16 1198K "10.5" Tube

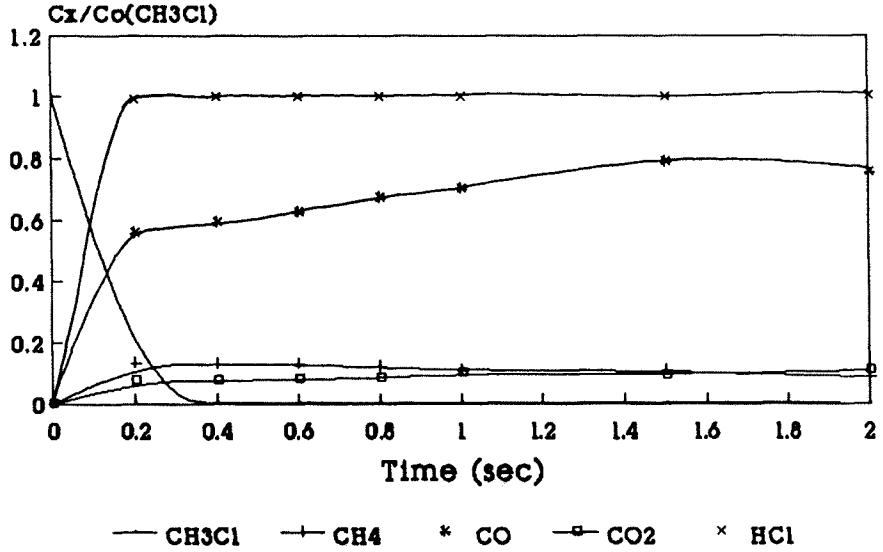


Fig. 16 1223K "10.5" Tube

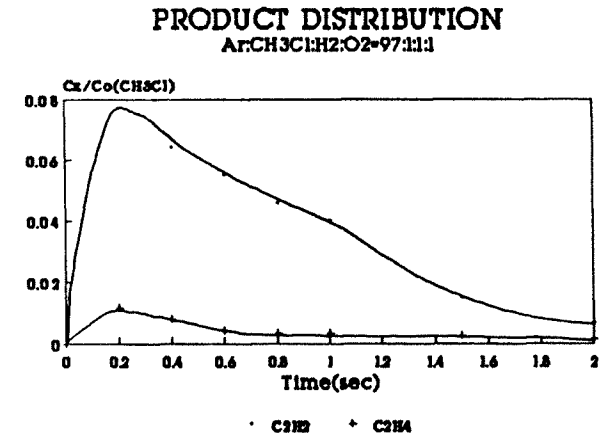


Fig. 17 1223K "10.5" Tube

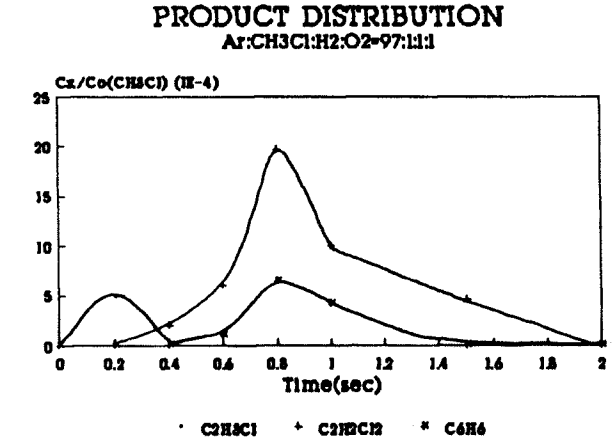


Fig. 18 1223K "10.5" Tube

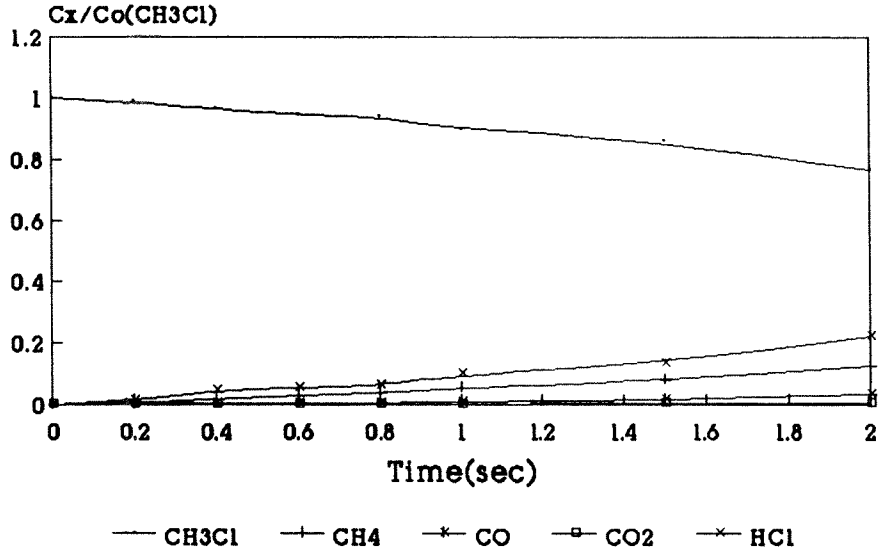


Fig. 19 1098K "10.5" Tube

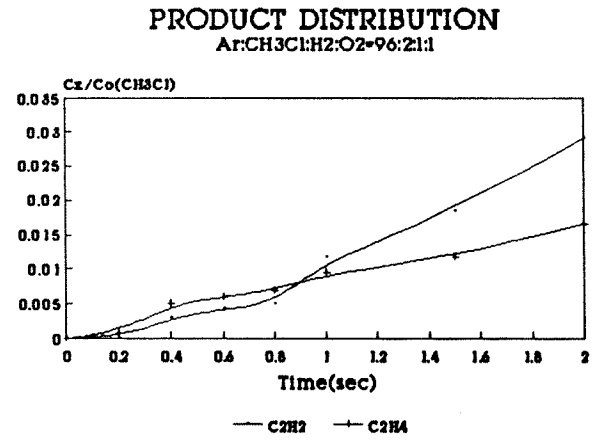


Fig. 20 1098K "10.5" Tube

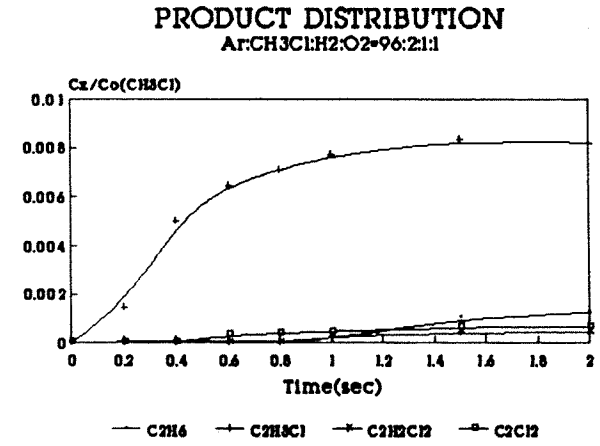


Fig. 21 1098K "10.5" Tube

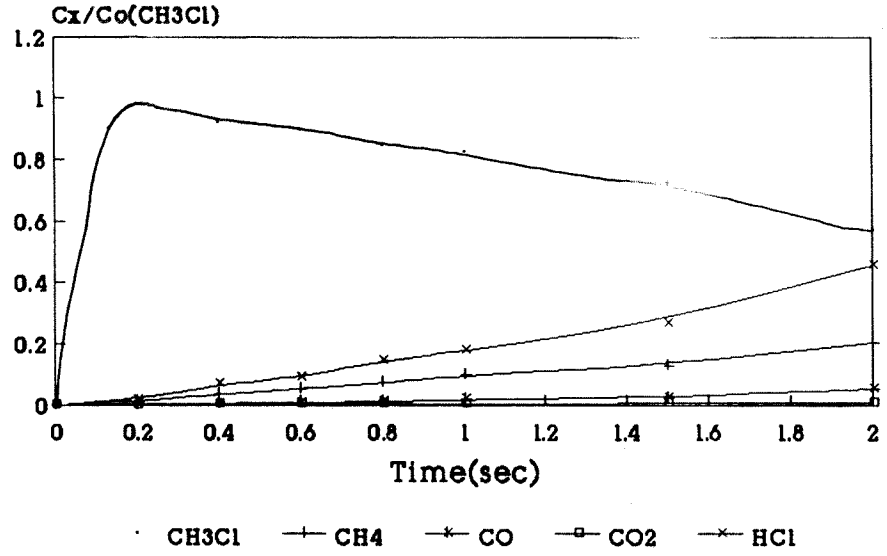
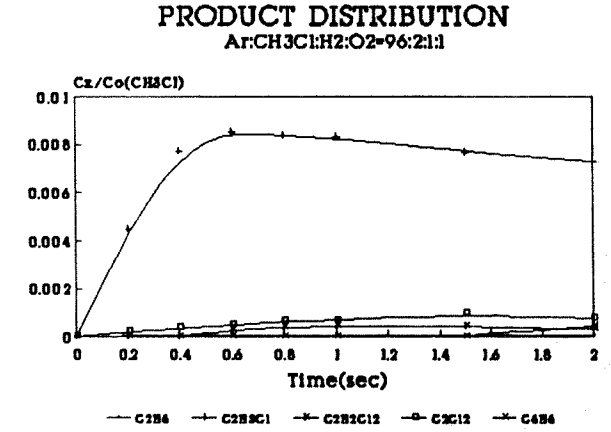


Fig. 22 1123K "10.5" Tube



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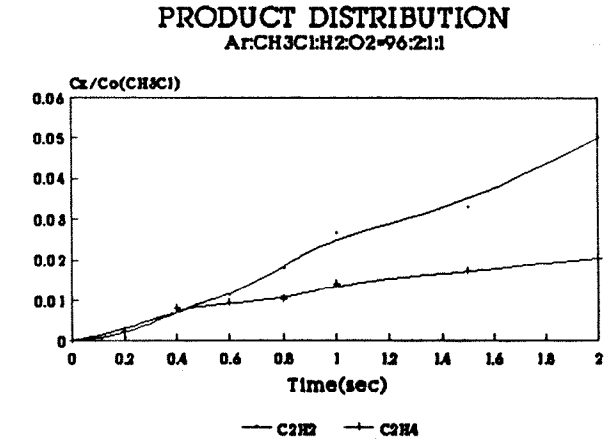


Fig. 24 1123K "10.5" Tube

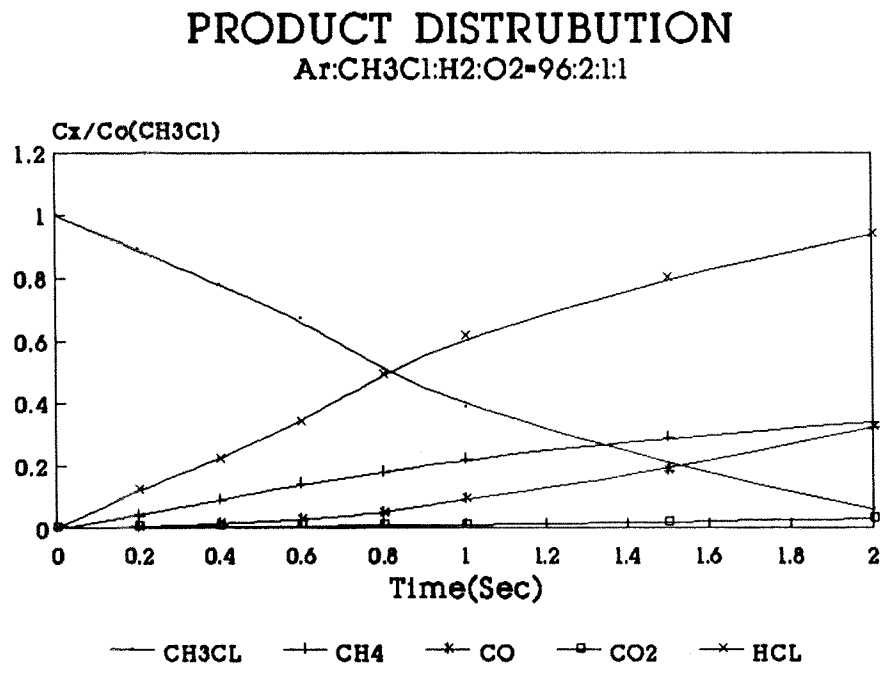


Fig. 25 1148K "10.5" Tube

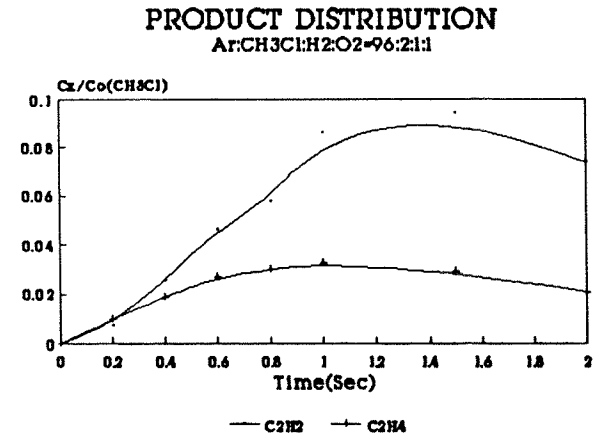


Fig. 26 1148K "10.5" Tube

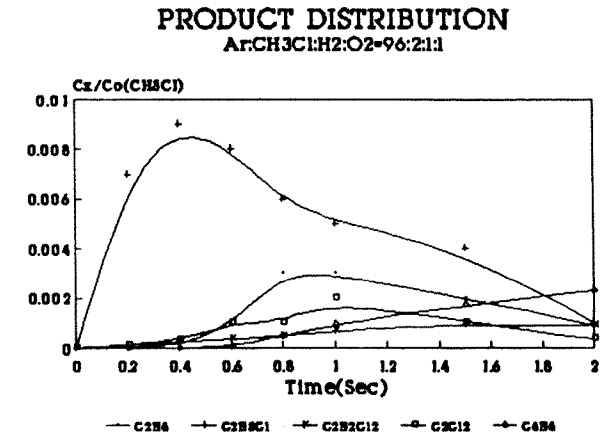


Fig. 27 1148K "10.5" Tube

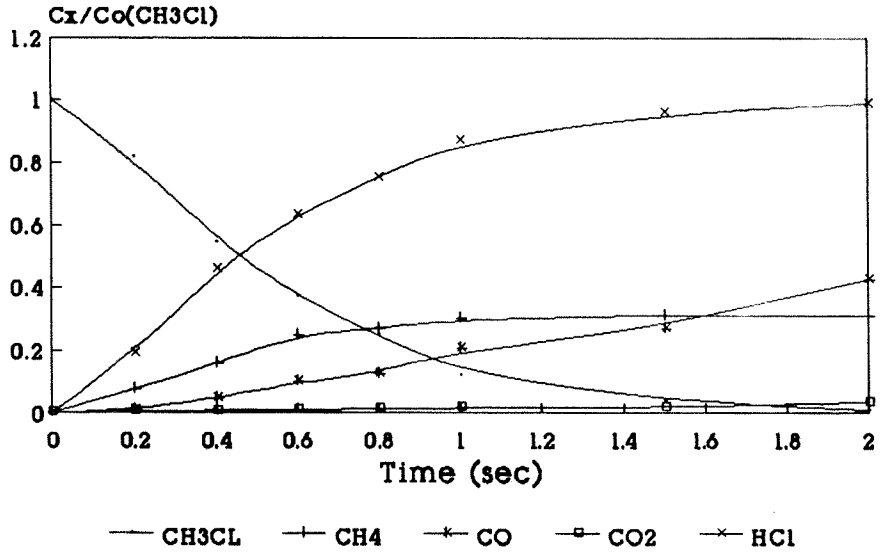


Fig. 28 1173K "10.5" Tube

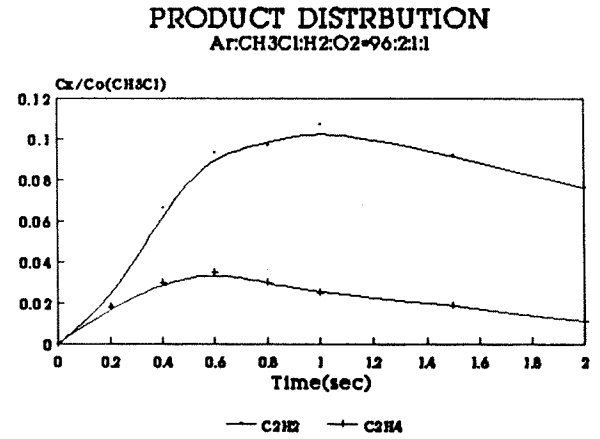


Fig. 29 1173K "10.5" Tube

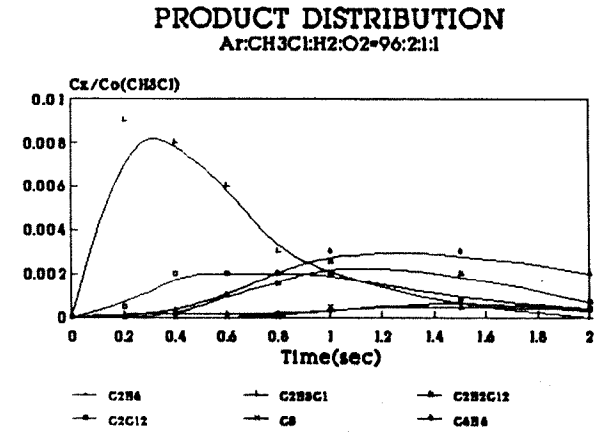


Fig. 30 1173K "10.5" Tube

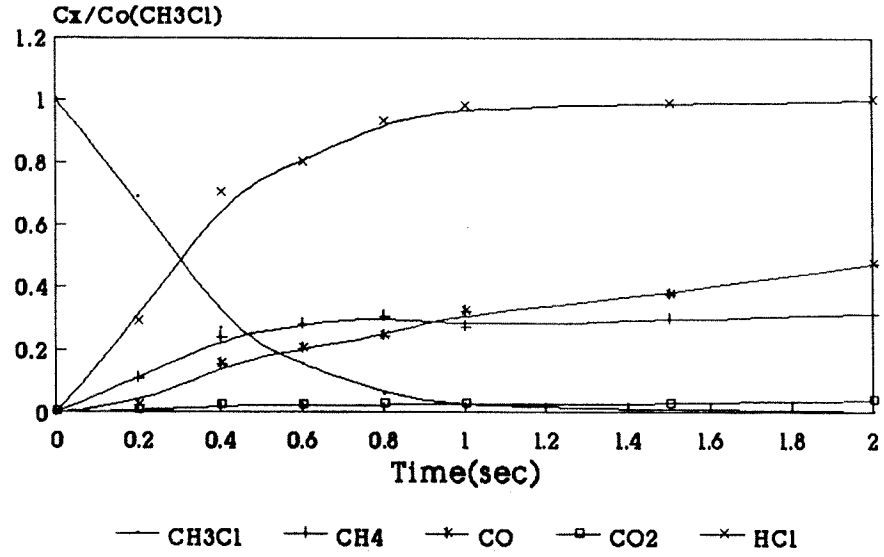


Fig. 31 1198K "10.5" Tube

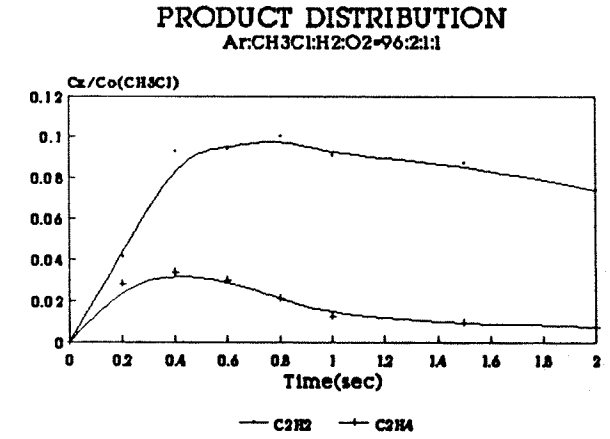


Fig. 32 1198K "10.5" Tube

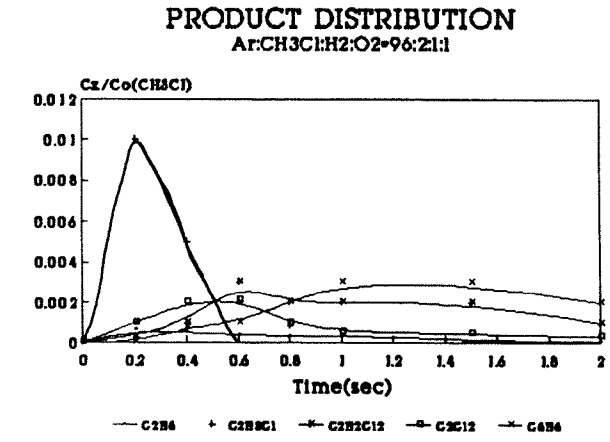


Fig. 33 1198K "10.5" Tube

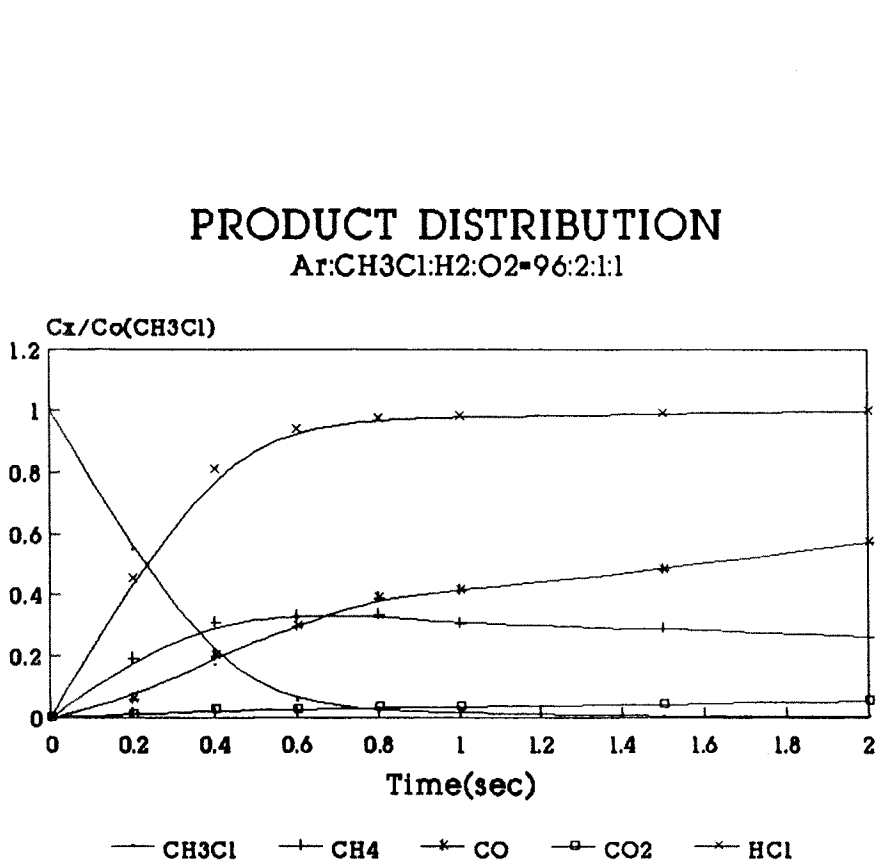


Fig. 34 1223K "10.5" Tube

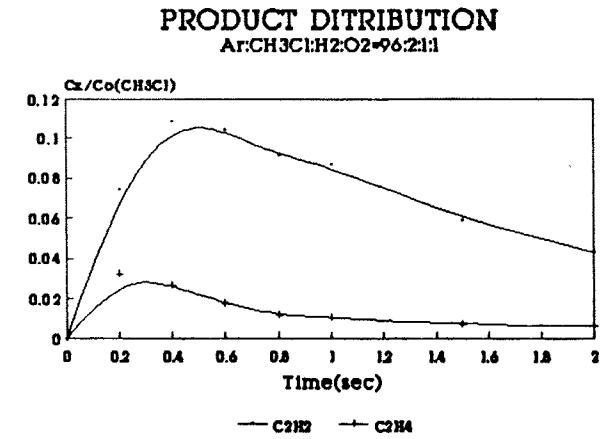


Fig. 34 1223K "10.5" Tube

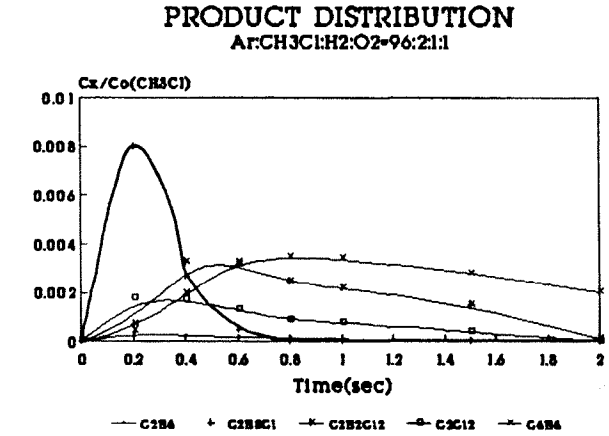


Fig. 34 1223K "10.5" Tube

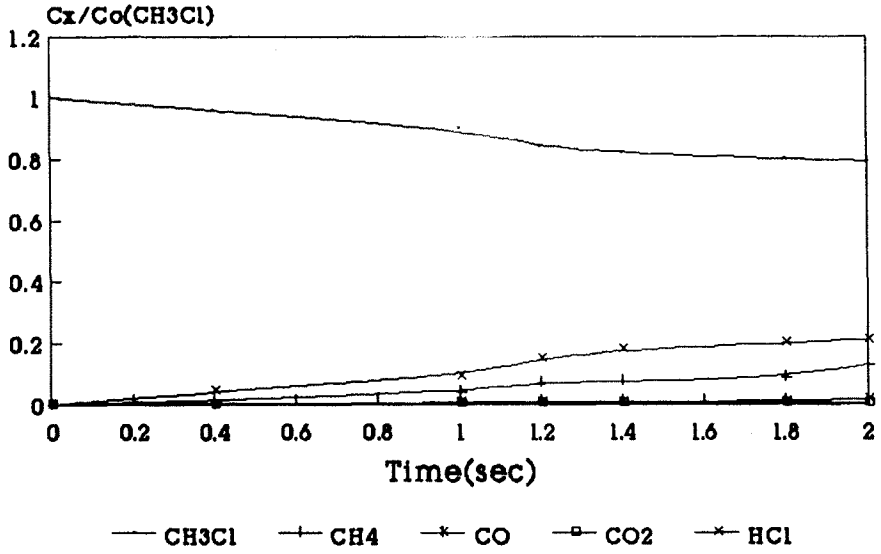
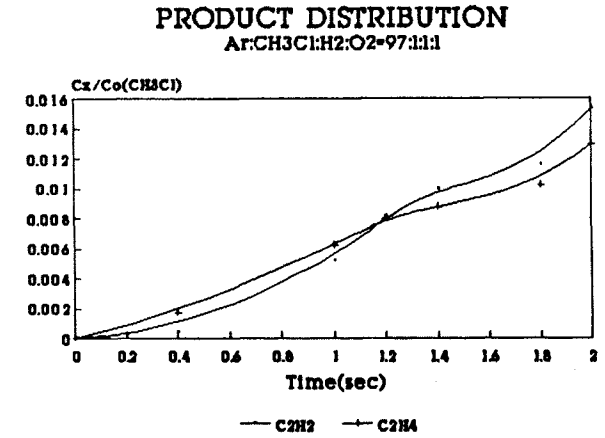


Fig. 78 1098K "16.0" Tube



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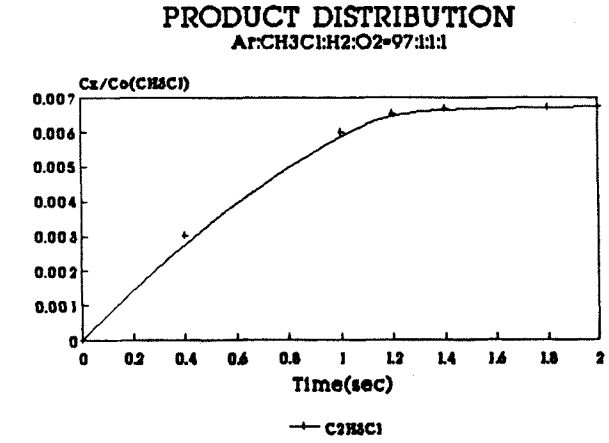

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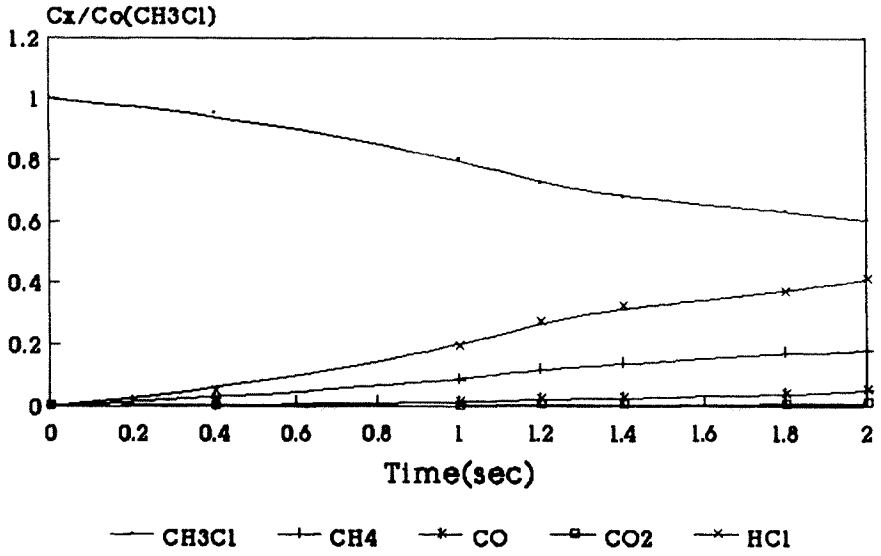


Fig. 81 1123K "16.0" Tube

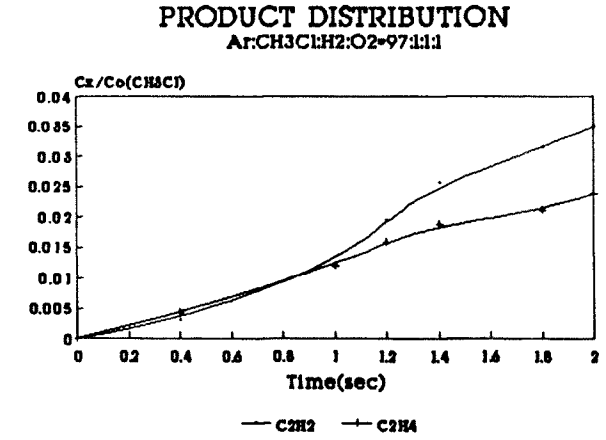
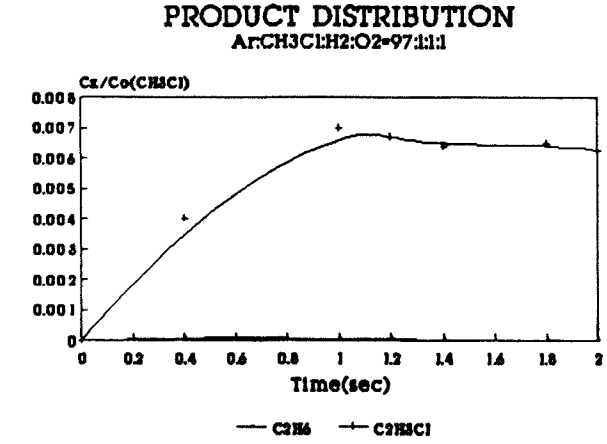


Fig. 82 1123K "16.0" Tube



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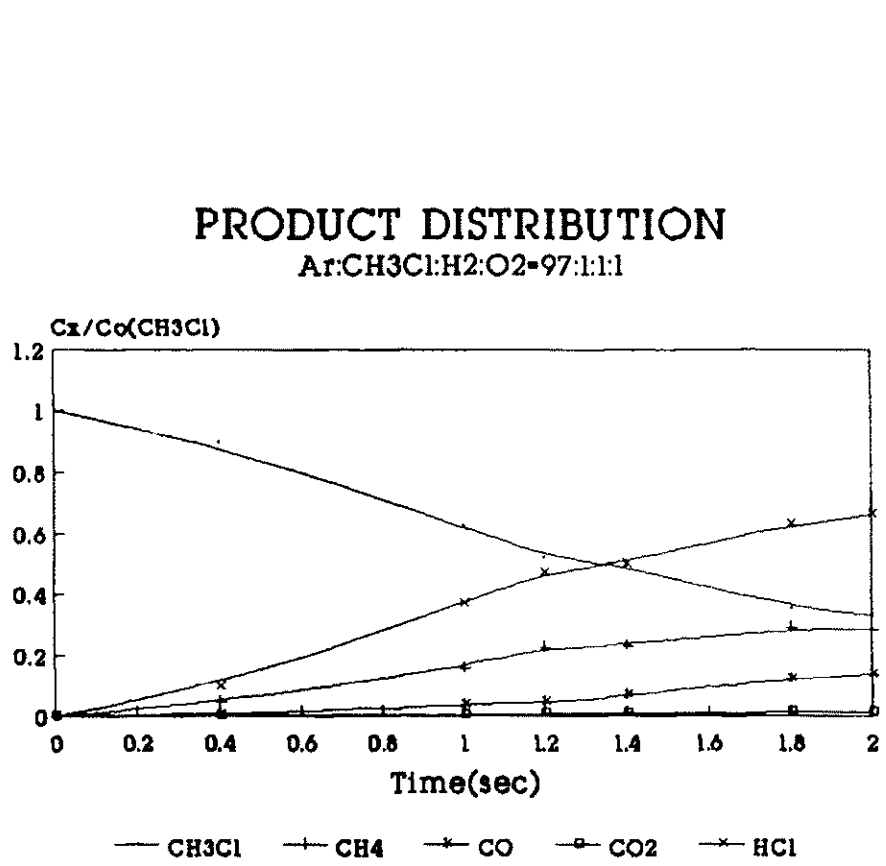


Fig. 84 1148K "16.0" Tube

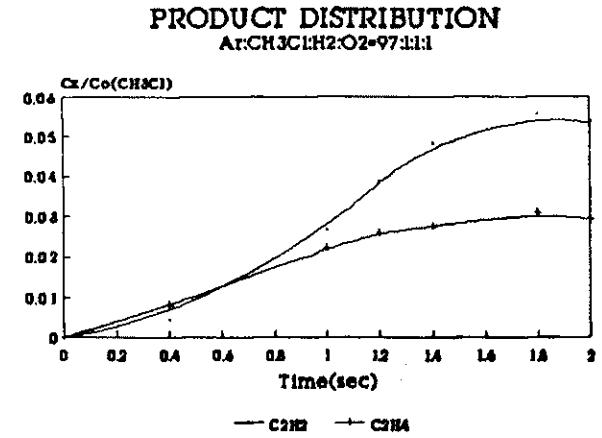


Fig. 84 1148K "16.0" Tube

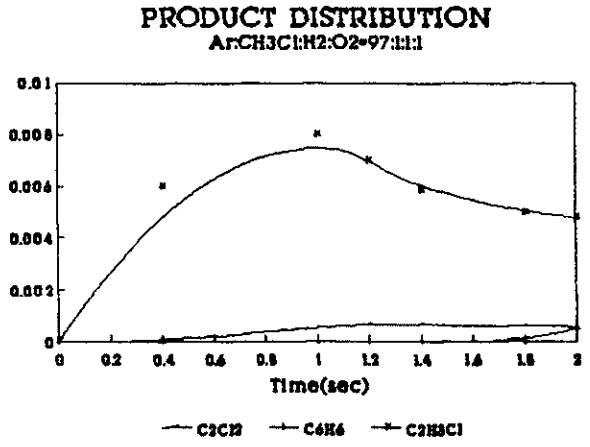


Fig. 84 1148K "16.0" Tube

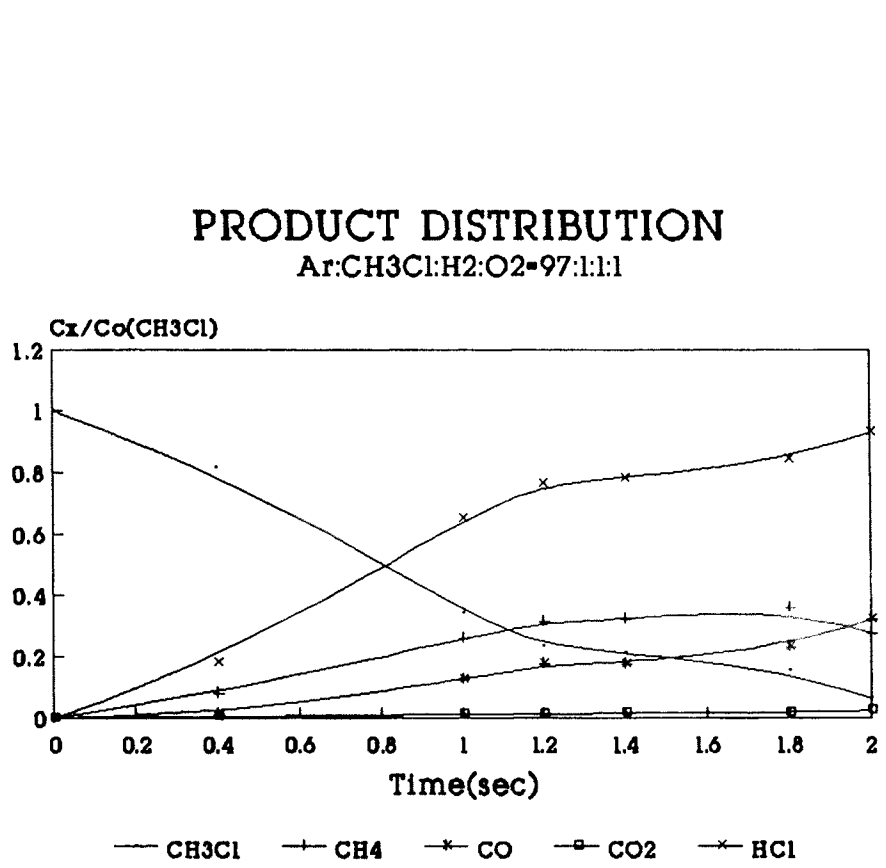


Fig. 87 1173K "16.0" Tube

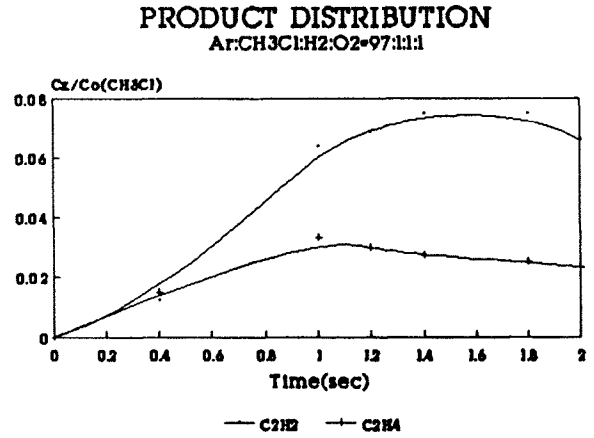


Fig. 88 1173K "16.0" Tube

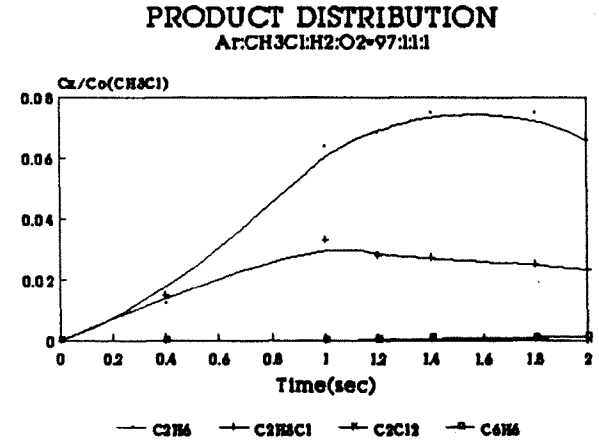


Fig. 89 1173K "16.0" Tube

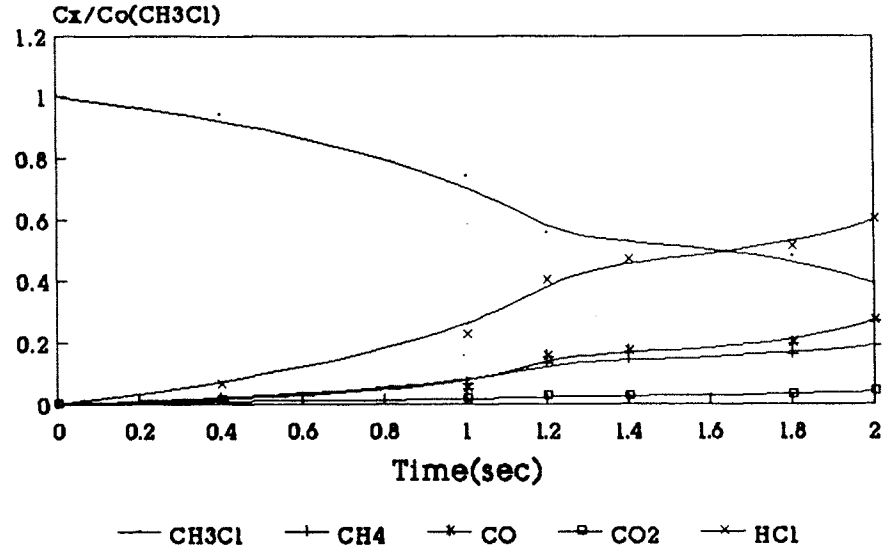


Fig. 90 1098K "16.0" Tube

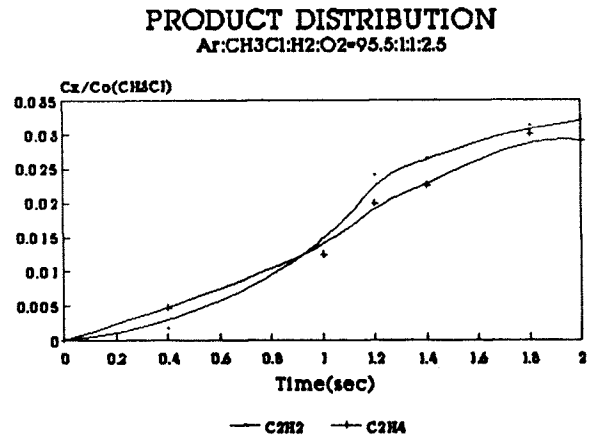


Fig. 91 1098K "16.0" Tube

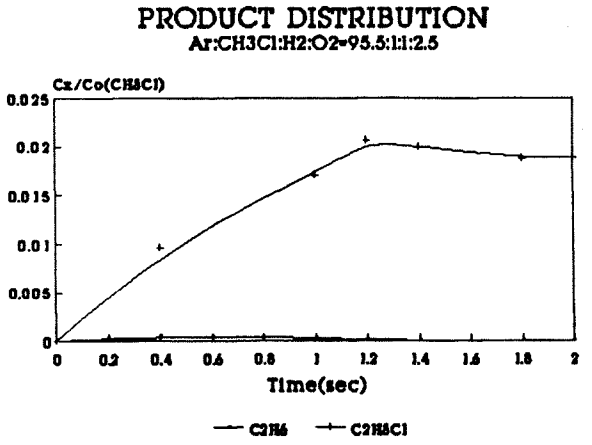


Fig. 92 1098K "16.0" Tube

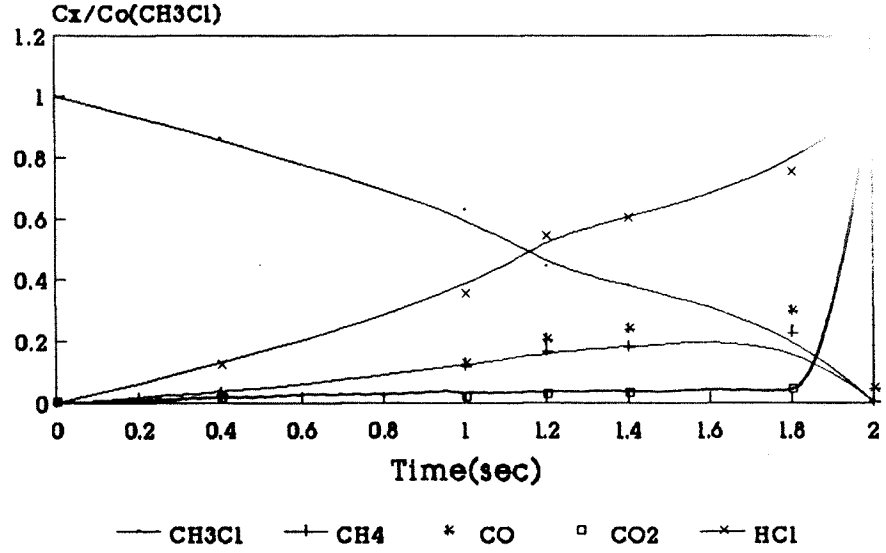


Fig. 93 1123K "16.0" Tube

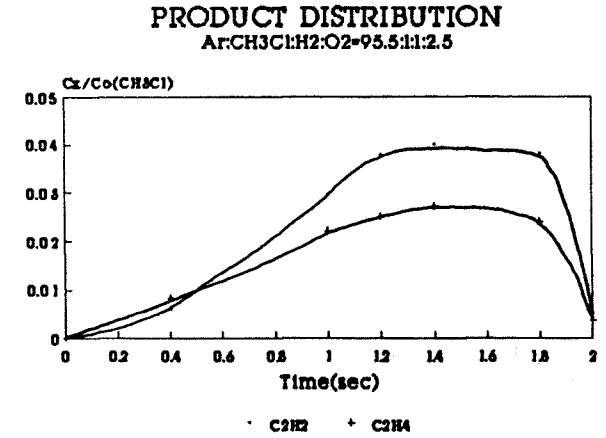


Fig. 94 1123K "16.0" Tube

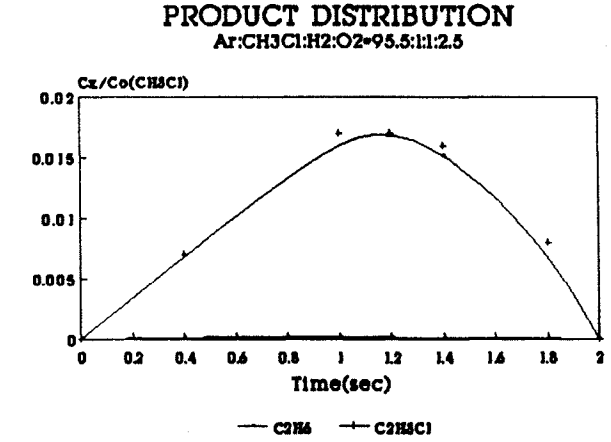


Fig. 96 1123K "16.0" Tube

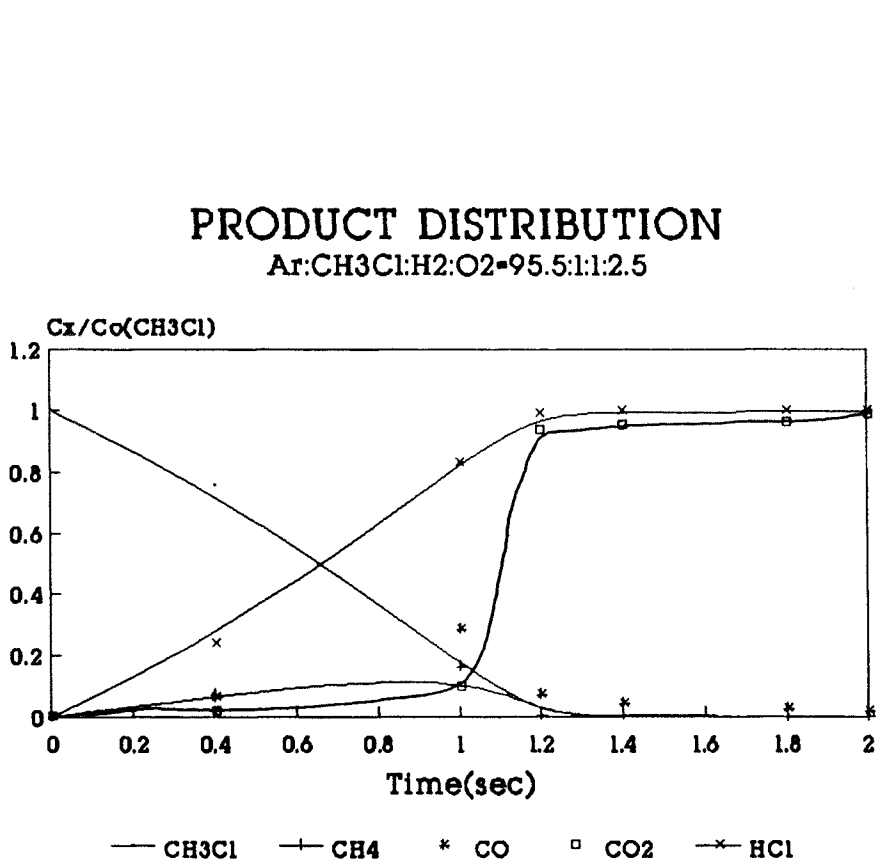


Fig. 96 1148K "16.0" Tube

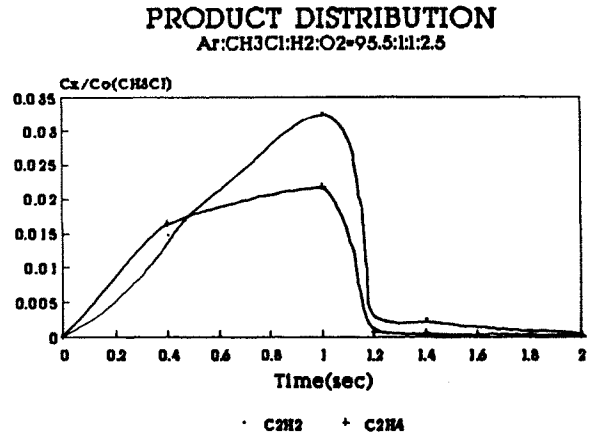
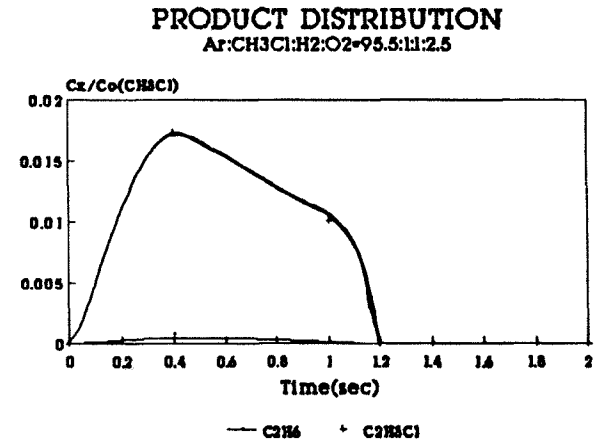


Fig. 97 1148K "16.0" Tube



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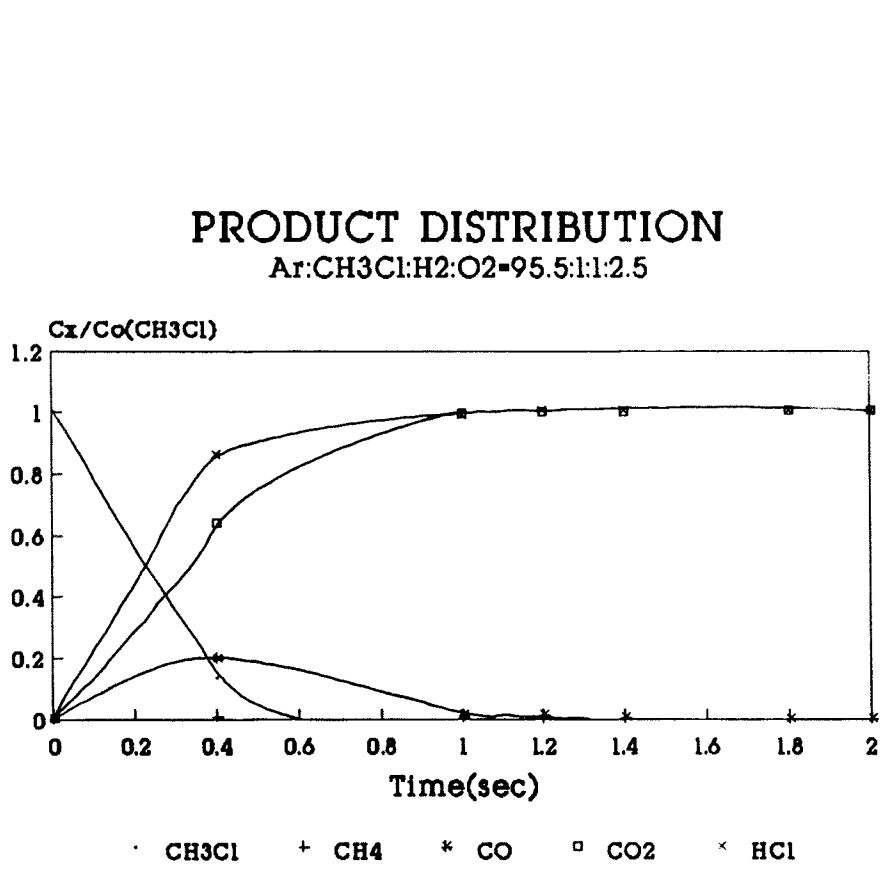

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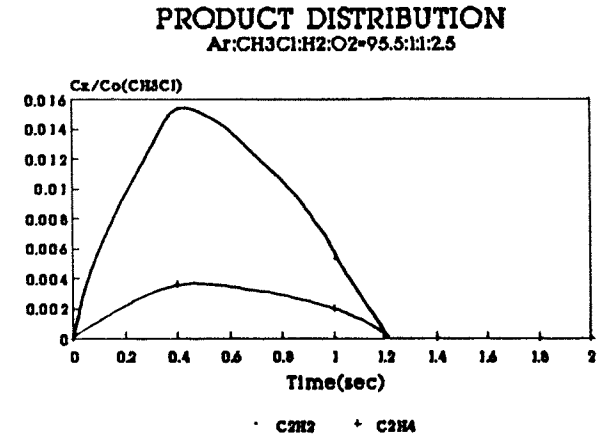

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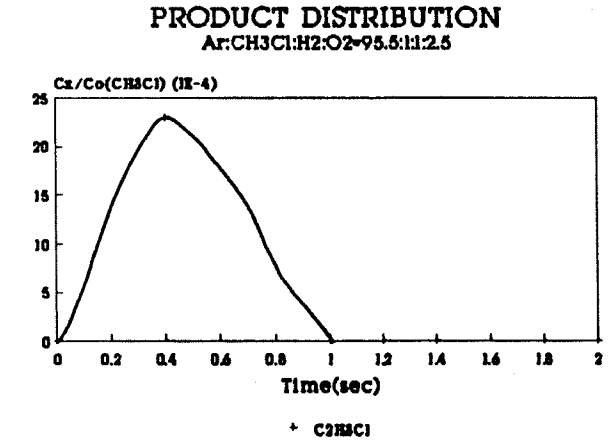


Fig. 101 1173K "16.0" Tube

3.1.3 Oxygen Content Effects

A. Oxygen Initiation Effect

We consider data from 10.5 mm ID reactor and two reactant ratios ($Ar:CH_3Cl:H_2:O_2$=97:1:1:1 and $Ar:CH_3Cl:H_2:O_2$ =96:2:1:1) CH3Cl/O2, 1/1 and 2/1 respectively. In order to show the effect of oxygen, the low temperature (1098K) results are taken for illustration. These results indicate that oxygen contributes to increased CH_3Cl conversion but also to major product formation (Figures 37-41). In order to verify the reliability of the results, another controll experiment was performed for ($Ar:CH_3Cl:H_2:O_2$=97:1:1:1 and $Ar:CH_3Cl:H_2:O_2$=95.5:1:1:2.5) in the 16.0 mm ID reactor. A more clear set of results (Figures 126-130) was obtained. This reason may stem from the following reactions:

$CH_3Cl = CH_3 + Cl$ (1) CH3 + O2 = CH2O + OH (2)

$CH_3Cl + O_2 = CH_2Cl + HO_2$ (3)

$H_2 + O_2 = H + HO_2$ (O_2 stimulates reactive H formation) (4)

$H + CH_3Cl = CH_3 + HCl$ (5)

$CH_3 + H = CH_4$ (The path of CH_4 formation) (6)

$CH_2Cl + CH_3 = CH_2ClCH_3$ (7)

$CH_2ClCH_3 = C_2H_4 + HCl$ (8)

$H + O_2 = OH + O$ (reactive H atoms abstract O from less reactive O_2 to produce more reactive OH and O) (9)

$CH_3 + CH_3 = C_2H_6$ (10)

C_2H_6 + (H, O, and OH) => C_2H_5 + (H_2, OH, and H_2O) (11)

$C_2H_5 = C_2H_4 + H$ (12)

$C_2H_4 + OH = C_2H_3 + H_2O$ (13)

$C_2H_3 = C_2H_2 + H$ (14)$CH_2Cl + CH_2Cl = CH_2ClCH_2Cl$ (15)

$CH_2ClCH_2Cl = C_2H_3Cl + HCl$ (16)

It can be seen that the reaction (2)-(3) show oxygen effect on CH_3Cl decay; the reactions (4)-(6) indicate oxygen stimulates CH_4 formation. Reactions (3), (5), (7), and (8) though (12) show that oxygen contributes to C_2H_4 formation. The reactions (2), (9), and (13)-(14) show oxygen contribution to C_2H_2 formation. The final result of reactions (3) and (16) is that oxygen also stimulates C_2H_3Cl production.

B. Oxygen Effect on the Complete Oxidation of All Species

Controlled oxidation of CH_3Cl and intermediate products (as C_2H_2, C_2H_4, C_2H_6, C_2H_3Cl, CO, $C_2H_2Cl_2$, C_2Cl_2, and C_6H_6) for above reaction systems via changing oxygen content in the reaction system or controlling reaction temperature can help us to evaluate the CH_3Cl combustion mechanism. Information about oxygen effect on complete oxidation of all species was obtained that when oxygen content is about stoichiometric ($O_2/CH_3Cl/H_2$ = 2.5/1/1) almost all of species are converted completely to CO_2 at 1173K and 1.2 sec residence time. We can predict that the temperature of CH_3Cl complete conversion to CO_2 will be reduced if the oxygen concentration is increased.

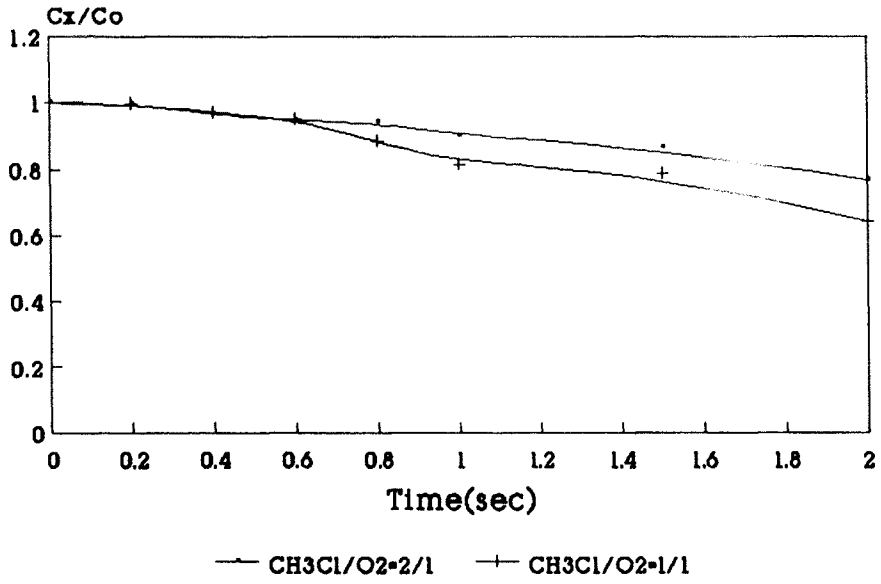


Fig. 37 1098K "10.5" Tube

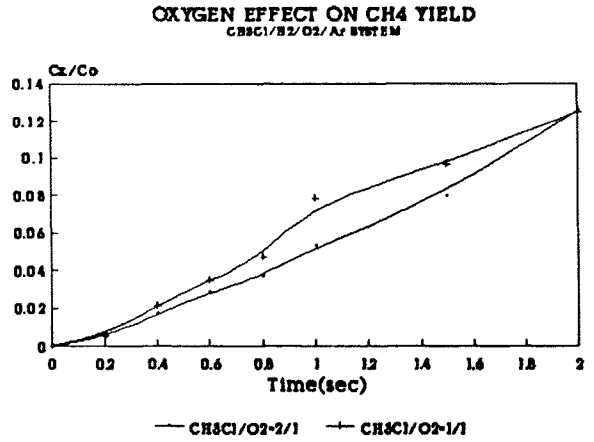


Fig. 38 1098K "10.5" Tube

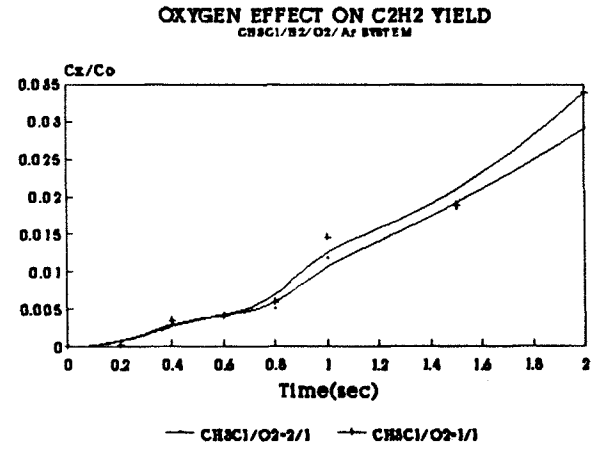
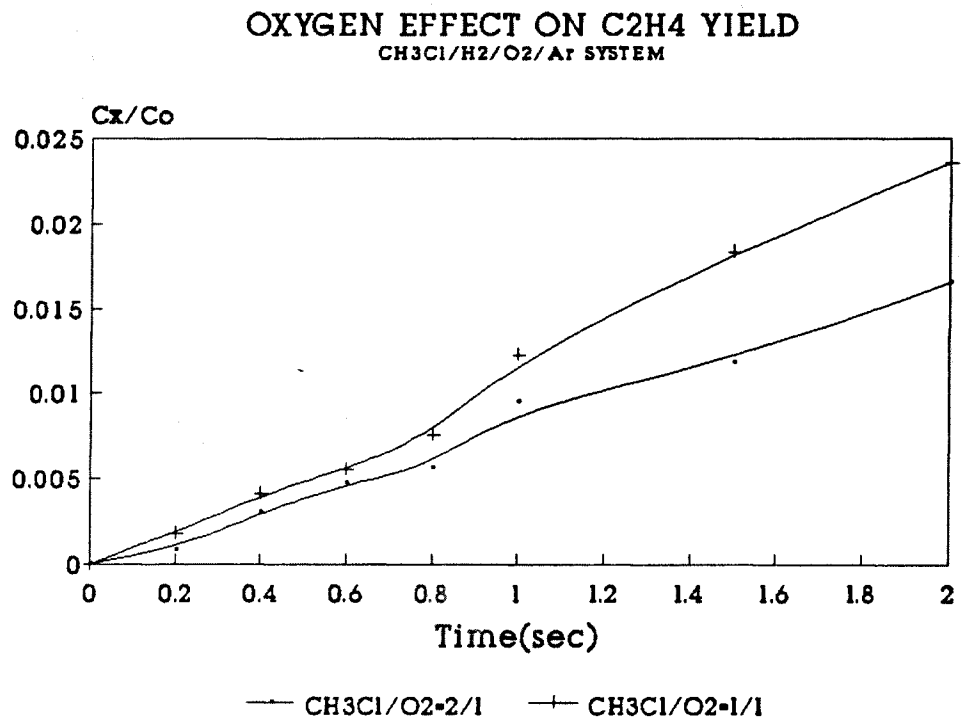


Fig. 39 1098K "10.5" Tube



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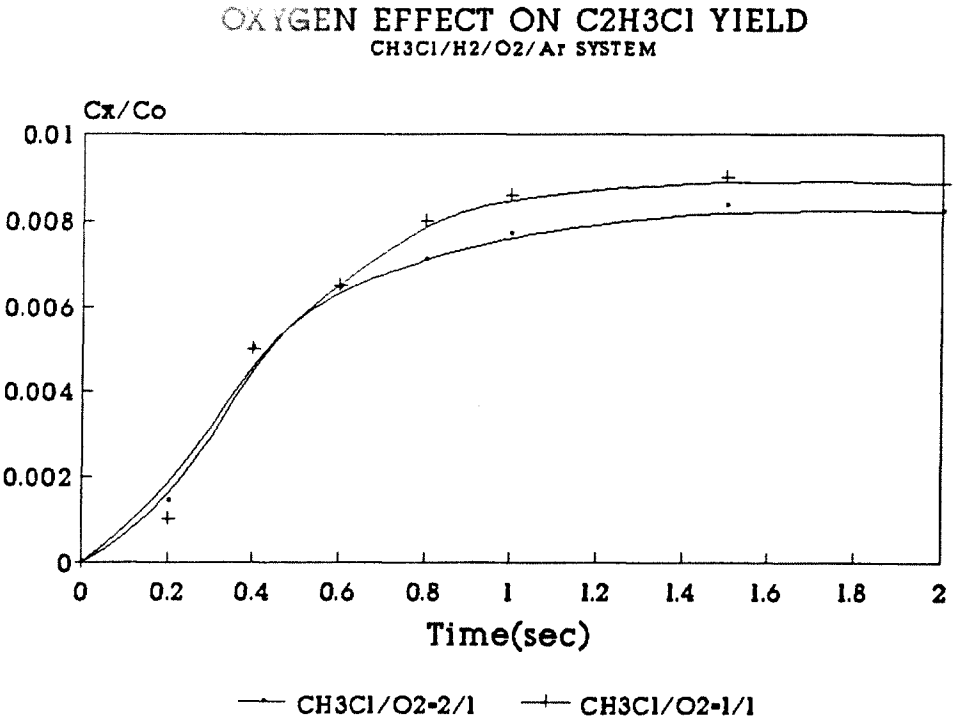

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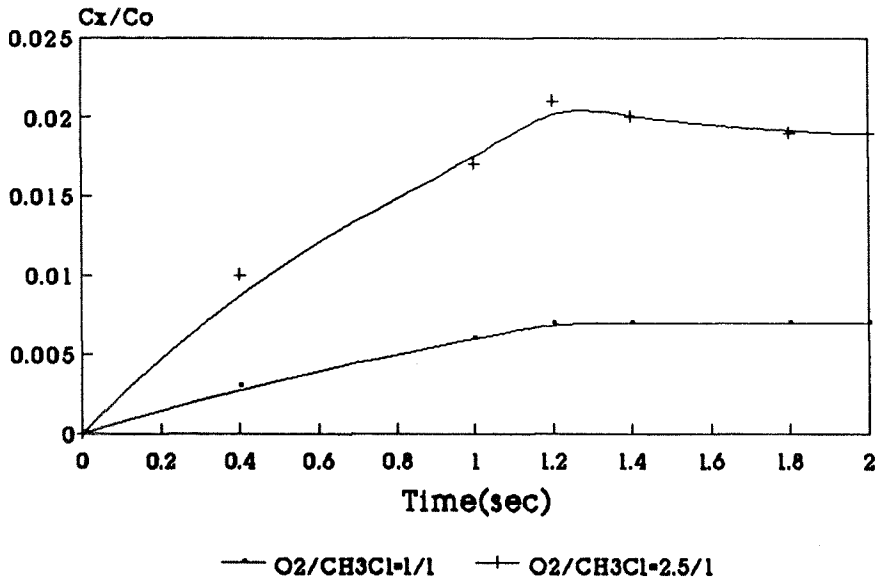


Fig. 126 1098K "16.0" Tube

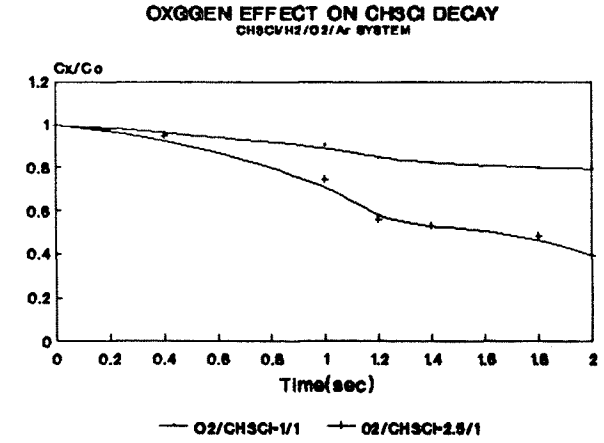
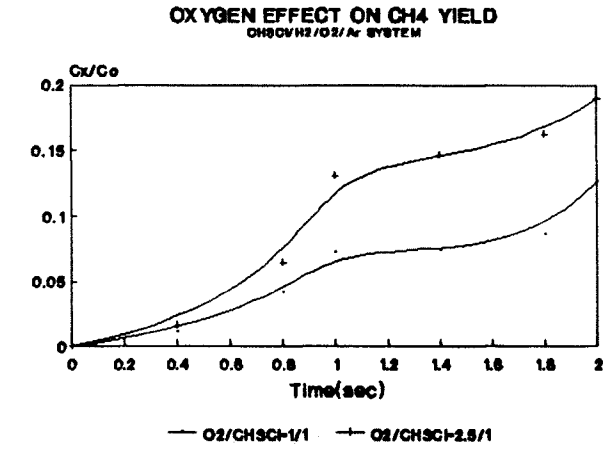


Fig. 127 1098K "16.0" Tube



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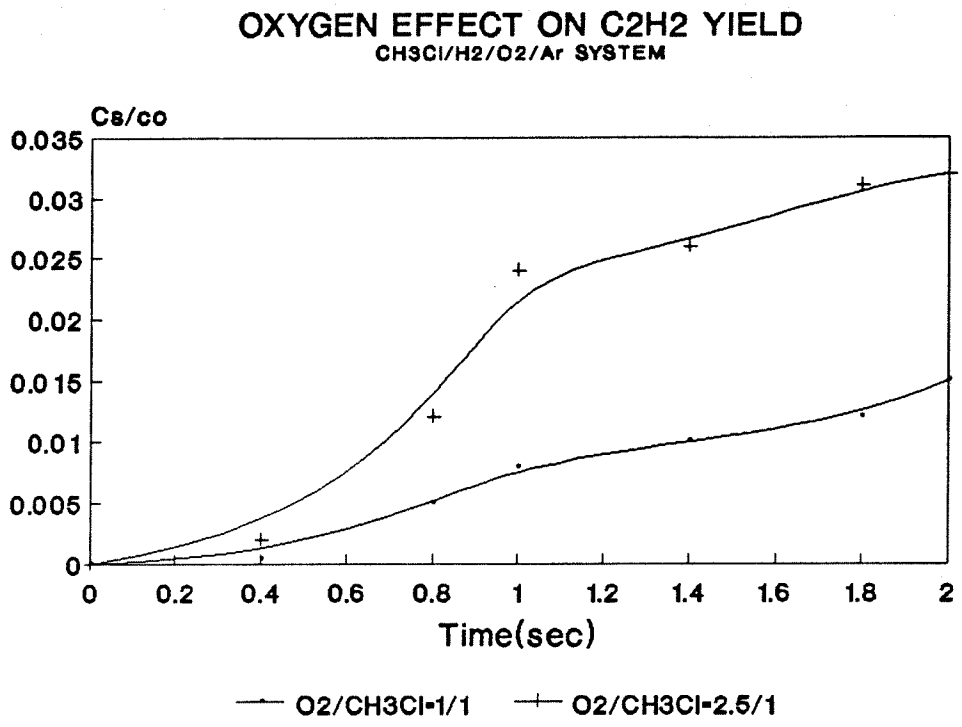

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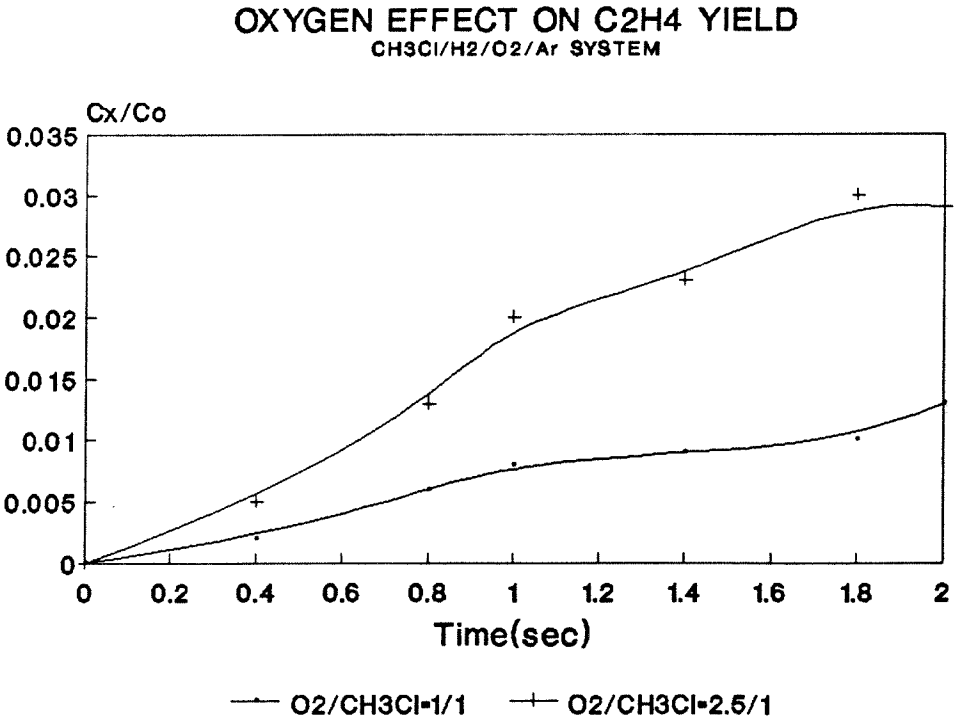


Fig. 130 1098K "16.0" Tube

3.1.4 Effects of S/V

In order to indicate the effect of S/V on CH_3Cl conversion and product distribution, the results for two types of reactor at the same reactant ratio ($Ar:CH_3Cl:H_2:O_2=97:1:1:1$) are compared. S/V increase contributes to increased CH_3Cl conversion (Figures 131-134) but also contributes to CH_4, C_2H_2, C_2H_4, C_2H_6, C_2H_3Cl, CO, and CO_2, $C_2H_2Cl_2$, C_2Cl_2, C_6H_6 formation (Figures 1-12 and 80-91). That is, When ID 10.5 mm reactor was used, these species formation temperatures were lowered and their concentration were increased. These reasons are likely due to effects of heat and mass transfer difference between two types of reactor. In view of higher temperature gradient presence for 16.0 mm ID reactor, experimental results obtained in 10.5 mm were used to validated our model.

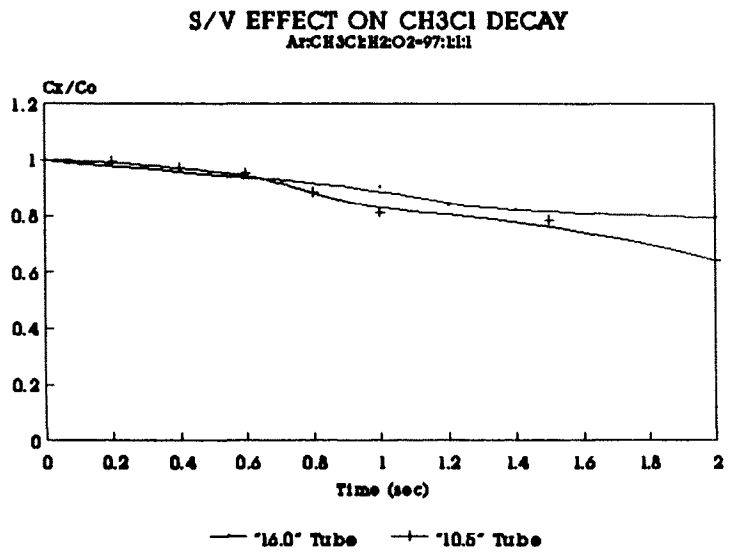


Fig. 131 1098K

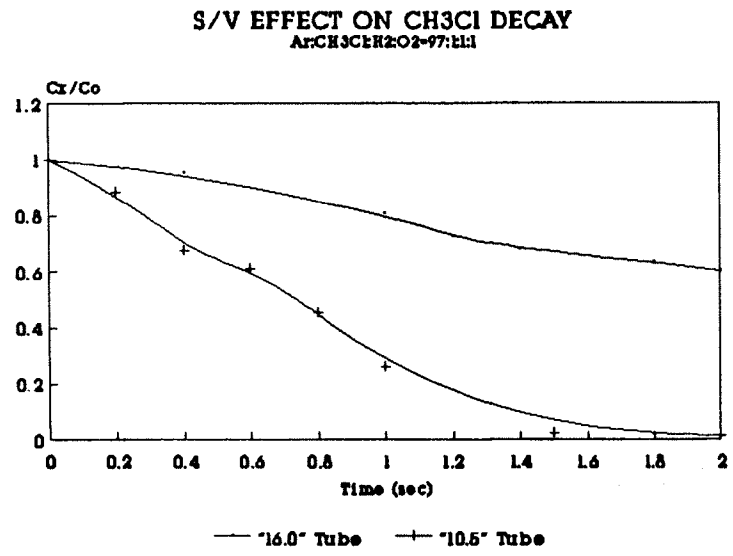


Fig. 132 1123K

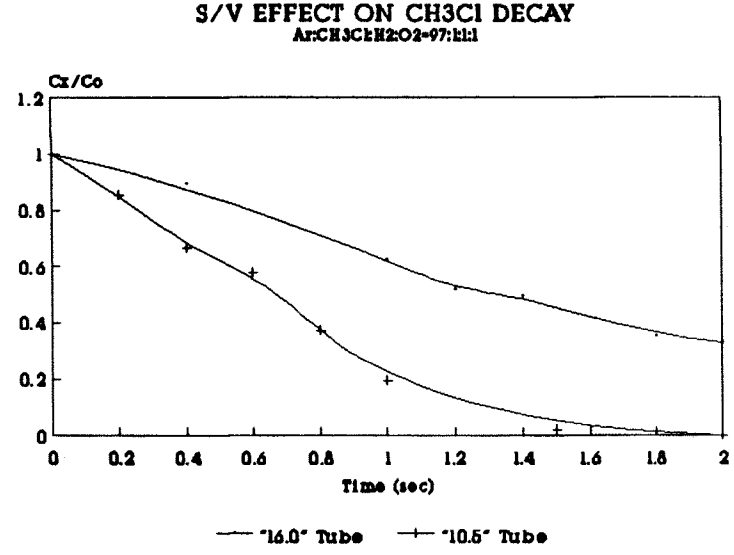


Fig. 133 1148K

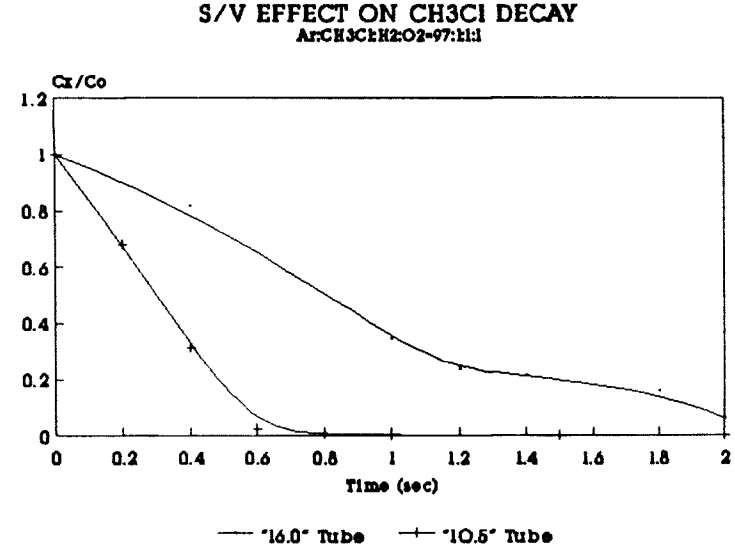


Fig. 134 1173K

3.2. Thermal Reaction of $CH_3Cl/CH_4/O_2/Ar$ Systems

In the thermal reaction systems of $CH_3Cl/CH_4/O_2/Ar$, CH_3Cl, CH_4, C_2H_4, C_2H_2, C_2H_3Cl, CO, CO_2, and HCl are major products. C_2H_6, $C_2H_2Cl_2$, C_2Cl_2, and C_6H_6 are small amounts of products.

3.2.1 Initial Conversion and Complete Conversion Temperatures

The temperature of initial conversion (about 5%) for CH_3Cl at 0.4 sec is 1098K. The temperature of complete conversion (99%) is 1173K at 1.0 sec for the ratio of $Ar:CH_3Cl:CH_4:O_2=96:1:1:4$ (close to stoichiometric). The ratios of CH_3Cl and CH_4 to O_2 and of S/V influence the conversion of CH_3Cl and affect the product distribution to a small extent as $CH_3Cl/H_2/O_2/Ar$ system.

3.2.2 Residence Time and Temperature Effects

The figures 42 - 77 and 102 - 125 show the effects of time and temperature, which are similar to that discussed earlier in $CH_3Cl/H_2/O_2/Ar$ system.

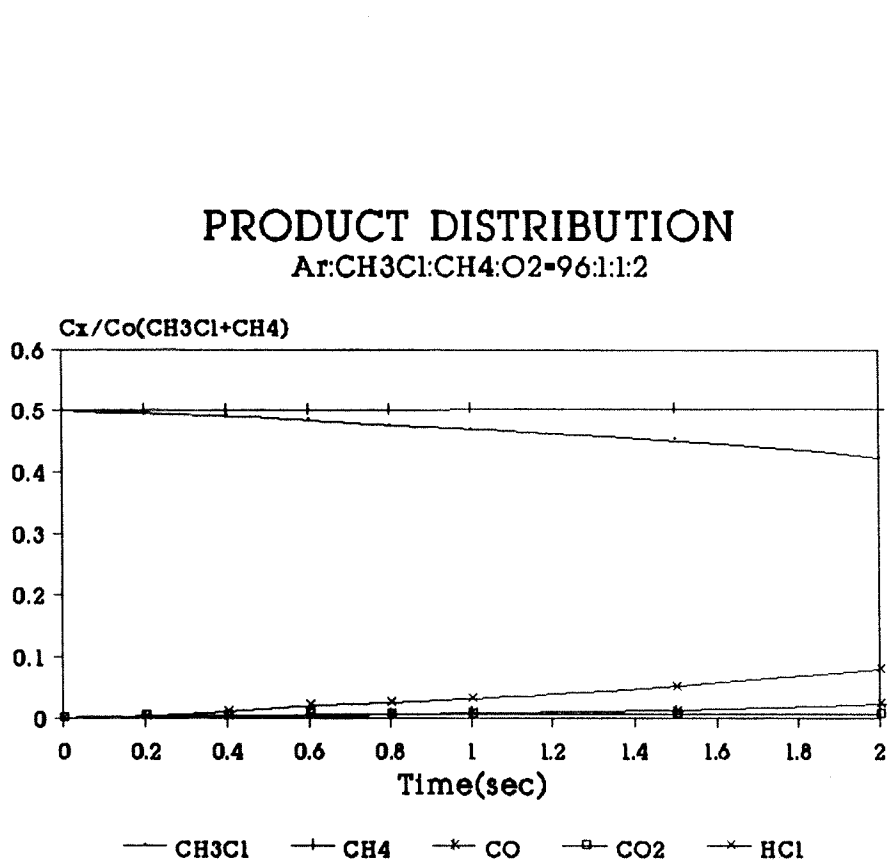


Fig. 42 1098K "10.5" Tube

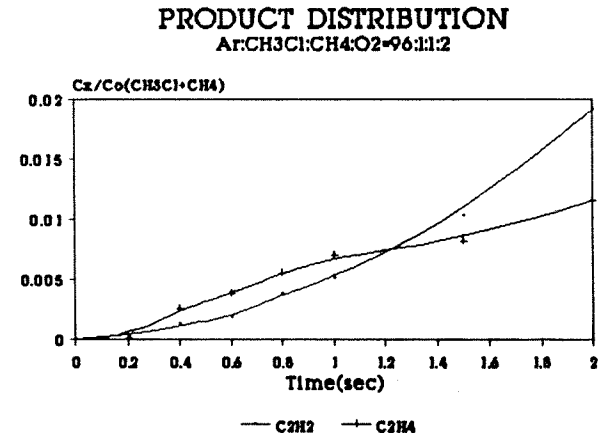


Fig. 43 1098K "10.5" Tube

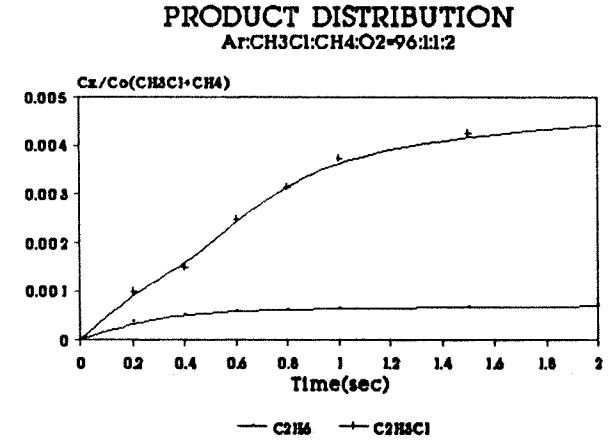


Fig. 44 1098K "10.5" Tube

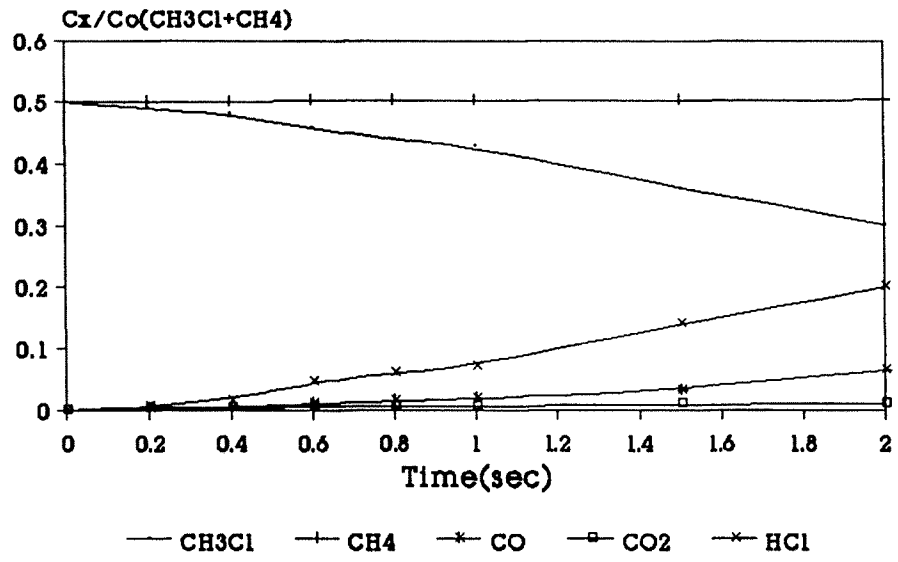
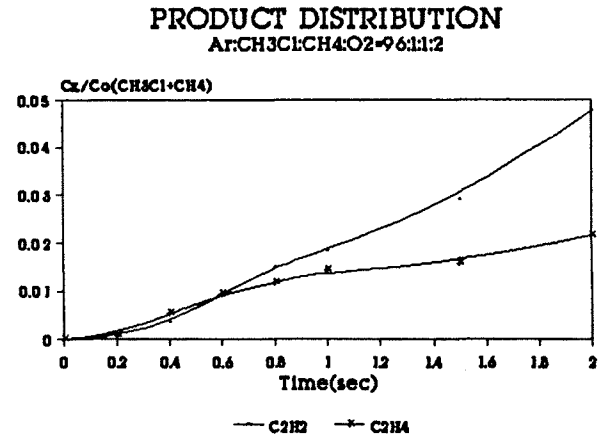


Fig. 45 1123K "10.5" Tube



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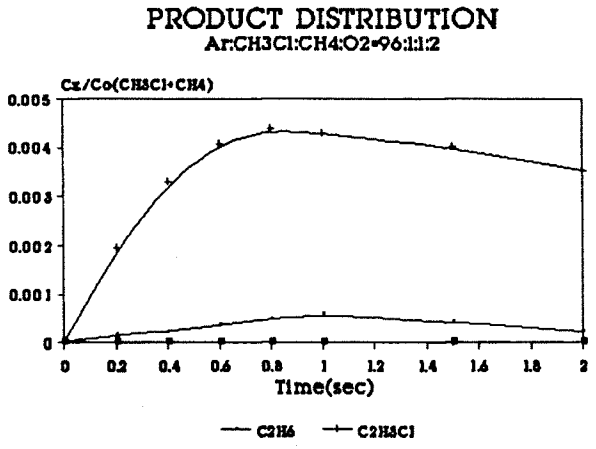

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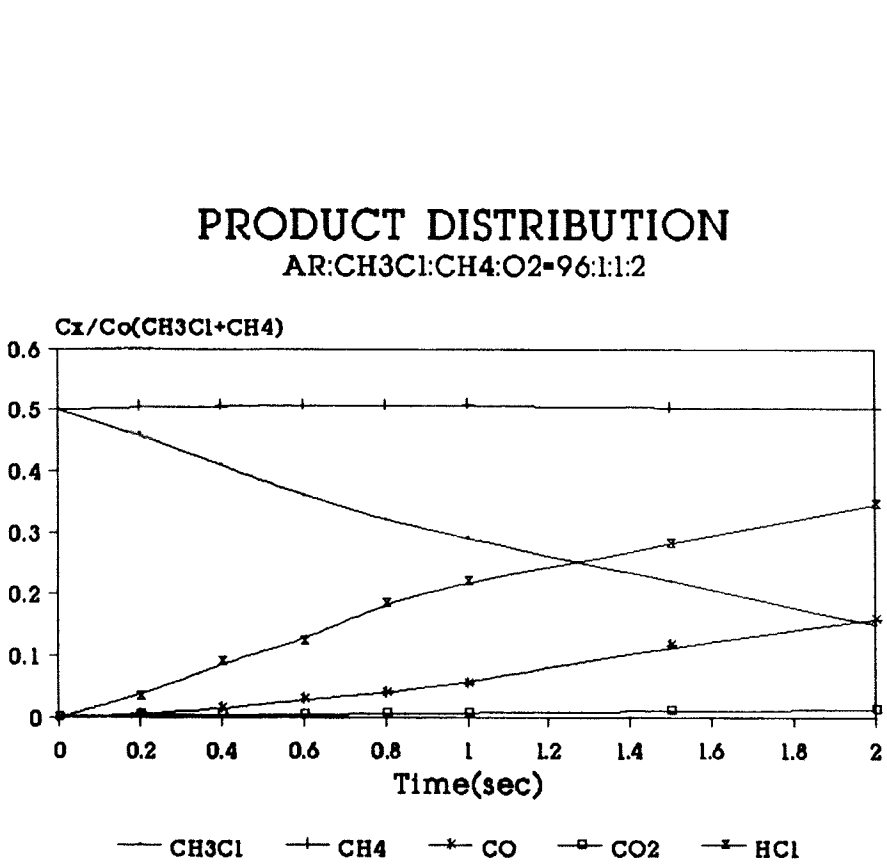


Fig. 48 1148K "10.5" Tube

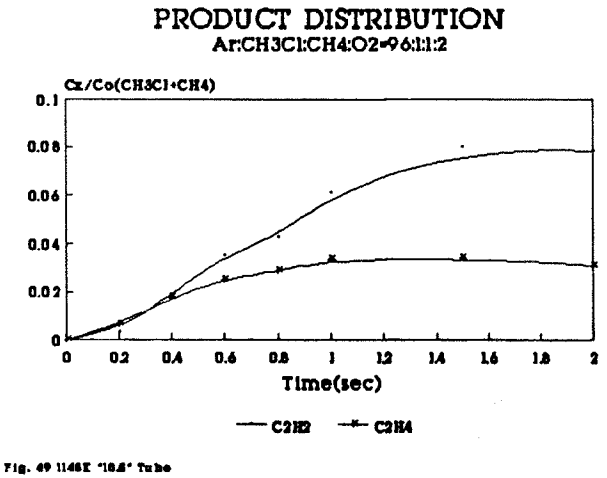
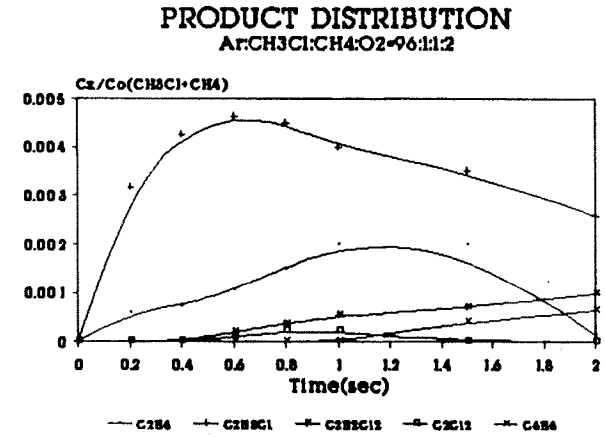


Fig. 49 1148K "10.5" Tube



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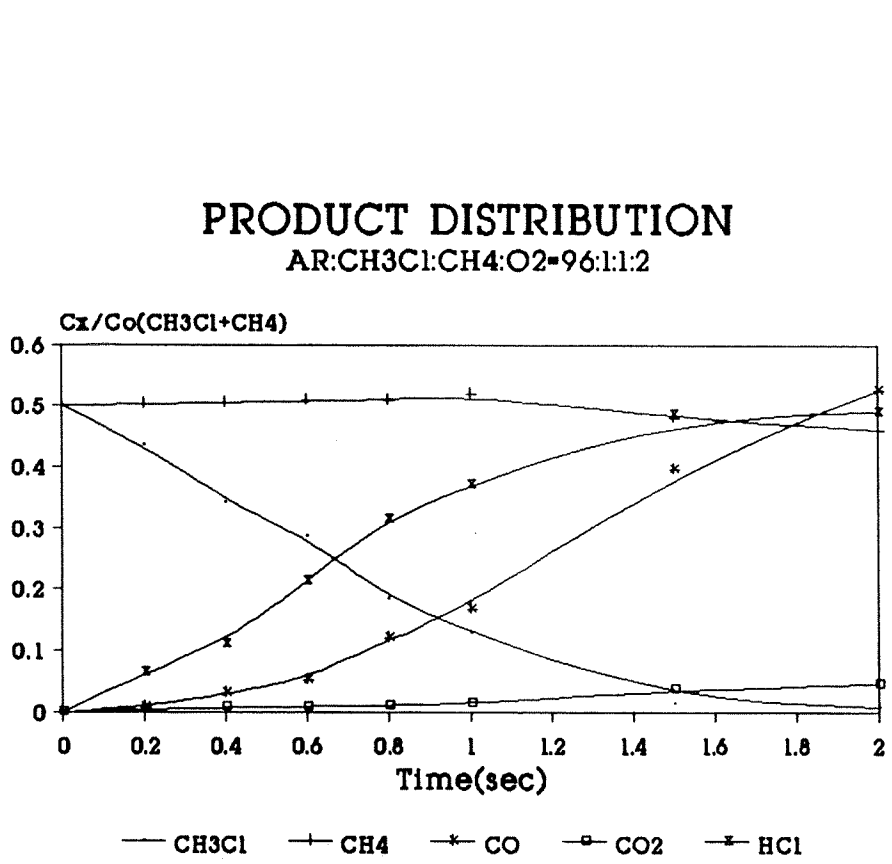
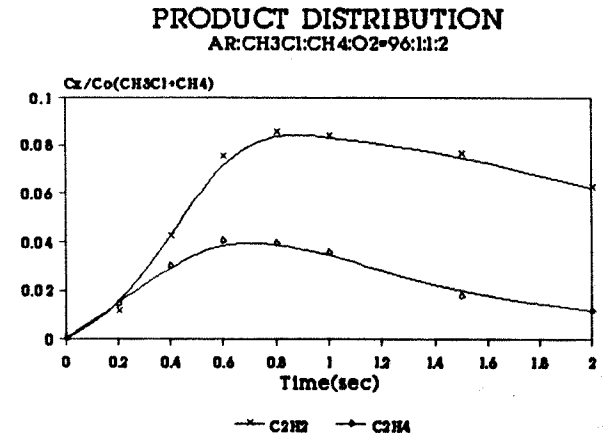


Fig. 51 1173K "10.5" Tube



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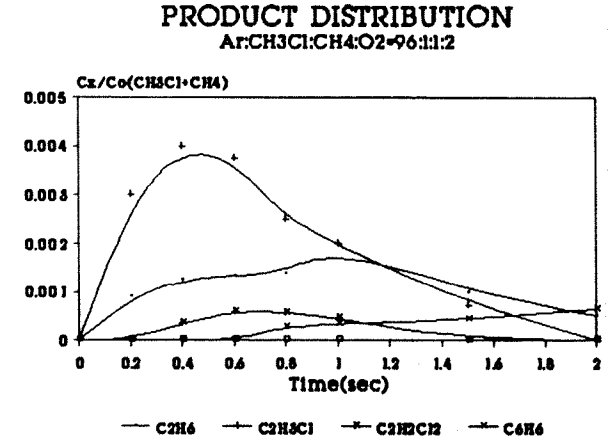

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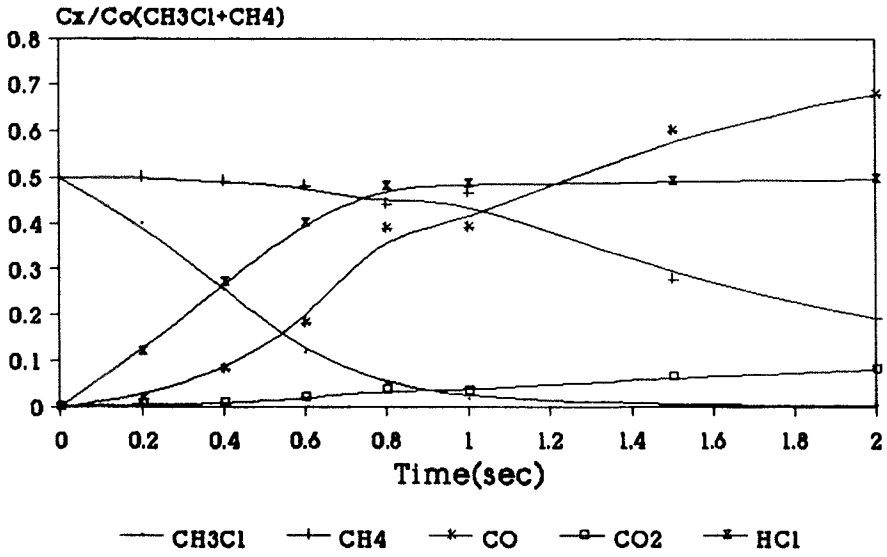

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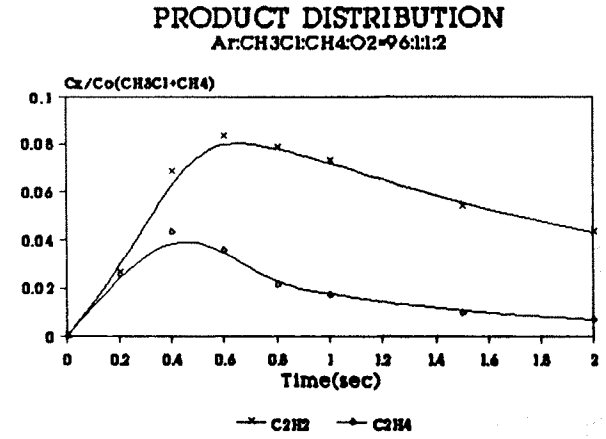

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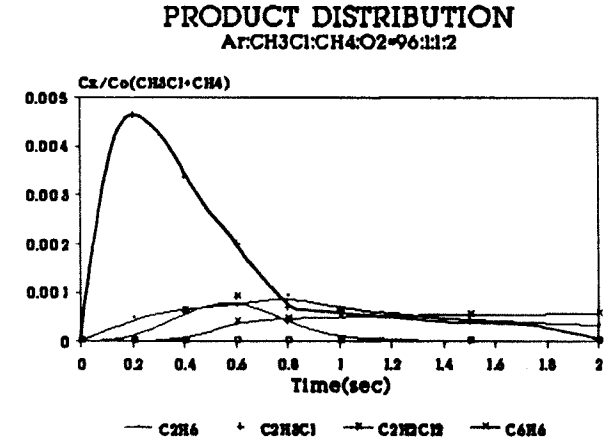

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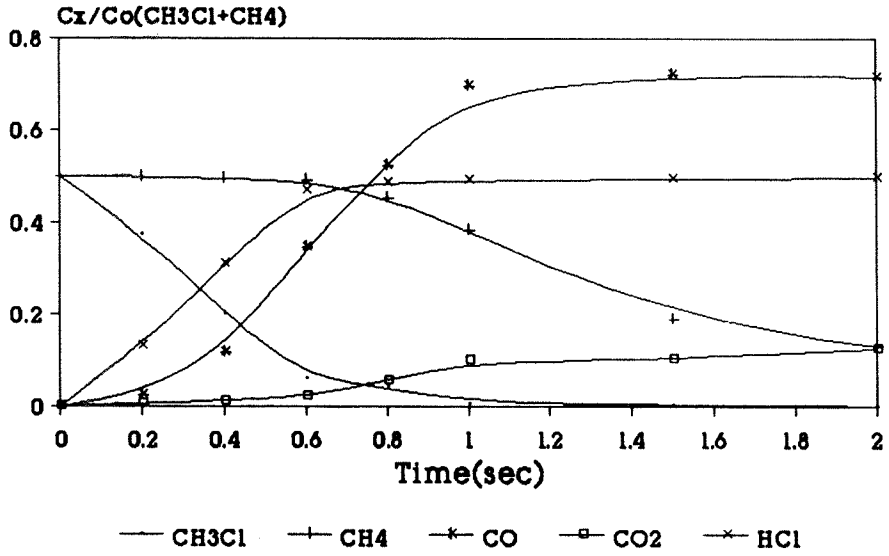

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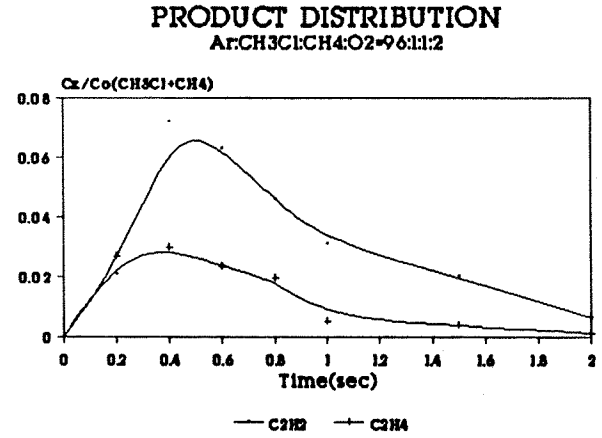
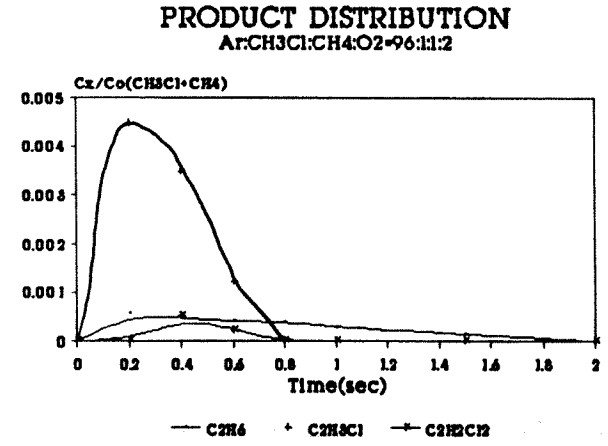


Fig. 68 1223K "18.5" Tube



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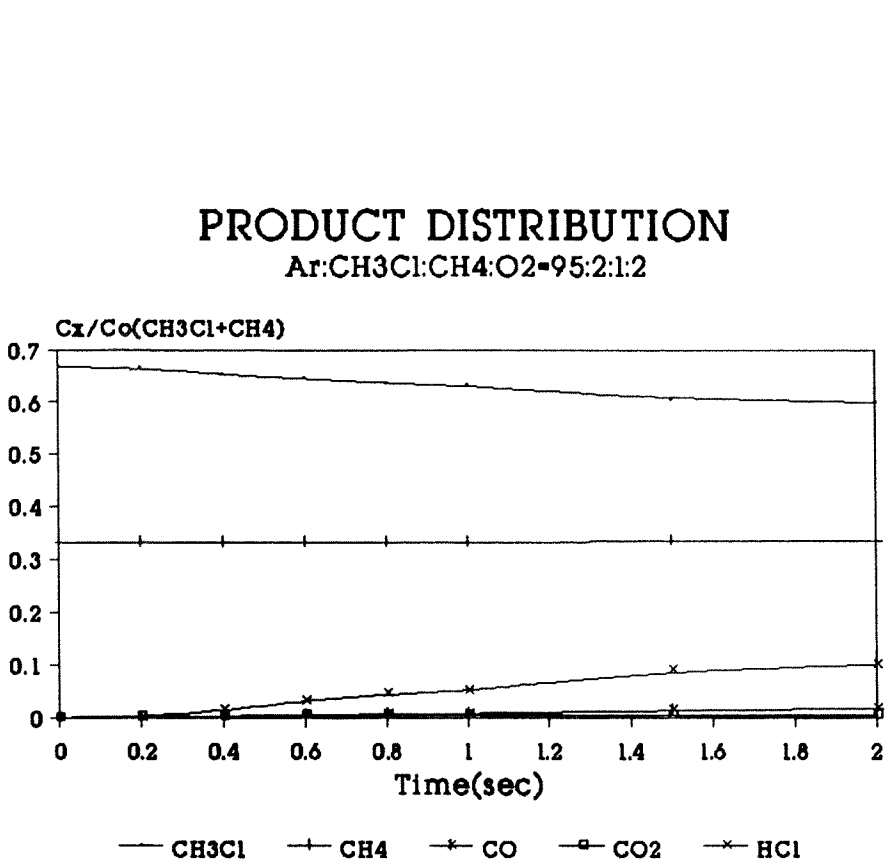
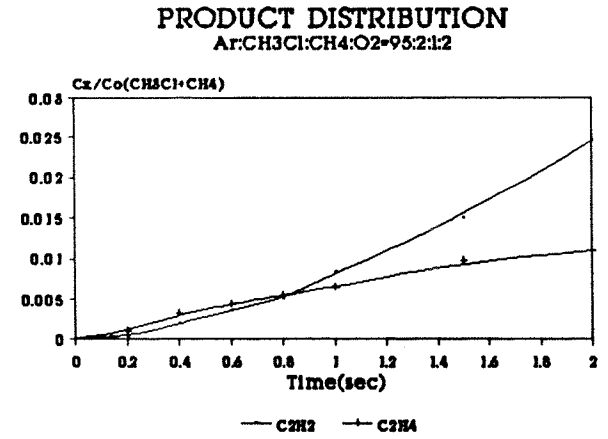


Fig. 60 1098k "10.5" Tube



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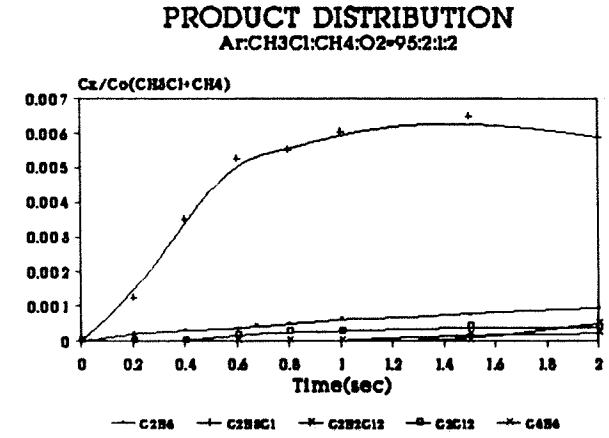

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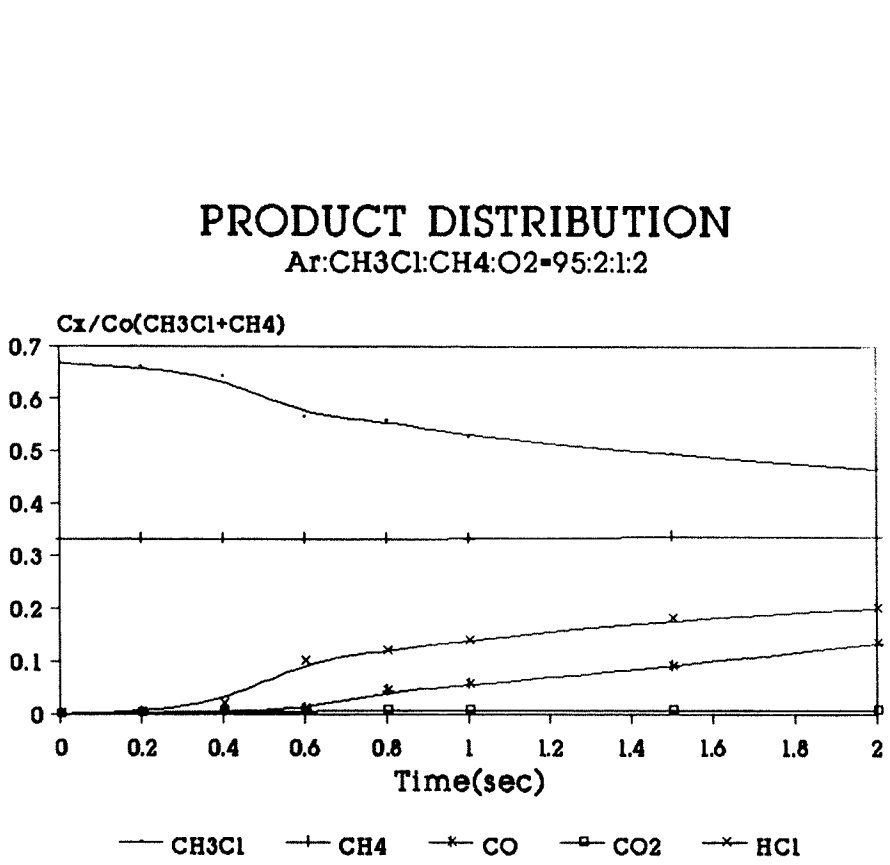

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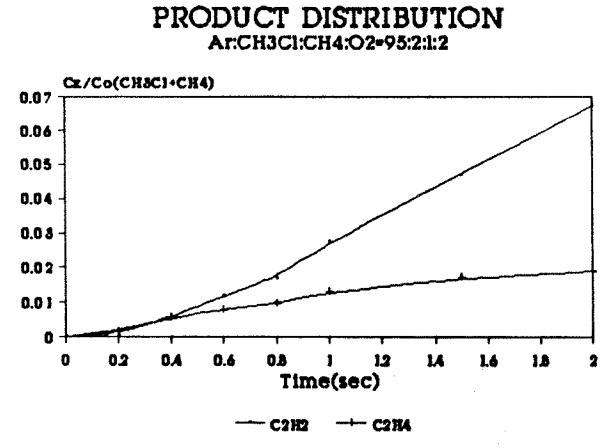

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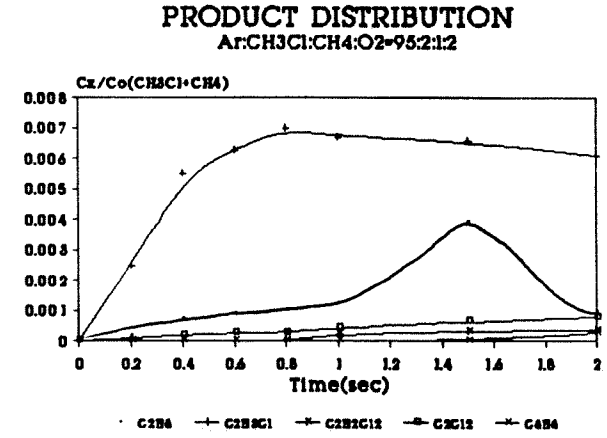

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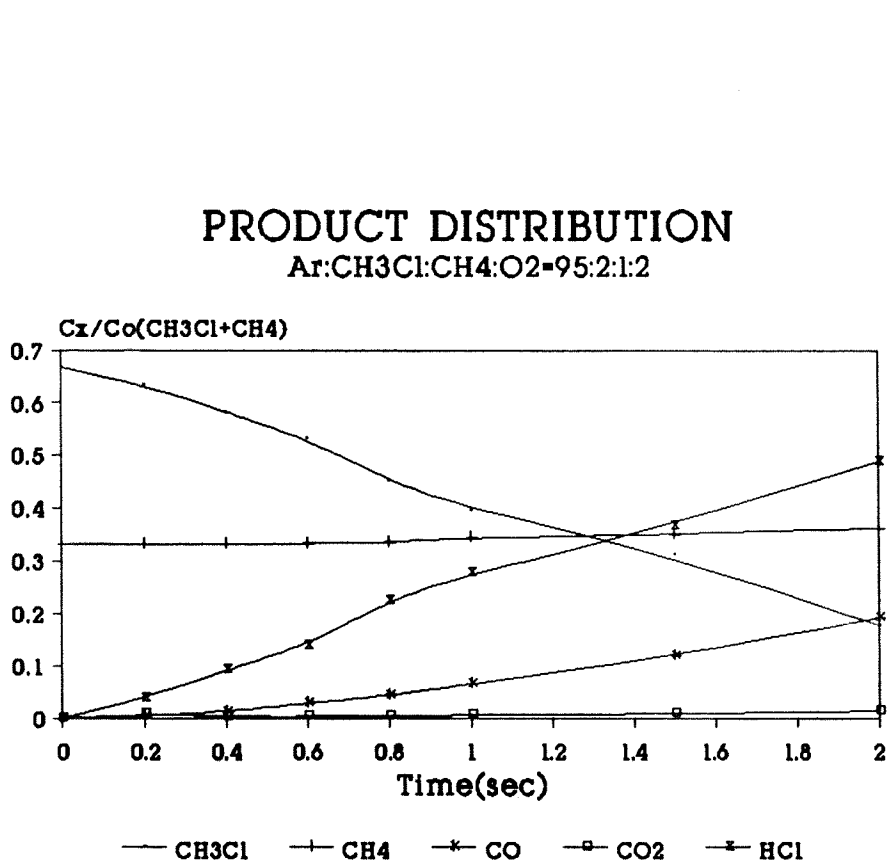
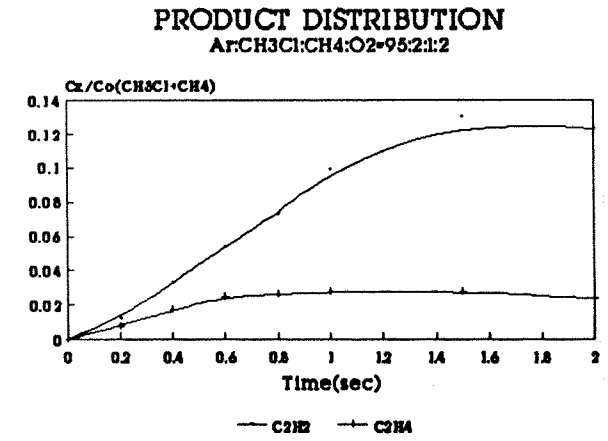


Fig. 66 1148K "10.5" Tube



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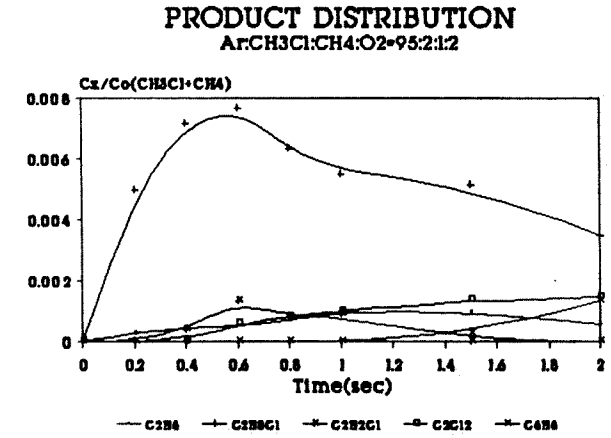

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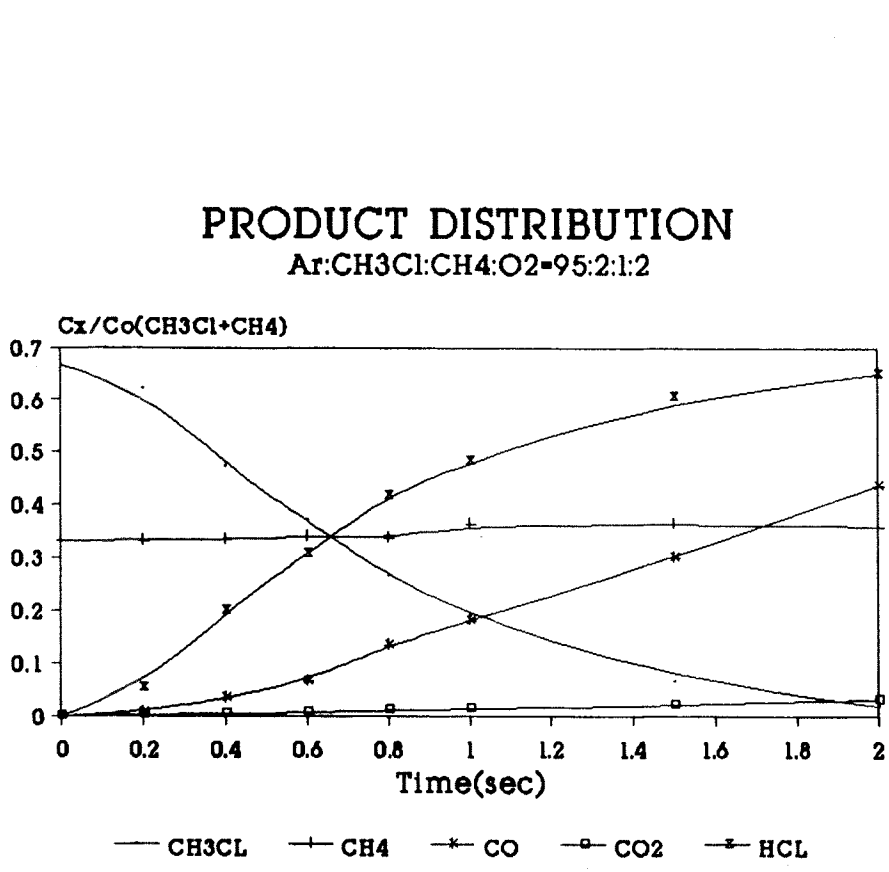

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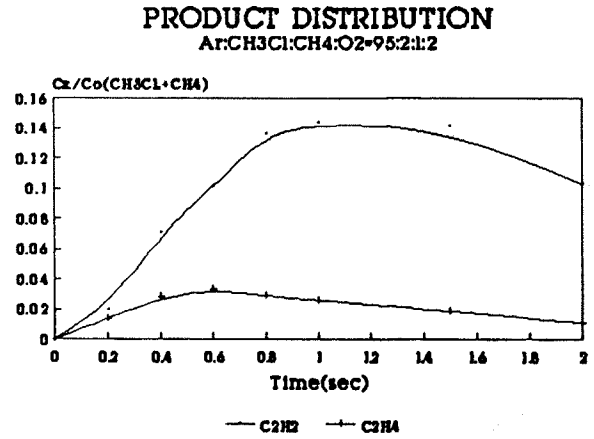

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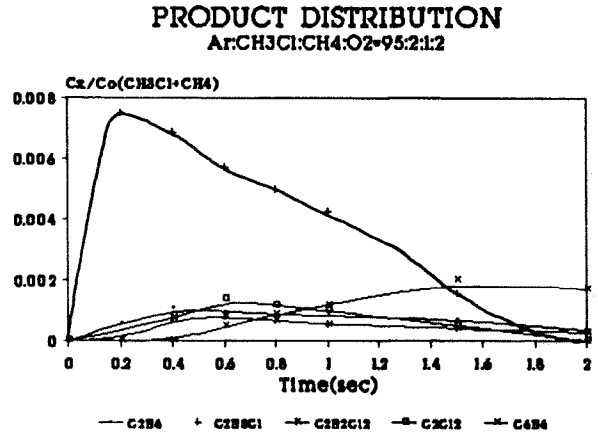

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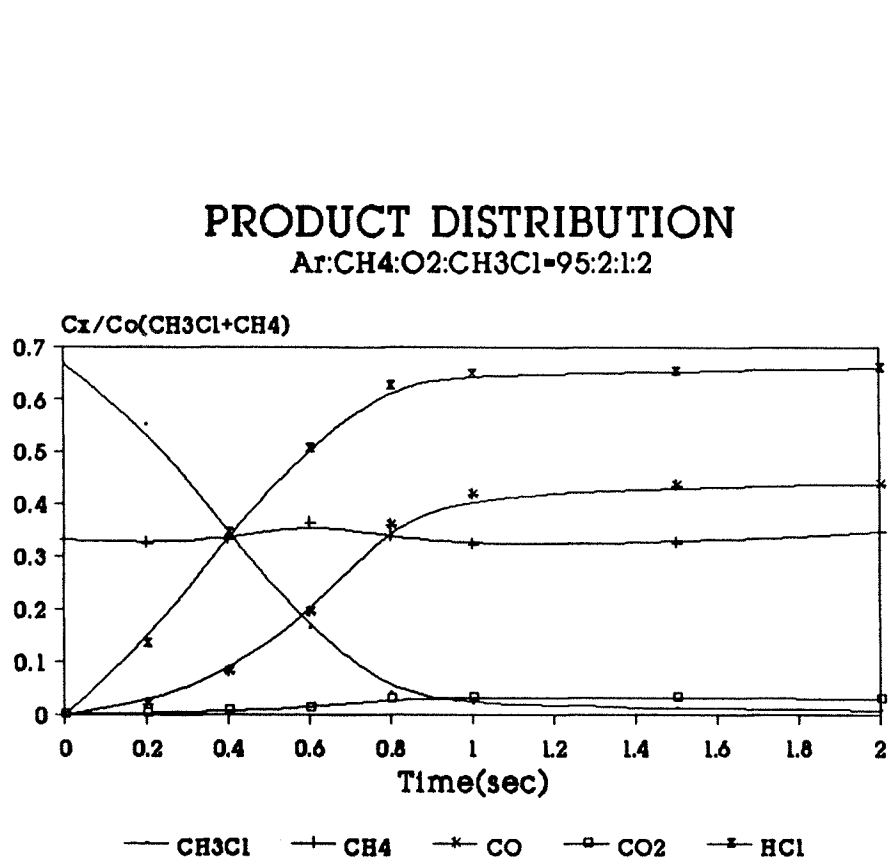

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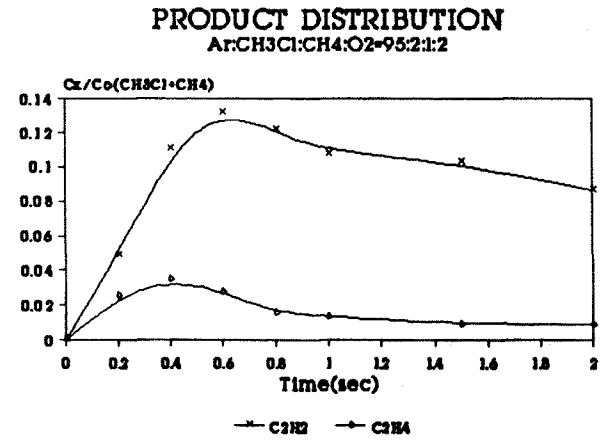

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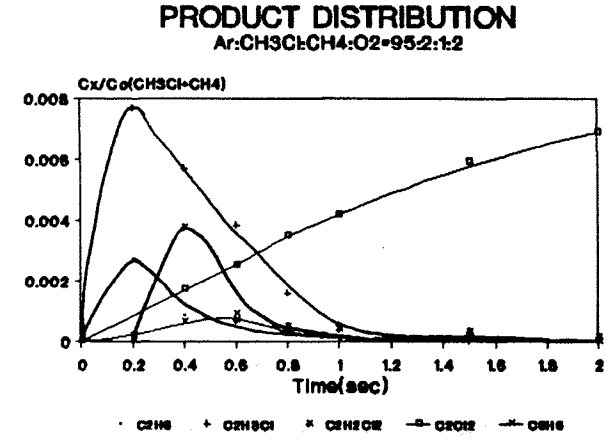

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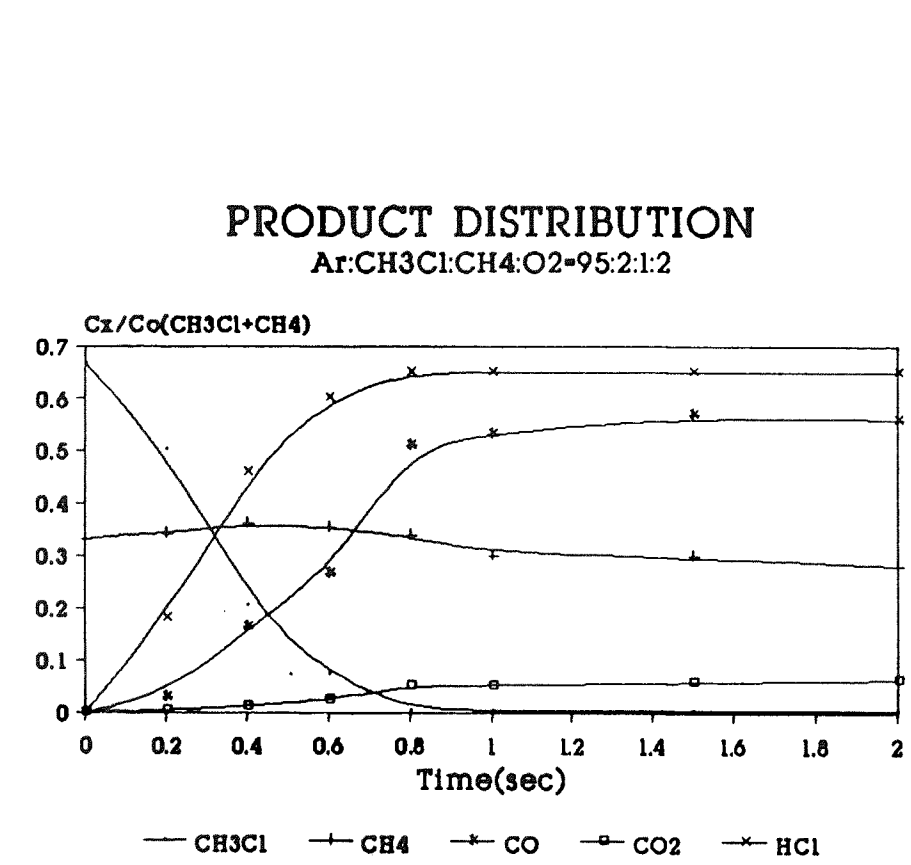

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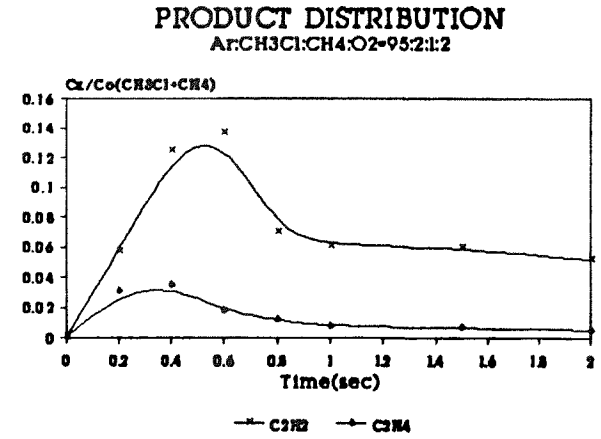

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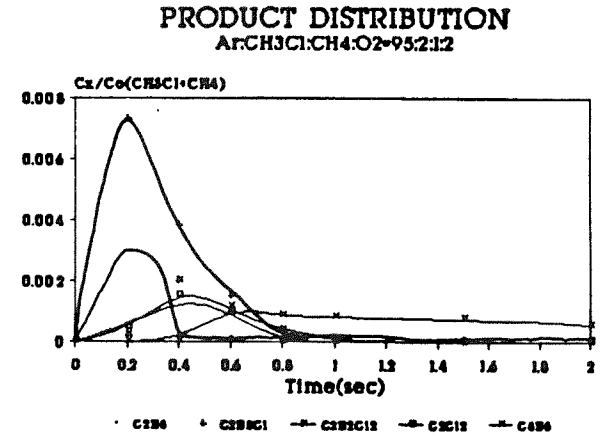

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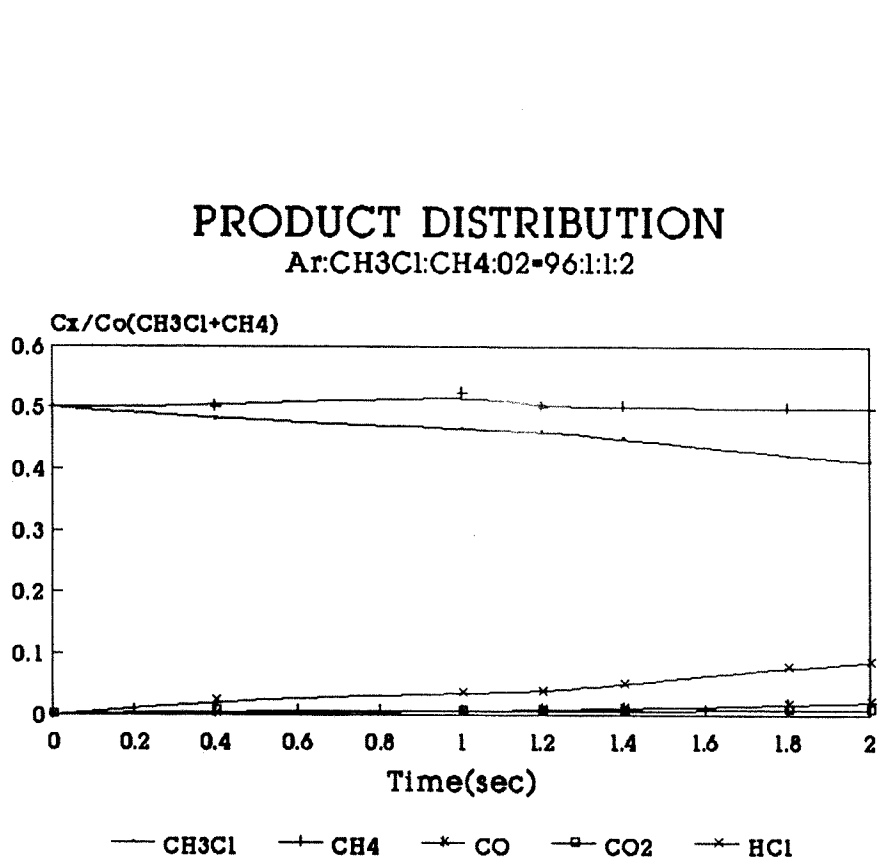

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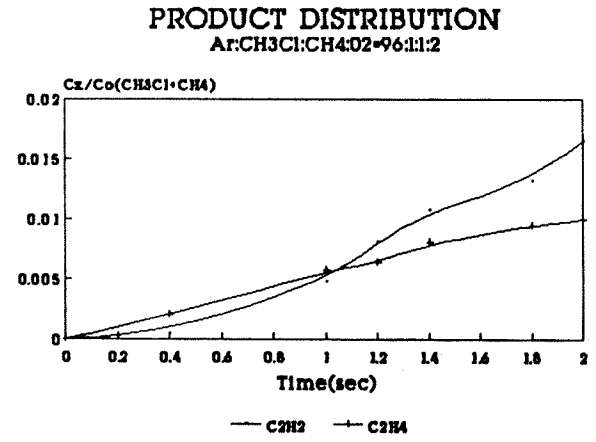

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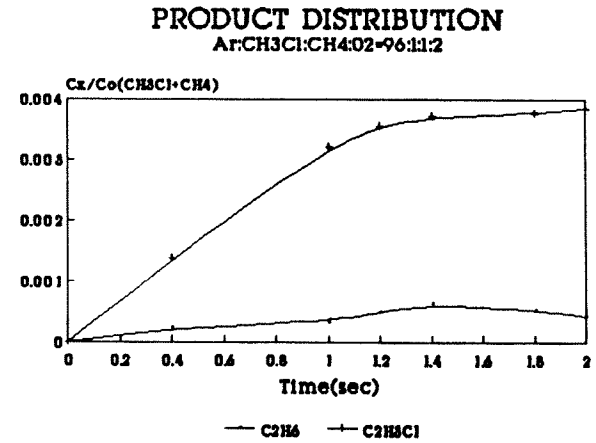

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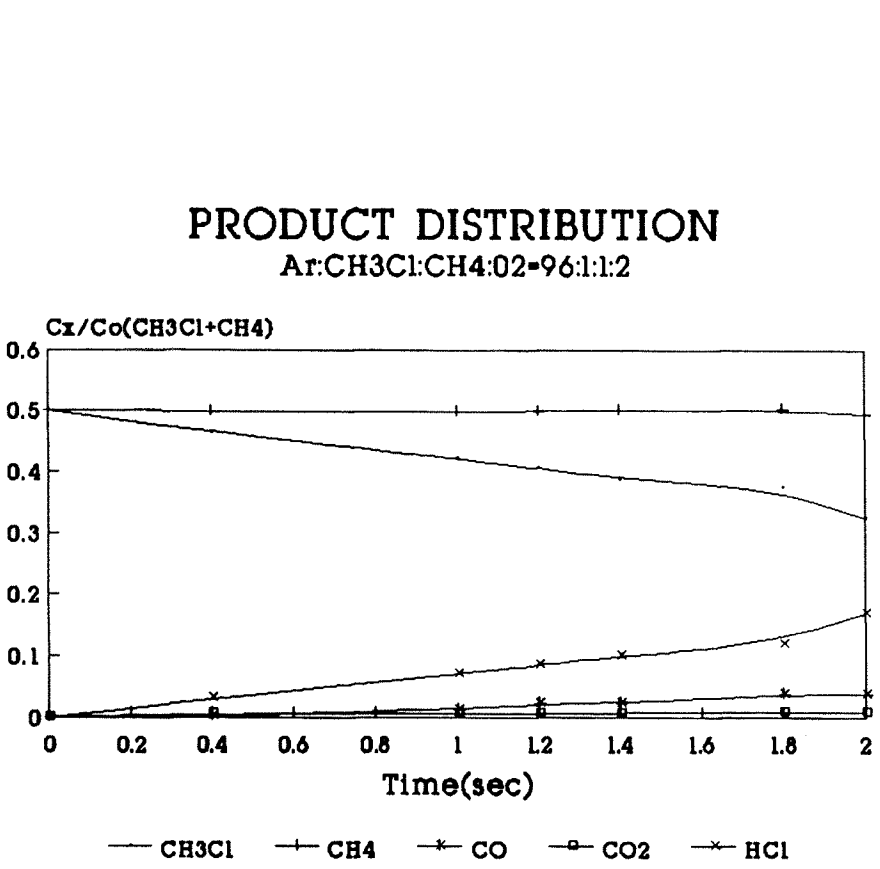

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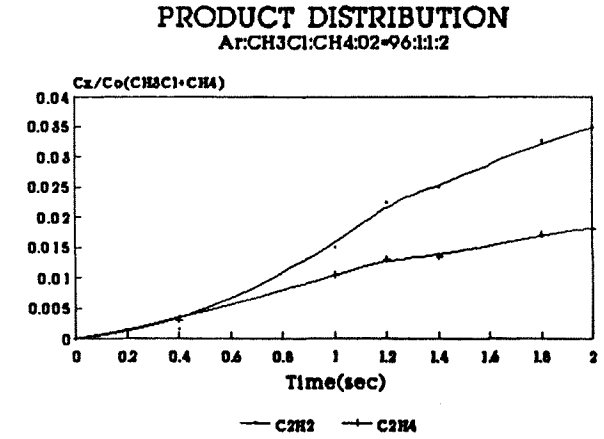

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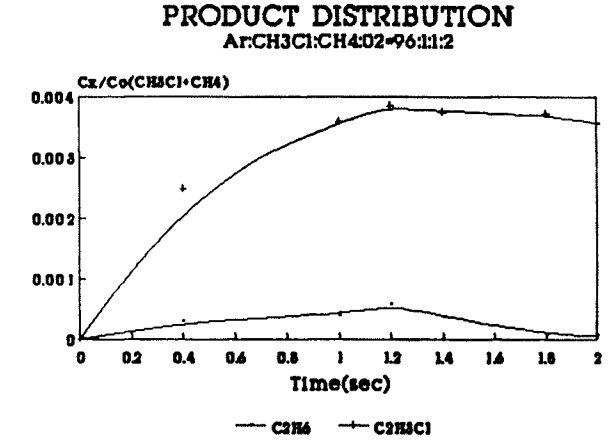

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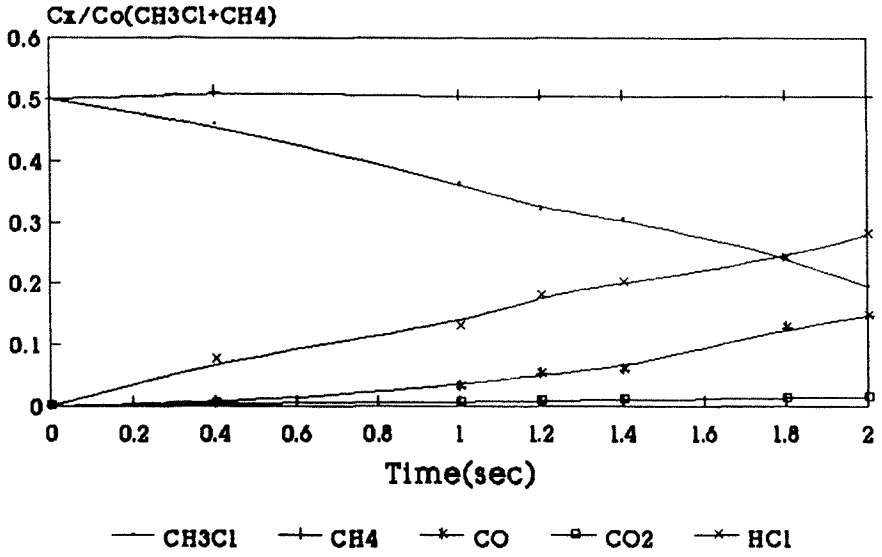

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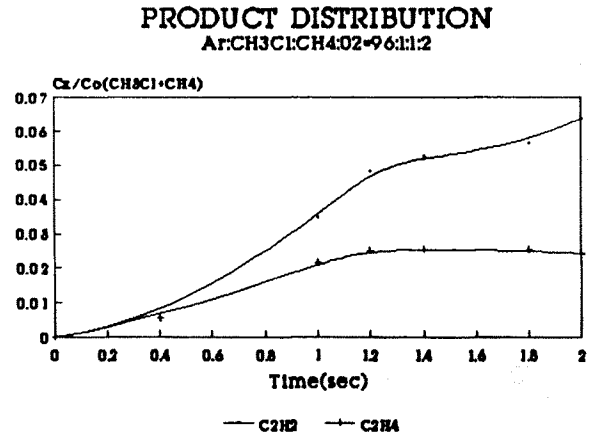

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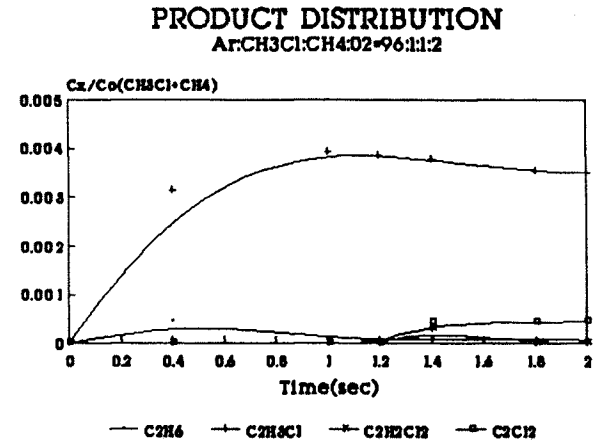

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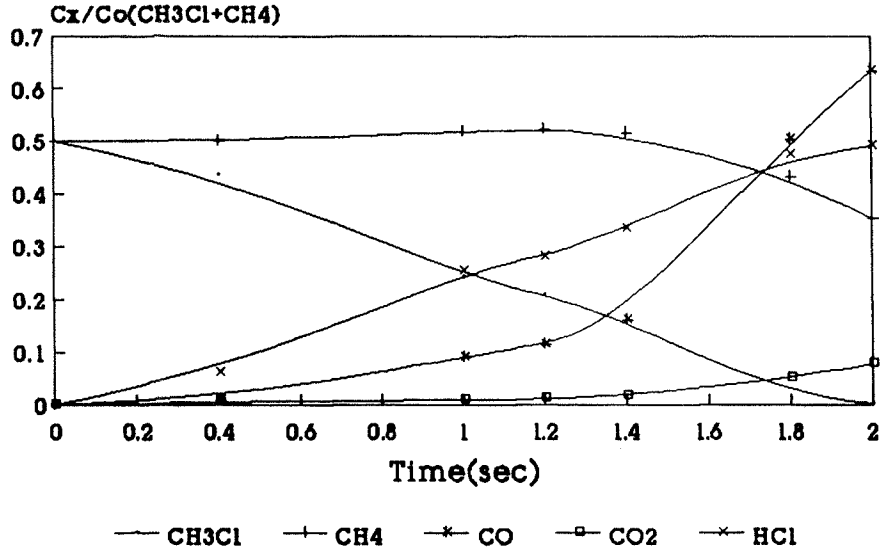

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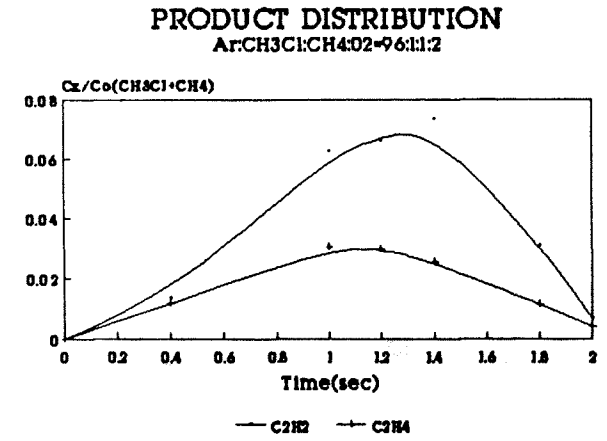

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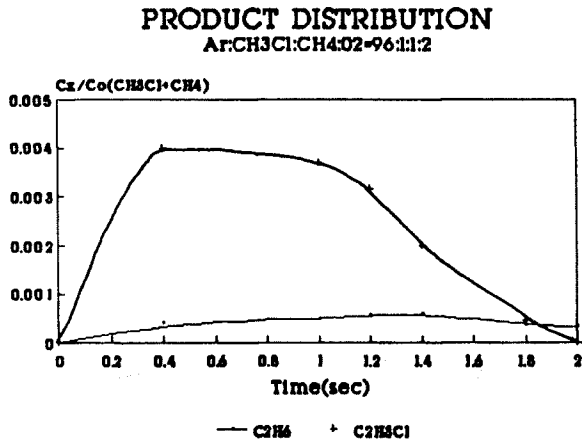

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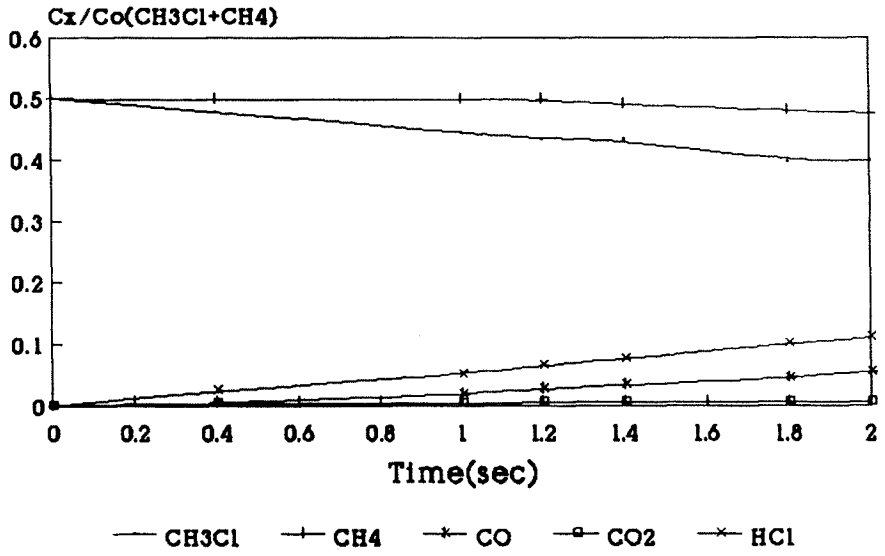

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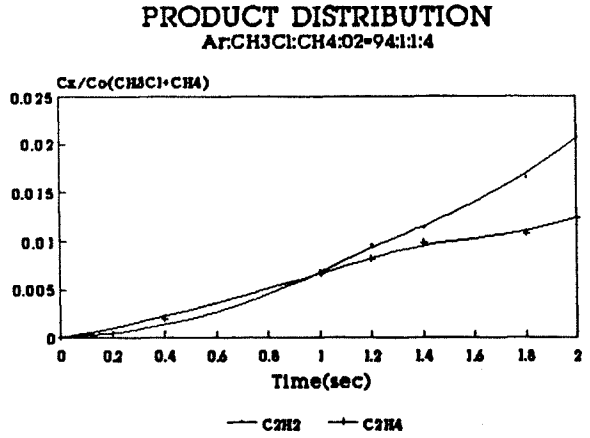

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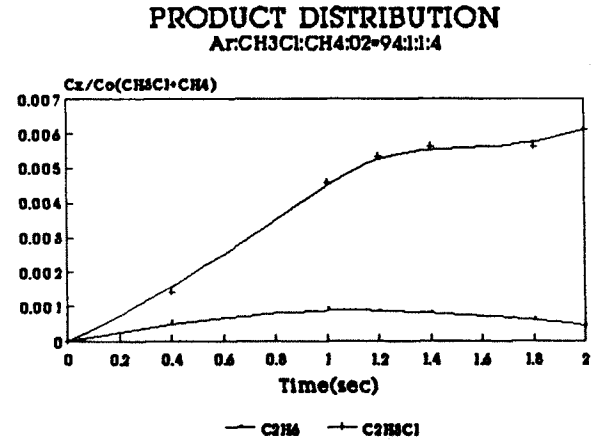

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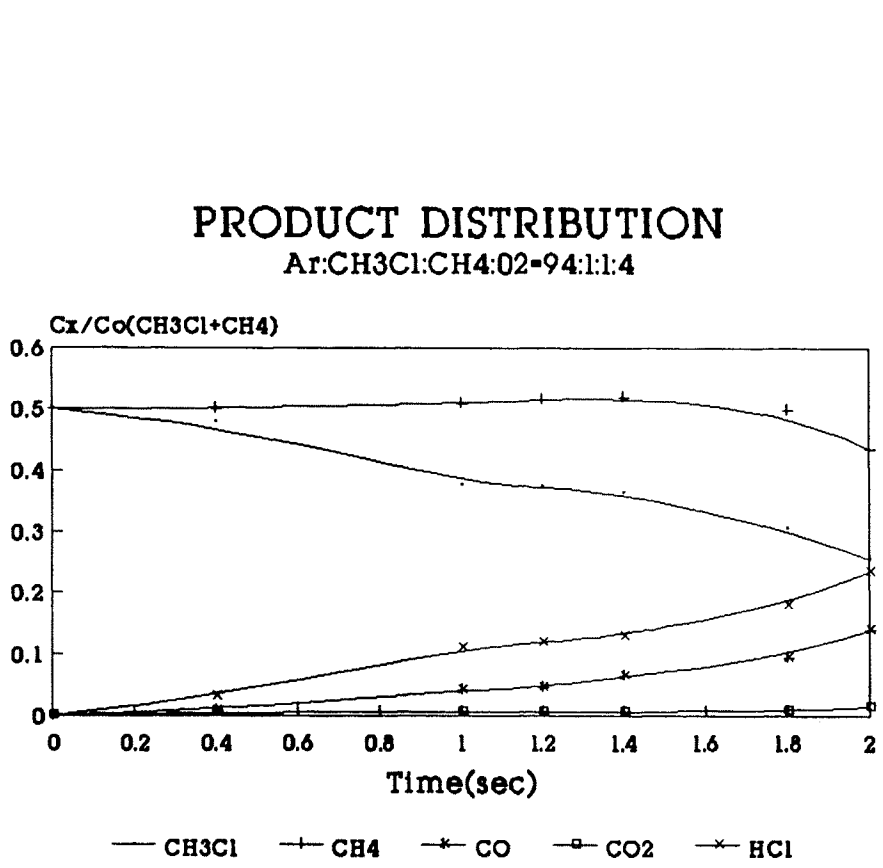

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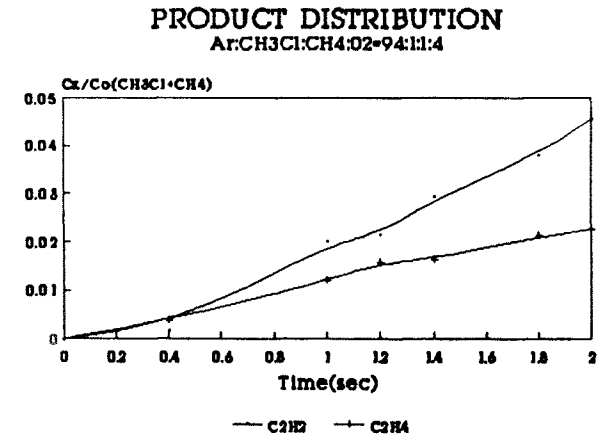

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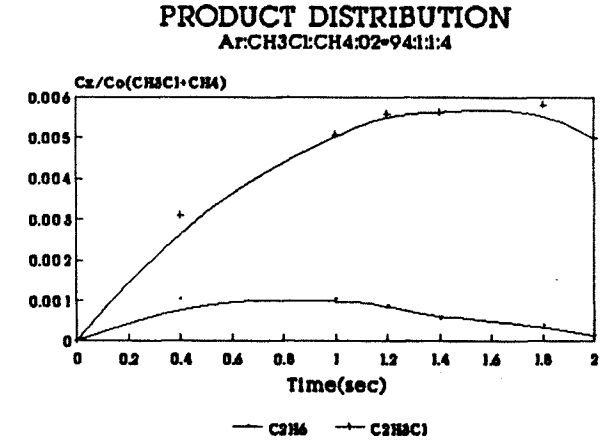

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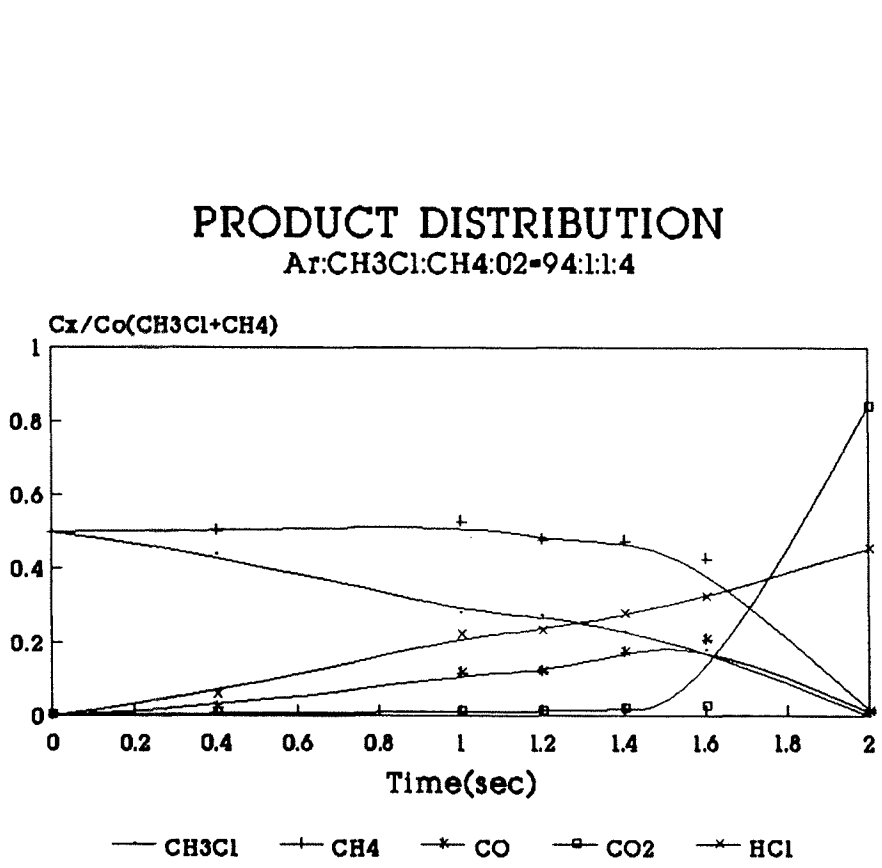

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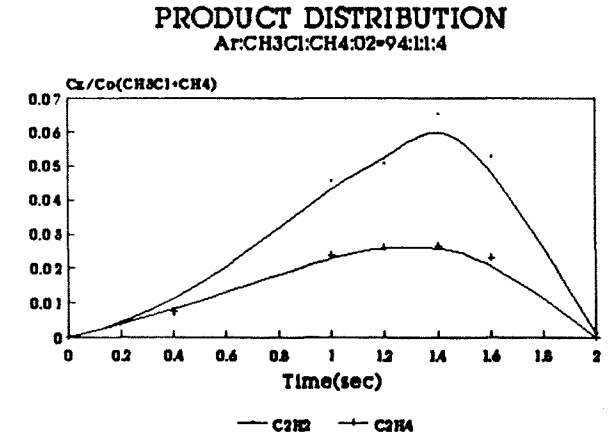

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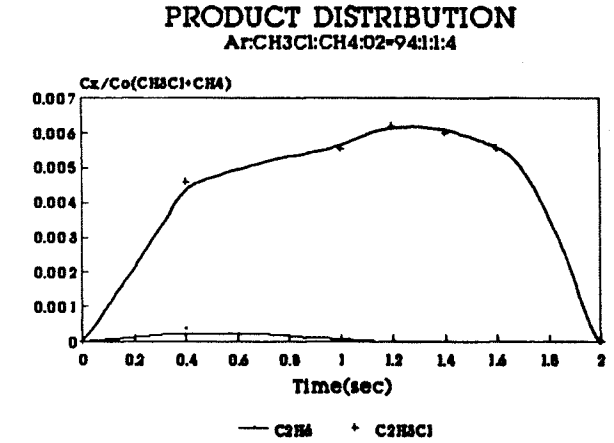

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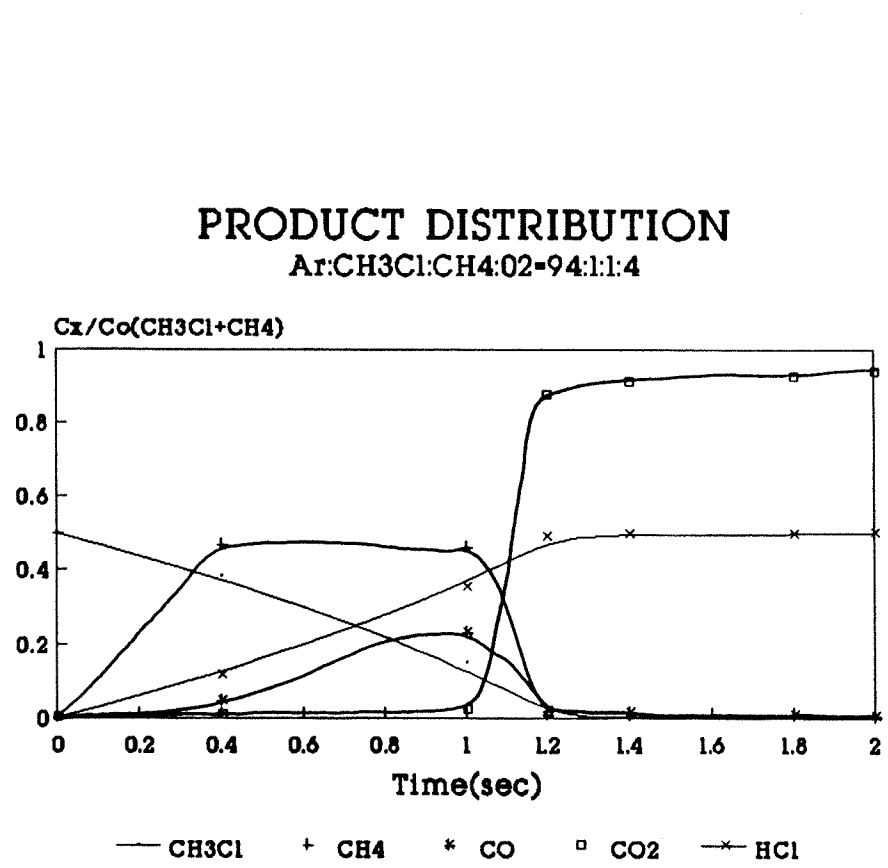

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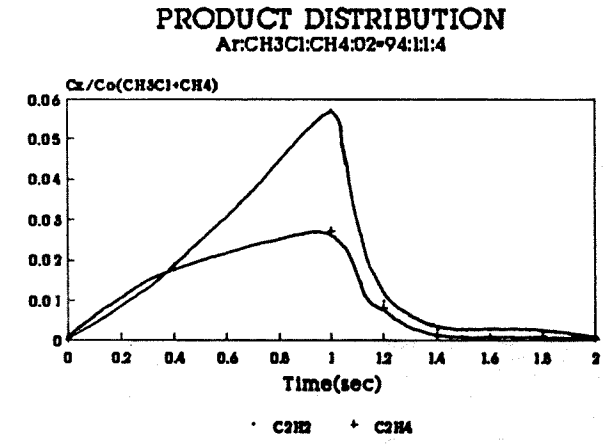

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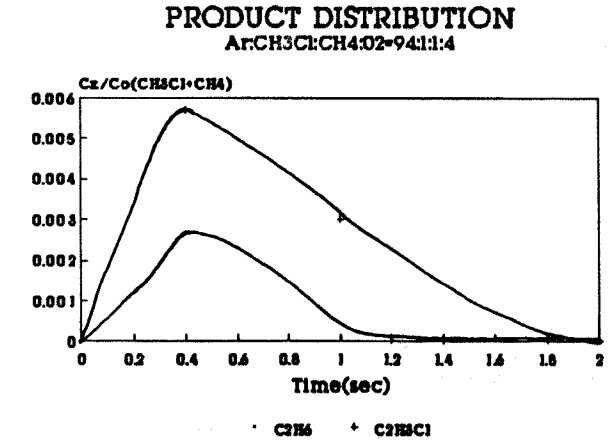

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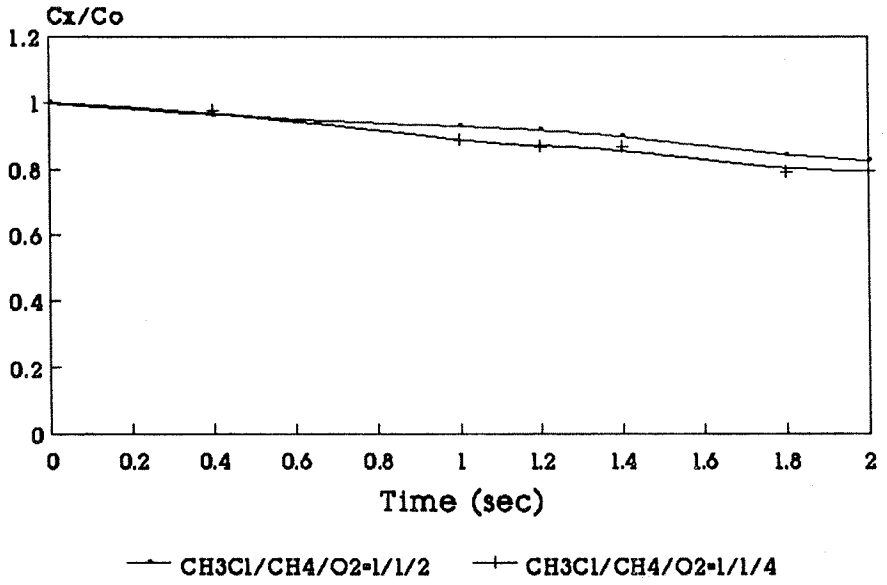

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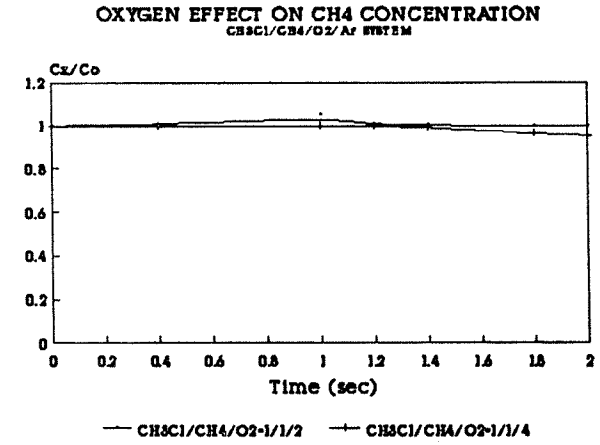

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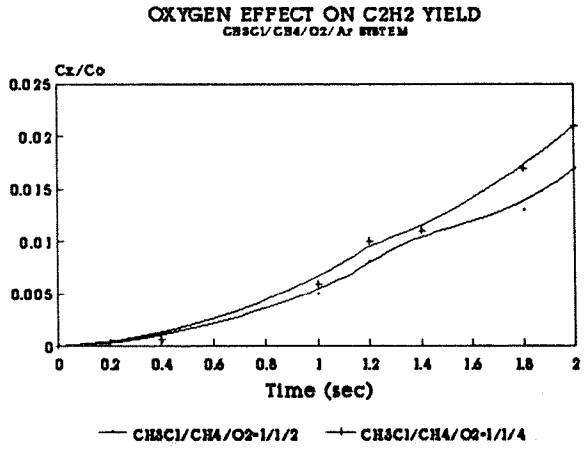

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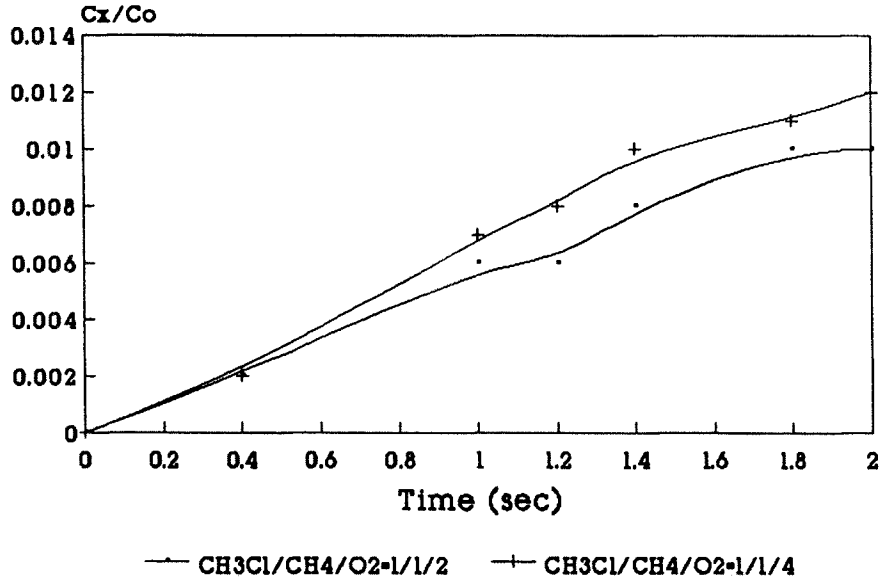

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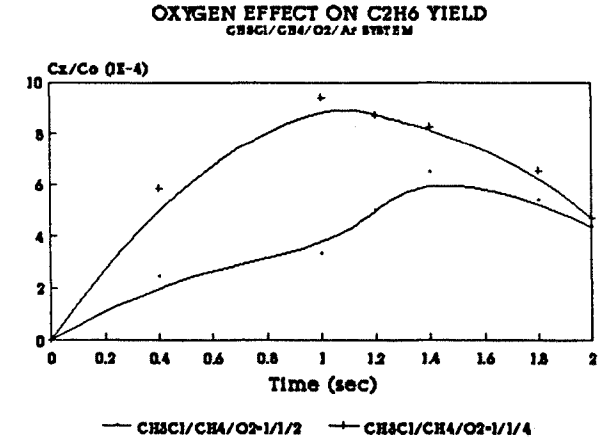

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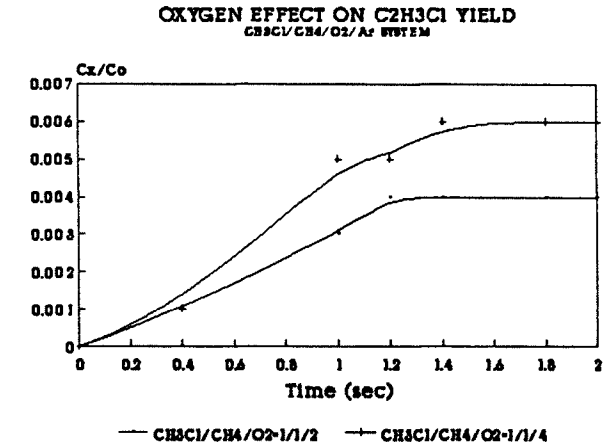

Fig. 140 1098K "16.0" Tube

3.2.3 Oxygen Content Effect

In order to discuss oxygen initiation effects in $CH_3Cl/CH_4/O_2/Ar$ system, Results at 1098K in the 16.0 mm ID reactor are used for illustration. These indicate that oxygen participates in initiation of CH_3Cl decay and contributes to intermediate product formation (Figures 135-140). These reasons may stem from the following reactions:

$CH_3Cl = CH_3 + Cl$ (1)

$CH_3 + O_2 = CH_2O + OH$ (2)

$CH_3Cl + O_2 = CH_2Cl + HO_2$ (3)

$CH_4 + O_2 = CH_3 + HO_2$ (4)

$CH_3Cl + Cl = CH_2Cl + HCl$ (5)

$CH_4 + Cl = CH_3 + HCl$ (6)

$CH_3 + HO_2 = CH_4 + O_2$ (7)

$CH_3 + HCl = CH_4 + Cl$ (8)

$CH_3 + CH_3Cl = CH_4 + CH_2Cl$ (9)

$CH_3 + CH_2Cl = CH_3CH_2Cl$ (10)

$CH_3CH_2Cl = C_2H_4 + HCl$ (11)

$CH_3 + CH_3 = C_2H_6$ (12)

$C_2H_6 + (Cl \text{ or } OH) = C_2H_5 + (HCl \text{ or } H_2O)$ (13)

$C_2H_5 = C_2H_4 + H$ (14)

$H + O_2 = OH + O$ (15)

$C_2H_4 + OH = C_2H_3 + H_2O$ (16)

$C_2H_3 = C_2H_2 + H$ (17)

$CH_2Cl + CH_2Cl = CH_2ClCH_2Cl$ (18)

$CH_2ClCH_2Cl = C_2H_3Cl + HCl$ (19)

Reactions (2) and (3) show oxygen contributes to CH_3Cl decay at very early time. The overall effects of reactions (1), (6), (7), (8), and (9) leads to a slightly increase in CH_4 at 1098K (see Figure 136); the result of reactions (1) - (6), and (10) - (14), lead to C_2H_4 formation. The general result of reactions (15) - (17) shows oxygen effect on C_2H_2 formation. Reactions (3), and (19) show oxygen's stimulation effect on C_2H_3Cl formation.

3.2.4 HCl Effect on CO Conversion to CO_2

When the concentration of CH_4 and O_2 is maintained at values of ca 1% and 2% respectively and CH_3Cl concentration is changed, the effect of HCl produced in reaction can be obtained. The following experimental results (Table 3) indicate that HCl inhibits oxidation of CO to CO_2. Since C[illegible] concentration of component II is two times that of component I, the concentration of HCl produced in II is about two times that of I under same reaction conditions. The data tell us that the concentration ratio of CO to CO_2 in II is greater than that in I, which means the greater, HCl concentration in reaction system; the lower, the conversion of CO to CO_2.

Table 3. The Effect of HCl Concentration in Products on CO Conversion

Temperature	Reactant Component	(HCl)	(CO)/(CO2)
825C	I	0.06	1.6
	II	0.14	2.0
850C	I	0.14	3.6
	II	0.42	8.3
875C	I	0.44	7.8
	II	0.83	9.4
900C	I	0.74	11.9
	II	1.45	13.9
925C	I	0.97	11.5
	II	1.94	13.0
950C	I	0.99	6.9
	II	1.98	10.3

* Reaction Time is at 1.0 second; ( ) denotes mole concentration.

I denotes Ar:CH_3Cl:CH_4:O_2 = 96:1:1:2.

II denotes Ar:CH_3Cl:CH_4:O_2 = 95:2:1:2.

3.3 Quantum Rice-Ramsperger-Kassel (QRRK) Analysis

Quantum Rice-Ramsperger-Kassel (QRRK) is a straightfoward method for calculating apparent rate constants of energized complexes. A brief description of its theoretical basis is derived from the article by Westmoreland and Dean [14]. The energized radical and molecular complexes are modeled using the QRRK analyses. The details of bimolecular QRRK method have been presented and discussed [14,15]. This computer code has been modified by Ritter and Bozzelli [16] to use gamma function instead of factorials. The QRRK computer code was used to determine the energy dependent rate constants for all reaction channels of the energized complexes and calculates rate constants as function of both temperature and pressure. The use of this formalism is important in determination of accurate rate constants needed for input to the mechanism, specifically in choice of the important reaction paths. This is also applied to accurate product distribution prediction from the activated complex.

QRRK analysis of the chemically activated system, using generic estimates or literature values for high pressure rate constants and species thermodynamic properties for the enthalpies of reaction, can yield thermodynamically and kinetically plausible apparent rate constants which are needed for the temperatures and pressures of our reaction systems. The input rate parameters used in

these calculations and results from the calculations are summarized in APPENDIX I Table A-E. In order to illustrate this calculation method, the reaction, C_2H_2 + OH => products as a example is presented:

The reaction of C_2H_2 with OH will be considered first as addition reaction to form the energized complex [HOCH*C.H]# (# denotes energized complex). It can further react as shown in reactions (2) to (3) or be stabilized and or return to initial reactant.

$$C_2H_2 + OH \underset{(63.7)}{\overset{(1)}{<=>}} [HOCH^*C.H]^{\#} \Rightarrow C_2H + H_2O \quad (74.2) \quad (2)$$

$$\Rightarrow HOC\#CH + H \quad (72.4) \quad (3)$$

$$\Rightarrow [.CH_2CHO]^{\#} \quad (3.2) \quad (4)$$

$$HOCH^*C.H \quad (28.3)$$

Reaction (2) is not important comparing with abstraction reaction C_2H_2 + OH = C_2H + H_2O. So this channel is omitted in QRRK analysis. Channel (3) has a higher energy barrier than channel (4). Based on BAC-MP4 potential-energy-surface information and statistical-theoretical methods presented by Miller [17], however, channel (3) is important path at combustion conditions. Reaction (4) is thermodynamically favorable relative to initial energy of the reactants (Isomerization through H shift from oxygen to carbon atom). The species .CH_2CHO can form CH_2CHO and H via beta scission reaction (5) or further isomerize (7) to product $CH_3C.O$. It is interesting that $CH_3C.O$ converts to

CH_2CO + H (9) but also reacts to form CH_3 + CO (8).

$$[.CH_2CHO]^{\#} \underset{(3.2)}{\Rightarrow} CH_2CO + H \quad (40.7) \quad (5)$$

$$\Leftrightarrow [CH_3C.O]^{\#} \quad (-5.4) \quad (7)$$

$$[CH_3C.O]^{\#} \underset{(8.4)}{\Rightarrow} CH_3 + CO \quad (8)$$

$$[CH_3C.O]^{\#} \Rightarrow CH_2CO + H \quad (9)$$

The energy diagram for above reaction channels is illustrated in Figure 141. The QRRK calculation results for this reaction system indicate that the reactions for CH_3 + CO and CH_2CO + H are the dominant channels. The rate constant for the HOC#CH + H channel increase faster than other channels with increasing temperature. When temperature increases from 1200K to 1500K, the rate constant for CH_3 + CO decreases slightly. The rate constant for CH_2CO + H increases slightly. The rate constant increase for HOC#CH + H is three times greater, however, which is agreement with data reported by Miller.

The important elementary reactions and their energy diagrams for the reaction systems C_2H_2 + O, C_2H_4 + O, and C_2H_4 + OH are shown in Figures 142-144.

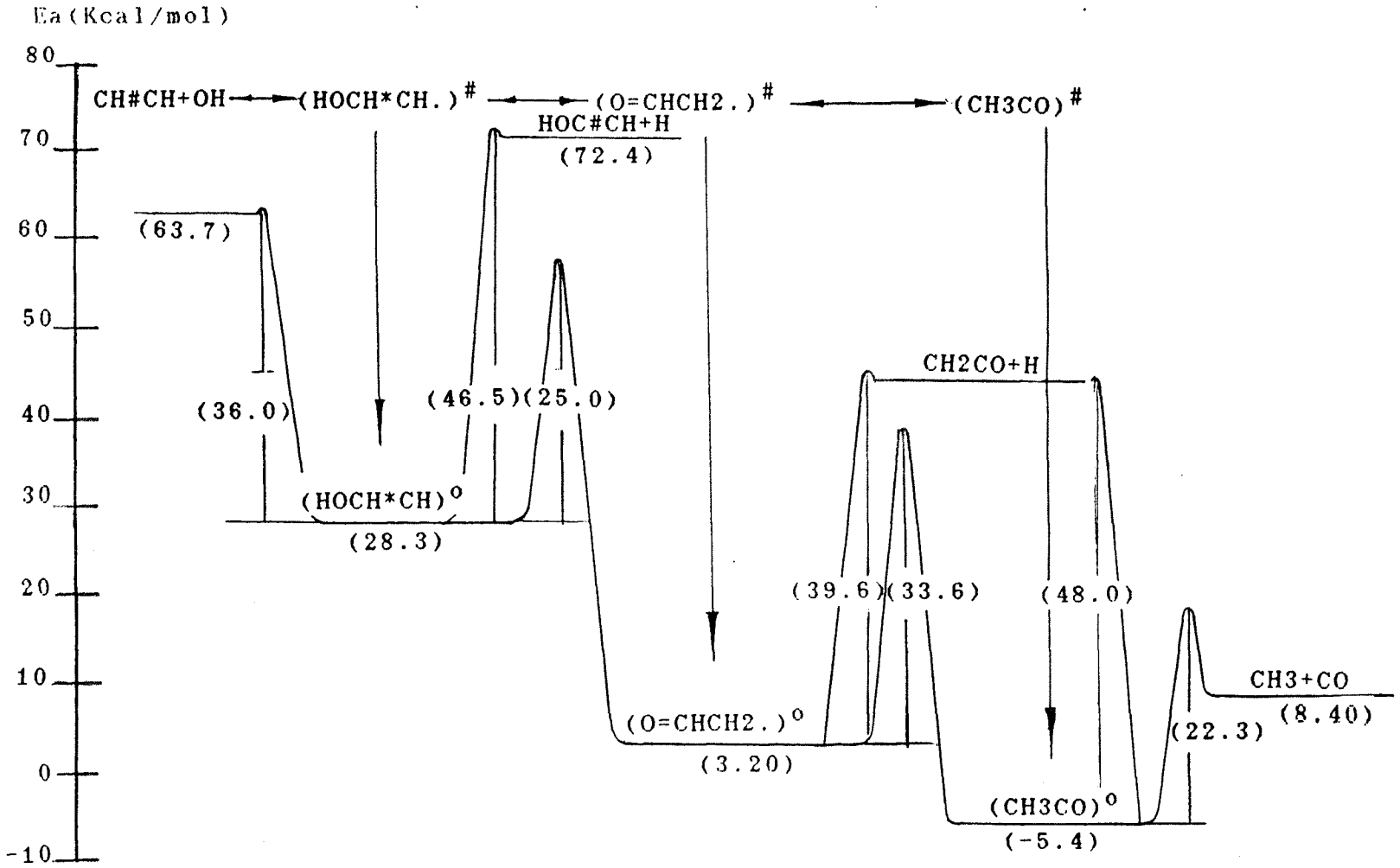

Figure 141. Energy Diagram for the Reaction C2H2+OH

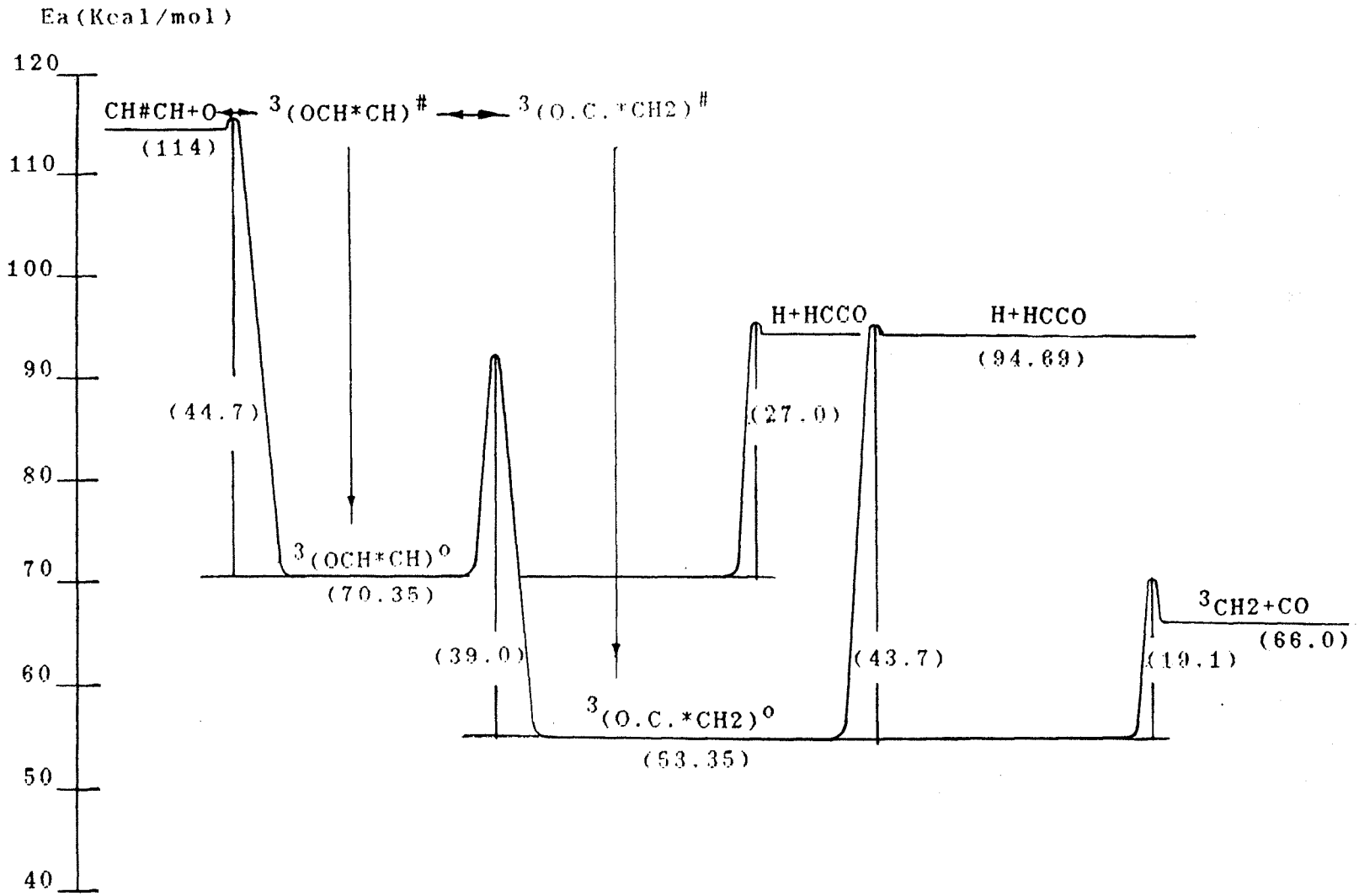

Figure 142. Energy Diagram for the Reaction C2H2+O

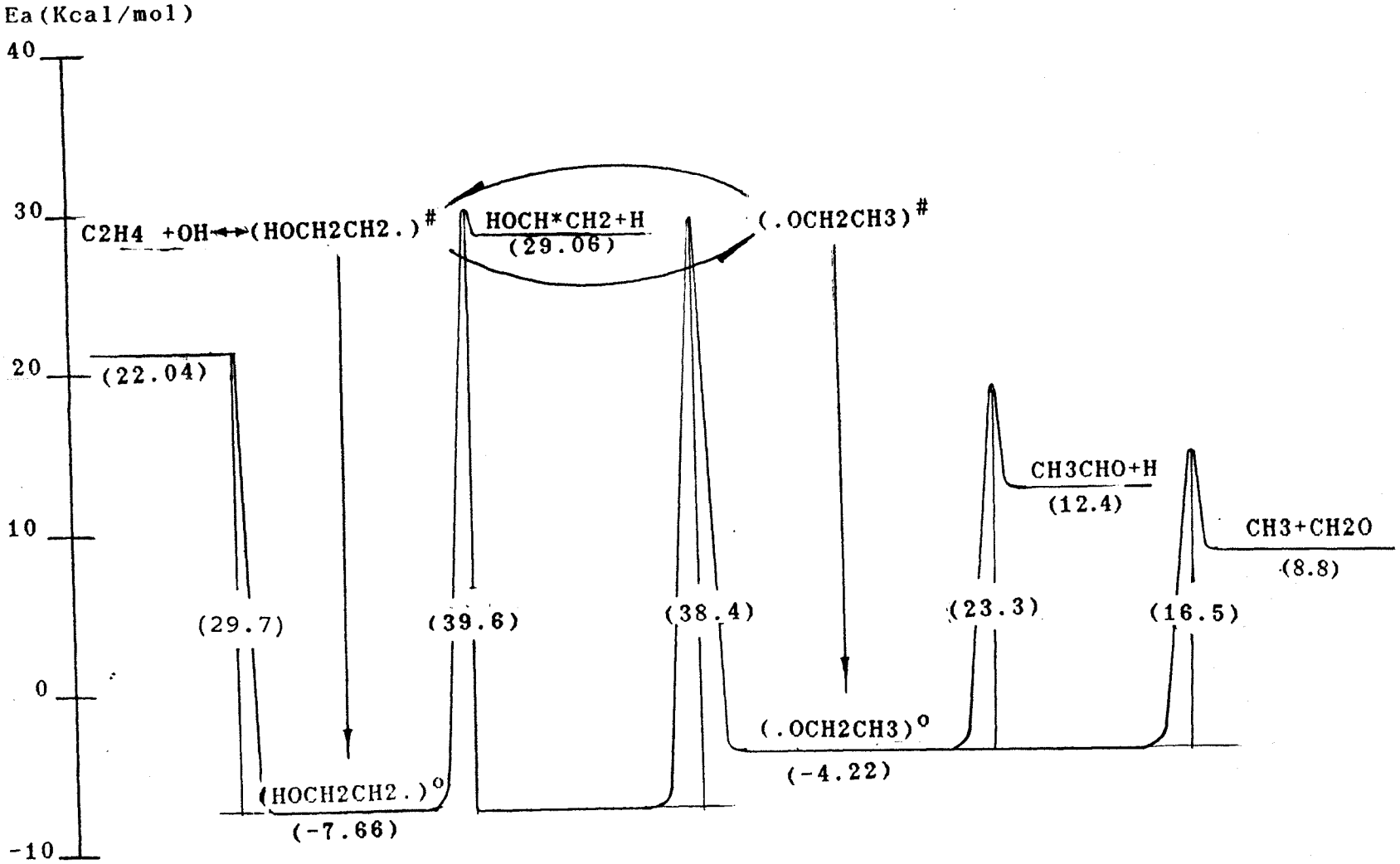

Figure 143. Energy Diagram for the Reaction C2H4+OH

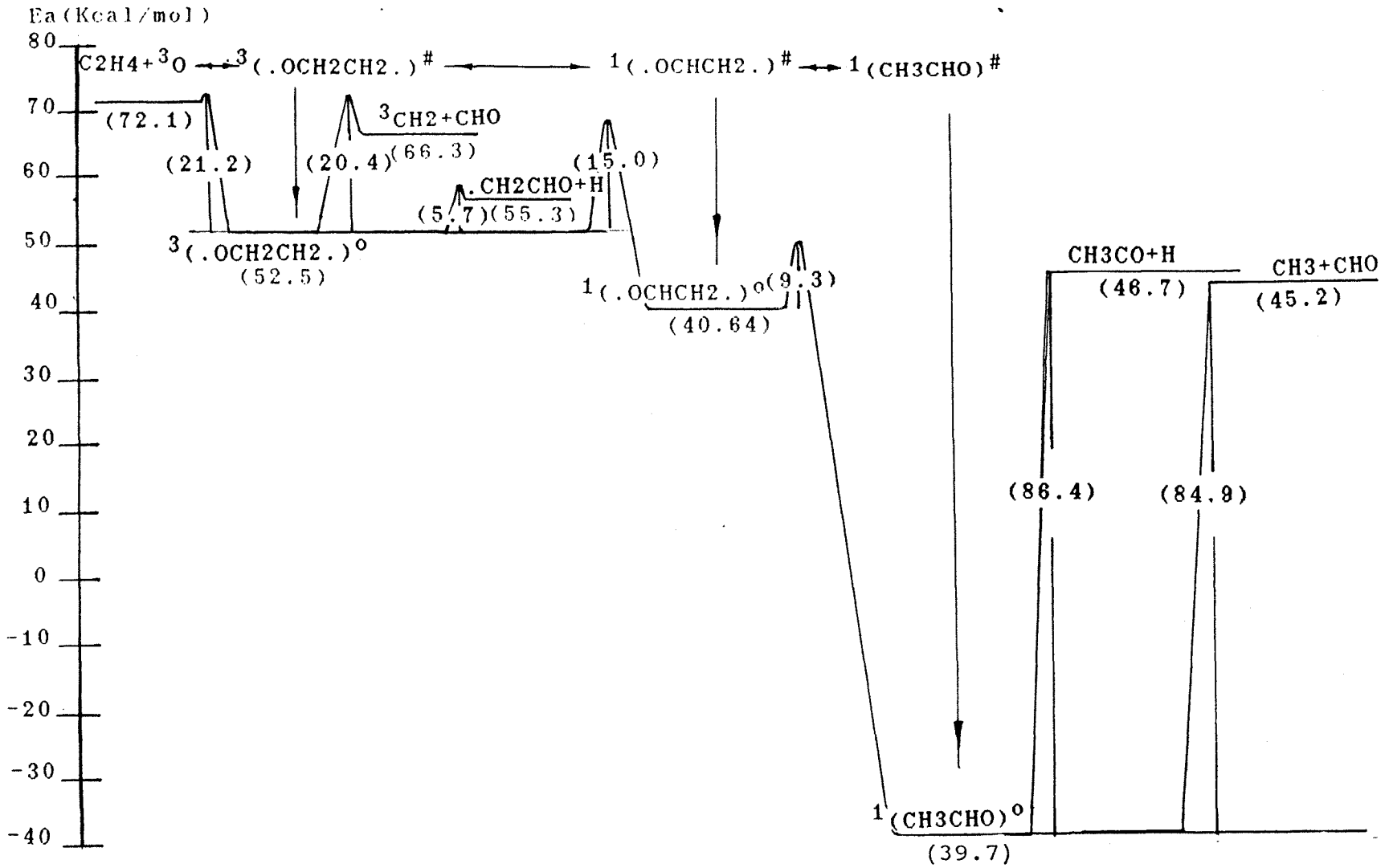

Figure 144. Energy Diagram for the Reaction C2H4+O

Table 4. Detailed Reaction Mechanism for CH3Cl/CH4/O2 Systems

	Reaction	A	n	Ea	Source*
1.	$C_2H_6+CH_3=C_2H_5+CH_4$ (LIKE CLARK&DOVE--OPT)	0.550	4.00	8300.	[1]
2.	$CH_3+C_2H_5=CH_4+C_2H_4$ (JPCRD)	5.50E+13	0.00	0.	[2]
3.	$CH_2Cl_2 = CHCl + HCl$	1.82E+36	-7.43	85730.	[2]
4.	$CH_2Cl_2 = CH_2Cl + Cl$	1.60E+40	-7.84	83550.	[2]
5.	$CH_2Cl = CH_2 + Cl$	1.26E+37	-6.91	90540.	[2]
6.	$CH_2Cl = CH_2S + HCl$	8.52E+27	-5.13	109640.	[2]
7.	$CH_2Cl_2 + H = CH_2Cl + HCl$	7.00E+13	0.00	7100.	[3]
8.	$CHCl_2 + H_2 = CH_2Cl_2 + H$	3.60E+12	0.00	15295.	[3]
9.	$CH_2Cl + H_2 = CH_3Cl + H$	1.79E+12	0.00	13059.	[3]
10.	$CH_2Cl_2 + Cl = CHCl_2 + HCl$	2.51E+13	0.00	3100.	[3]
11.	$CH_3Cl + H = CH_3 + HCl$	3.72E+13	0.00	7600.	[3]
12.	$CH_4 = CH_3 + H$	1.03E+33	-5.58	111800.	[2]
13.	$CH_4 + H = CH_3 + H_2$ (TSA)	2.20E+04	3.00	8748.	[16]
14.	$CH_4 + Cl = CH_3 + HCl$	3.09E+13	0.00	3600.	[3]
15.	$CH_3Cl + Cl = CH_2Cl + HCl$	3.16E+13	0.00	3300.	[3]
16.	$CH_2Cl_2 + CH_3 = CH_4 + CHCL_2$	6.76E+10	0.00	7200.	[3]
17.	$CH_2Cl_2 + CH_3 = CH_3Cl + CH_2Cl$	1.40E+11	0.00	4900.	[3]
18.	$CH_3Cl + CH_3 = CH_4 + CH_2Cl$	3.39E+11	0.00	9400.	[3]
19.	$CHCl_2 + CHCl_2 = C_2H_2Cl_4$	9.08E+45	-10.56	13170.	[46]
20.	$CHCl_2 + CHCl_2 = C_2H_2Cl_3 + Cl$	1.36E+30	-5.23	14180.	[46]
21.	$CHCl_2 + CHCl_2 = C_2HCl_3 + HCl$	6.72E+35	-7.11	13210.	[46]
22.	$CH_2Cl + CH_2Cl = C_2H_4Cl_2$	1.00E+13	0.00	0.	[4]
23.	$CH_2Cl + CH_2Cl = CH_2ClCH_2 + Cl$	4.67E+29	-4.95	14070.	[2]
24.	$CH_2Cl + CH_2Cl = C_2H_3Cl + HCl$	1.88E+35	-6.73	13160.	[2]
25.	$CH_2Cl + CHCl_2 = C_2H_3Cl_3$	6.41E+33	-10.22	12910.	[2]
26.	$CH_2Cl + CHCl_2 = CH_2ClCl_2 + HCl$	3.75E+36	-7.22	13620.	[2]
27.	$CH_2Cl + CHCl_2 = CHClCHCl + HCl$	1.22E+37	-7.20	13640.	[2]
28.	$CH_2Cl + CH_3 = C_2H_5Cl$	5.01E+13	0.00	0.	[46]
29.	$CH_2Cl + CH_3 = C_2H_4 + HCl$	3.50E+28	-4.49	9130.	[2]
30.	$CH_2Cl + CH_3 = C_2H_5 + Cl$	9.27E+19	-2.07	10130.	[2]
31.	$CHCl_2 + CH_3 = CH_3CHCl_2$	2.28E+41	-8.68	11620.	[2]
32.	$CHCl_2 + CH_3 = C_2H_3Cl + HCl$	1.35E+30	-4.96	11550.	[2]
33.	$CHCl_2 + CH_3 = CH_3CHCl + Cl$	2.74E+25	-3.45	12810.	[2]
34.	$CH_2Cl + H = CH_3Cl$	3.08E+27	-5.02	4380.	[2]
35.	$CH_2Cl + H = CH_3 + Cl$	4.49E+15	-0.50	760.	[2]
36.	$CH_2Cl + H = CH_2S + HCl$	1.04E+06	1.65	3320.	[46]
37.	$CHCl_2 + H = CH_2Cl_2$	4.81E+26	-4.82	3810.	[2]
38.	$CHCl_2 + H = CH_2Cl + Cl$	1.25E+14	-0.03	570.	[2]
39.	$C_2H_3Cl + H = CH_2ClCH_2$	5.01E+23	-4.21	8470.	[46]
40.	$C_2H_3Cl + H = C_2H_4 + Cl$ (REC)	1.59E+14	0.00	5040.	[5]
41.	$C_2H_3Cl + H = C_2H_3 + HCl$ (REC)	6.65E+37	-7.09	18400.	[5]
42.	$C_2HCl_3 + H = CH_2ClCCl_2$	1.51E+23	-4.18	7520.	QRRK
43.	$C_2HCl_3 + H = C_2H_2Cl_3$	2.87E+22	-4.09	10890.	QRRK
44.	$C_2HCl_3 + H = CH_2Cl_2 + Cl$	1.45E+13	-0.01	5830.	QRRK
45.	$C_2HCl_3 + H = CHClCHCl + Cl$	7.37E+12	-0.01	9220.	QRRK

46.	$C_2H_3Cl_3 = CHClCHCl + HCl$	1.39E+20	-2.03	60450.	DISSOC
47.	$C_2H_3Cl_3 = CH_2CCl_2 + HCl$	3.13E+19	-2.02	60330.	DISSOC
48.	$CH_2CHCl_2 = C_2H_2Cl + HCl$	2.94E+21	-2.37	59460.	DISSOC
49.	$CH_2CHCl_2 = CH_2CHCl + Cl$	3.17E+42	-8.10	92670.	DISSOC
50.	$C_2H_2Cl_4 = C_2HCl_3 + HCl$	8.62E+21	-2.57	51870.	DISSOC
51.	$C_2H_4Cl_2 = C_2H_3Cl + HCl$	6.76E+19	-1.93	58710.	DISSOC
52.	$C_2H_5Cl = C_2H_4 + HCl$	6.31E+13	0.00	57400.	DISSOC
53.	$C_2H_5Cl = C_2H_5 + Cl$	2.35E+43	-8.50	96980.	DISSOC
54.	$C_2H_5Cl + Cl = HCl + CH_2CHCl$	3.55E+13	0.00	1500.	QRRK
55.	$C_2H_5Cl + Cl = HCl + CH_2ClCH_2$	1.12E+13	0.00	1500.	QRRK
56.	$C_2H_5Cl + H = HCl + C_2H_5$	1.00E+14	0.00	7900.	QRRK
57.	$C_2H_3Cl = C_2H_2 + HCl$	1.62E+28	-4.29	75780.	DISSOC
58.	$C_2H_3Cl = C_2H_3 + Cl$	1.71E+38	-7.13	96370.	DISSOC
59.	$C_2H_6 = C_2H_5 + H$	6.22E+47	-9.76	111250.	DISSOC
60.	$C_2H_6 = CH_3 + CH_3$	5.34E+54	-11.12	112210.	DISSOC
61.	$C_2H_4 = C_2H_2 + H_2$ (DISSOC,WAR)	8.52E+43	-8.32	121240.	[7]
62.	$C_2H_4 = C_2H_3 + H$ (DISSOC,DEAN)	8.53E+30	-5.87	118240.	[46]
63.	$CH_2Cl_2 + H = C_2H_2Cl + Cl$	7.21E+12	0.00	7510.	QRRK
64.	$CHClCHCl + H = C_2H_2Cl + Cl$	3.44E+13	-0.03	5890.	QRRK
65.	$C_2H_6 + H = C_2H_5 + H_2$ (REC)	3.24E+06	2.63	6300.	[5]
66.	$C_2H_6 + Cl = C_2H_5 + HCl$ (REC)	5.43E+13	0.00	246.	[5]
67.	$C_2H_6 + O = C_2H_5 + OH$ (REC)	2.62E+08	2.05	5400.	[5]
68.	$C_2H_6 + OH = C_2H_5 + H_2O$ (REC)	9.07E+09	1.99	1480.	[5]
69.	$C_2H_5 = C_2H_4 + H$ (DISSOC,DEAN)	1.83E+39	-7.75	52820.	[46]
70.	$C_2H_5 + H = CH_3 + CH_3$ (QRRK)	1.35E+22	-2.17	7000.	[2]
71.	$C_2H_5 + O = CH_2O + CH_3$	1.00E+13	0.00	0.	[6]
72.	$C_2H_5 + O_2 = C_2H_4 + HO_2$	2.00E+12	0.00	4996.	[7]
73.	$C_2H_5 + HO_2 = C_2H_4 + H_2O_2$ (TSA)	3.01E+11	0.00	0.	[16]
74.	$C_2H_4 + OH = CH_3 + CH_2O$ (REC)	1.57E+16	-1.47	12179.	[5]
75.	$C_2H_4 + OH = CH_2CHO + H$ (REC)	3.50E+14	-0.87	11650.	[5]
76.	$C_2H_4 + OH = C_2H_3 + H_2O$ (REC)	9.41E+13	0.00	8330.	[5]
77.	$CH_2CHO = CH_3 + CHO$	7.10E+15	0.00	81280.	[47]
78.	$CH_2CHO + OH = CH_2CO + H_2O$	1.00E+13	0.00	0.	[7]
79.	$CH_2CHO + O = CH_2CO + OH$	5.00E+12	0.00	1790.	[7]
80.	$CH_2CHO + H = CH_2CO + H_2$	4.00E+13	0.00	4210.	[7]
81.	$C_2H_4 + O = CH_2CHO + H$ (REC)	2.70E+13	-0.20	1760.	[5]
82.	$C_2H_4 + O = CH_3 + CHO$ (REC)	2.70E+30	-4.54	39390.	[5]
83.	$C_2H_4 + O_2 = C_2H_3 + HO_2$ (TSA)	4.22E+13	0.00	57623.	[16]
84.	$C_2H_4 + H = C_2H_3 + H_2$ (REC)	1.31E+05	3.10	11400.	[5]
85.	$C_2H_4 + Cl = C_2H_3 + HCl$ (REC)	2.00E+13	0.00	10000.	[5]
86.	$C_2H_3 = C_2H_2 + H$ (REC)	3.84E+22	-2.21	36500.	[5]
87.	$C_2H_3 + O_2 = CH_2CHO + O$ (BOZ)	1.66E+19	-1.83	7749.	[54]
88.	$C_2H_3 + O_2 = C_2H_2 + HO_2$ (BOZ)	5.08E+23	-3.61	8041.	[54]
89.	$C_2H_3 + O_2 = CH_2O + CHO$ (BOZ)	5.64E+27	-4.73	8487.	[54]
90.	$C_2H_2 + Cl = C_2H + HCl$ (REC)	1.00E+14	0.00	27700.	[5]
91.	$C_2H_2 + O = CH_2 + CO$ (REC)	7.11E+14	-0.66	1900.	[5]
92.	$C_2H_2 + O = HCCO + H$ (REC)	7.04E+09	0.76	590.	[5]
93.	$C_2H_2 + OH = CH_3 + CO$ (REC)	2.69E+17	-1.44	3810.	[5]
94.	$C_2H_2 + OH = CH_2O + H$ (REC)	1.22E+13	-0.32	2840.	[5]
95.	$C_2H_2 + OH = C_2H + H_2O$ (REC)	3.37E+08	2.00	14000.	[5]

96.	$CH_4 + O_2 = CH_3 + HO_2$	7.94E+13	0.00	55900.	[46]
97.	$CH_4 + O = CH_3 + OH$	1.20E+07	2.10	7620.	[2]
98.	$CH_4 + OH = CH_3 + H_2O$	1.60E+06	2.10	2462.	[2]
99.	$CH_4 + HO_2 = CH_3 + H_2O_2$	1.81E+11	0.00	18580.	[16]
100.	$CH_3 + O_2 = CH_2O + OH$	1.56E+14	0.00	30802.	[2]
101.	$CH_3 + O_2 = CH_2O + O$	2.88E+15	-1.15	30850.	[2]
102.	$CH_3 + O = CH_2O + H$	1.05E+14	0.00	0.	[11]
103.	$CH_3 + OH = CH_2O + H$	3.87E+12	-0.19	13741.	[12]
104.	$CH_3 + HO_2 = CH_3O + OH$	2.00E+13	0.00	0.	[16]
105.	$CH_3O + O_2 = CH_2O + HO_2$	1.00E+13	0.00	7165.	[7]
106.	$CH_2O + CH_3 = CH_4 + CHO$ (WAR)	1.00E+11	0.00	6090.	[7]
107.	$CH_2O + H = CHO + H_2$ (WAR)	2.50E+13	0.00	3990.	[7]
108.	$CH_2O + O = CHO + OH$	3.50E+13	0.00	3510.	[4]
109.	$CH_2O + OH = CHO + H_2O$	3.00E+13	0.00	1190.	[4]
110.	$CH_2O + HO_2 = CHO + H_2O_2$	1.00E+12	0.00	8000.	[13]
111.	$CH_2O + Cl = CHO + HCl$	5.00E+13	0.00	500.	[49]
112.	$CH_2O + M = CHO + H + M$	5.00E+16	0.00	76200.	[7]
113.	$CH_2O + O_2 = CHO + HO_2$ (TRANG)	2.05E+13	0.00	38945.	[16]
114.	$CHO = H + CO$ (WARNATZ)	2.50E+14	0.00	16790.	[7]
115.	$CHO + H = CO + H_2$	2.00E+14	0.00	0.	[4]
116.	$CHO + O_2 = CO + HO_2$	3.00E+12	0.00	0.	[4]
117.	$CO + OH = CO_2 + H$	4.40E+06	1.50	-741.	[15]
118.	$CO + HO_2 = CO_2 + OH$	1.51E+14	0.00	23600.	[13]
119.	$CO + O_2 = CO_2 + O$	2.50E+12	0.00	47800.	[15]
120.	$CO + CH_3O = CO_2 + CH_3$	1.57E+13	0.00	11800.	[16]
121.	$H + O_2 = O + OH$	2.20E+14	0.00	16790.	[46]
122.	$O + H_2 = H + OH$	1.80E+10	1.00	8826.	[46]
123.	$O + H_2O = OH + OH$	1.50E+10	1.14	17240.	[46]
124.	$H + H2O = H2 + OH$	4.60E+08	1.60	18560.	[46]
125.	$H + OH + M = H_2O + M$	7.50E+23	-2.60	0.	[46]
126.	$O_2 + M = O + O + M$	1.20E+14	0.00	107550.	[46]
127.	$H + O + M = OH + M$	2.29E+14	0.00	3900.	[46]
128.	$H + HO_2 = OH + OH$	1.69E+14	0.00	874.	[46]
129.	$H + HO_2 = H_2 + O_2$	2.50E+13	0.00	690.	[46]
130.	$H + HO_2 = O + H_2O$	5.50E+13	0.00	1816.	[46]
131.	$O + HO_2 = OH + O_2$	2.00E+13	0.00	0.	[46]
132.	$OH + HO_2 = H_2O + O_2$	2.00E+13	0.00	0.	[46]
133.	$O + HCl = OH + Cl$	5.24E+12	0.00	6400.	[46]
134.	$OH + HCl = Cl + H_2O$	2.45E+12	0.00	1100.	[46]
135.	$H + H + M = H_2 + M$	6.40E+17	-1.00	0.	[46]
136.	$Cl + Cl + M = Cl_2 + M$	1.25E+15	0.00	-1630.	[46]
137.	$H + Cl + M = HCl + M$	1.00E+17	0.00	0.	[46]
138.	$H + HCl = H_2 + Cl$	2.30E+13	0.00	3500.	[46]
139.	$Cl + HO_2 = O_2 + HCl$	3.00E+13	0.00	0.	[46]
140.	$Cl + HO_2 = ClO + OH$	2.42E+13	0.00	950.	[46]
141.	$ClO + CO = Cl + CO_2$	6.03E+11	0.00	17400.	[46]
142.	$CHClO + H = CHO + HCl$	8.33E+13	0.00	7400.	[46]
143.	$CHClO + H = CH_2O + Cl$	6.99E+14	-0.58	6360.	[46]
144.	$CH_3 + ClO = CH_3O + Cl$	3.33E+11	0.46	30.	[46]
145.	$CH_3 + ClO = CH_2O + HCl$	3.47E+18	-1.90	2070.	[46]

146.	$CH_2Cl_2 + O_2 = CHCl_2 + HO_2$	1.35E+13	0.00	51800.	[46]
147.	$CH_2Cl_2 + HO_2 = CHCl_2 + H_2O_2$	6.67E+12	0.00	18270.	[46]
148.	$CH_2Cl_2 + OH = CHCl_2 + H_2O$	4.23E+12	0.00	2269.	[46]
149.	$CH_2Cl_2 + O = CHCl_2 + OH$	1.10E+13	0.00	6500.	[46]
150.	$CH_2Cl + O_2 = CH_2O + ClO$	1.91E+14	-1.27	3810.	[46]
151.	$CH_2Cl + O_2 = CHClO + OH$	4.00E+13	0.00	34000.	[46]
152.	$CH_2Cl + O = CH_2ClO$ (QRRK)	1.29E+15	-1.98	1100.	QRRK
153.	$CH_2Cl + O = CH_2O + Cl$ (QRRK)	5.59E+13	-0.13	710.	QRRK
154.	$CH_2Cl + OH = CH_2O + HCl$ (QRRK)	1.24E+22	-2.72	3860.	QRRK
155.	$CH_2Cl + OH = CH_2O + Cl$ (QRRK)	2.00E+12	0.29	3270.	QRRK
156.	$CH_2Cl + HO_2 = CH_2ClO + OH$	1.33E+13	0.00	0.	[2]
157.	$CH_2ClO = CHClO + H$	1.83E+27	-5.13	21170.	[2]
158.	$CH_2ClO = CH_2O + Cl$	4.53E+31	-6.41	22560.	[2]
159.	$CHClO = CHO + Cl$	8.86E+29	-5.15	92920.	[2]
160.	$CHClO = CO + HCl$	1.10E+30	-5.19	92960.	[2]
161.	$CH_2Cl + ClO = CH_2ClO + Cl$	4.15E+12	0.70	1110.	[2]
162.	$CH_2Cl + ClO = CHClO + HCl$	4.13E+19	-2.22	2360.	[2]
163.	$CH_2Cl + CH_2O = CH_3Cl + CHO$	2.00E+11	0.00	6000.	[2]
164.	$CH_3Cl + O_2 = CH_2Cl + HO_2$	2.02E+13	0.00	54000.	[46]
165.	$CH_3Cl + O = CH_2Cl + OH$	1.70E+13	0.00	7300.	[3]
166.	$CH_3Cl + OH = CH_2Cl + H_2O$	2.45E+12	0.00	2700.	[3]
167.	$CH_3Cl + HO_2 = CH_2Cl + H_2O_2$	1.00E+13	0.00	21660.	[18]
168.	$H_2O_2 + Cl = HCl + HO_2$	1.02E+12	0.00	800.	[3]
169.	$ClO + CH_4 = CH_3 + HOCl$ (NIST)	6.03E+11	0.00	15000.	[49]
170.	$ClO + CH_3Cl = CH_2Cl + HOCl$	3.03E+11	0.00	10700.	[49]
171.	$OH + HOCl = H_2O + ClO$ (DEMO)	1.81E+12	0.00	990.	[49]
172.	$H + HOCl = HCl + OH$ (DEM)	3.01E+12	0.00	0.	[49]
173.	$Cl + HOCl = Cl_2 + OH$ (DEM)	1.81E+12	0.00	260.	[49]
174.	$Cl + HOCl = HCl + ClO$	7.62E+12	0.00	180.	[49]
175.	$O + HOCl = OH + ClO$ (DEM)	6.03E+12	0.00	4370.	[49]
176.	$Cl + OH = HOCl$	1.69E+18	-3.01	1790.	[46]
177.	$Cl + OH = H + ClO$	1.73E+12	-0.10	38050.	[46]
178.	$O + Cl_2 = Cl + ClO$ (BAU)	2.51E+12	0.00	2720.	[17]
179.	$H + Cl_2 = HCl + Cl$ (BAU)	8.59E+13	0.00	1170.	[17]
180.	$C_2H_6 + O_2 = C_2H_5 + HO_2$	7.94E+13	0.00	55900.	[46]
181.	$C_2H + O_2 = CO + CHO$	2.41E+12	0.00	0.	[16]
182.	$C_2H + O = CH + CO$	1.00E+13	0.00	0.	[7]
183.	$C_2H + OH = CH_2 + CO$	1.81E+13	0.00	0.	[16]
184.	$C_2H + C_2H_4 = C\#CC\#C + H$	1.21E+13	0.00	0.	[16]
185.	$C_2H + C_2H_3 = C\#CC\#C$	1.21E+14	0.00	0.	[23]
186.	$C_2H + C_2H_6 = C_2H_5 + C_2H_2$	3.61E+12	0.00	0.	[16]
187.	$HCCO + O_2 = CO + CO + OH$	1.60E+12	0.00	854.	[48]
188.	$HCCO + O = CO + CO + H$	1.00E+14	0.00	0.	[34]
189.	$HCCO + H = CH_2S + CO$	1.50E+14	0.00	0.	[34]
190.	$HCCO + M = CH + CO + M$	6.00E+15	0.00	29600.	[34]
191.	$CH + O = CO + H$	1.50E+14	0.00	0.	[34]
192.	$C_2H_2 + O_2 = C_2H + HO_2$	1.21E+13	0.00	74520.	[16]
193.	$C_2H_2 + HO_2 = CH_2CO + OH$	6.03E+09	0.00	7949.	[16]
194.	$CH_2CO + OH = HCCO + H_2O$	7.50E+12	0.00	2000.	[48]
195.	$CH_2CO + H = CH_3 + CO$	1.13E+13	0.00	3428.	[35]

196.	$CH_2CO + O = HCCO + OH$	1.00E+13	0.00	8000.	[43]
197.	$C_2H_3 + H = C_2H_2 + H_2$ (REC)	9.64E+13	0.00	0.	[5]
198.	$C_2H_3 + O = CH_2CO + H$	9.64E+13	0.00	0.	[16]
199.	$C_2H_3 + CH_3O = CH_2O + C_2H_4$	2.42E+13	0.00	0.	[16]
200.	$C_2H_3 + CH_2O = C_2H_4 + CHO$	5.43E+03	2.81	5862.	[16]
201.	$C_2H_3 + H_2O_2 = C_2H_4 + HO_2$	1.21E+10	0.00	-596.	[16]
202.	$C*CC*C. + C_2H_3 = C_6H_6 + H_2$	1.84E-13	7.07	-3610.	[40]
203.	$C_2H_3 + C_2H_3 = C*CC*C$	1.00E+12	0.00	0.	[20]
204.	$C*CC*C + H = C*CC*C. + H_2$	6.30E+10	0.70	5990.	[19]
205.	$C*CC*C + CH_3 = C*CC*C. + CH_4$	7.00E+13	0.00	18501.	[36]
206.	$C_2H_3 + C_2H_2 = C*CC*C.$	2.88E+12	0.00	45800.	[20]
207.	$C_2H_3 + C_2H_2 = C\#CC*C + H$	1.58E+13	0.00	25096.	[21]
208.	$C_2H_2 + C_2H_2 = C\#CC*C$	1.83E+13	0.00	39540.	[52]
209.	$C_2H_2 + C_2H_2 = C\#CC*C. + H$	1.00E+12	0.00	66000.	[20]
210.	$C\#CC*C + C_2H_2 = C_6H_6$	4.47E+11	0.00	30092.	[22]
211.	$C\#CC*C + Cl = C\#CC*C. + HCl$	1.00E+16	0.00	1000.	[50]
212.	$C\#CC*C + C_2H = C\#CC*C. + C_2H_2$	3.98E+13	0.00	0.	[21]
213.	$C\#CC*C. + C_2H_3 = C_6H_6$	2.87E+14	0.00	817.	[23]
214.	$C_2H + C_2H_2 = C\#CC*C.$	1.00E+13	0.00	0.	[23]
215.	$CH_2 + C_2H_2 = C\#CC. + H$	2.70E+12	0.00	0.	[37]
216.	$CH_3 + C_2H_2 = C\#CC + H$	6.19E+12	0.00	16999.	[38]
217.	$CH_3 + C_2H_2 = CC*C.$	1.61E+40	-8.58	20331.	[24]
218.	$CH_3 + C_2H_2 = C*C*C + H$	6.74E+19	-2.03	31593.	[24]
219.	$CH_3 + C\#CC. = C\#CCC$	5.00E+12	0.00	0.	[39]
220.	$CH_3 + C_2H_2 = C*CC.$	6.03E+11	0.00	7704.	[16]
221.	$C\#CC = C*C*C$	2.10E+11	0.00	60002.	[38]
222.	$C*CC. + C_2H_5 = C*CC + C_2H_5$	7.24E+11	0.00	16396.	[51]
223.	$C*CC. = C*C*C + H$	2.63E+13	0.00	59791.	[53]
224.	$C*C*C + C*C*C. = C_6H_5 + H$	2.20E+11	0.00	1999.	[39]
225.	$C*C*C. + C*C*C. = C_6H_6$	3.00E+11	0.00	0.	[39]
226.	$C_2H_2 + C\#CC*C. = C_5H_5$	7.01E+14	-0.86	6371.	[40]
227.	$C_6H_5 + H = C_6H_6$	3.16E+13	0.00	0.	[41]
228.	$C_6H_6 + H = C_6H_5 + H_2$	3.01E+12	0.00	8100.	[25]
229.	$C_6H_5 + O = C_5H_5 + OH$	2.90E+13	0.00	4250.	[26]
230.	$C_6H_6 + OH = C_6H_5 + H_2O$	1.45E+13	0.00	4490.	[27]
231.	$C_6H_6 + OH = C_6H_5OH + H$	1.31E+13	0.00	10600.	[27]
232.	$C_6H_6 + Cl = C_6H_5Cl + H$	3.60E+12	0.00	30990.	[29]
233.	$C_6H_6 + CH_3 = C_6H_5CH_3 + H$	1.20E+12	0.00	15940.	[30]
234.	$CH_4 + CH_3 = C_2H_5 + H_2$	1.00E+13	0.00	23000.	[31]
235.	$C_2H_3 + CH_4 = C_2H_4 + CH_3$	1.44	4.02	5473.	[16]
236.	$C_2H + CH_4 = C_2H_2 + CH_3$	1.80E+12	0.00	497.	[16]
237.	$CH_2 + CH_4 = CH_3 + CH_3$	4.30E+12	0.00	10039.	[32]
238.	$CH_2S + CH_4 = CH_3 + CH_3$	4.00E+13	0.00	0.	[16]
239.	$CH_2S + C_2H_6 = C_2H_5 + CH_3$	1.20E+14	0.00	0.	[16]
240.	$CH_2S + O_2 = CO + OH + H$	3.00E+13	0.00	0.	[16]
241.	$CH_2S + O = CO + H + H$	1.51E+13	0.00	0.	[16]
242.	$CH_2S + OH = CH_2O + H$	3.01E+13	0.00	0.	[16]
243.	$CH_2S + H_2O_2 = CH_2O + OH$	3.01E+13	0.00	0.	[16]
244.	$CH_2S + CH_3 = C_2H_4 + H$	1.81E+13	0.00	0.	[16]
245.	$CH_2S + C_2H = C_2H_2 + CH$	1.81E+13	0.00	0.	[16]

246.	$CH_2S + CH_3O = CH_3 + CH_2O$	1.81E+13	0.00	0.	[16]
247.	$CH_2S + H_2 = CH_3 + H$	7.00E+13	0.00	0.	[16]
248.	$CH_2S + H = CH_2 + H$	2.00E+14	0.00	0.	[16]
249.	$CH_2S + M = CH_2 + M$	2.00E+12	0.00	0.	[16]
250.	$C_2H_6 + HO_2 = H_2O_2 + C_2H_5$	6.00E+12	0.00	19407.	[7]
251.	$C_2H_3 + CHO = C_2H_4 + CO$	9.04E+13	0.00	0.	[16]
252.	$C_2H_6 + C_2H_3 = C_2H_5 + C_2H_4$	1.50E+13	0.00	10000.	[42]
253.	$C_2H_3 + Cl_2 = C_2H_2Cl + Cl$ (TIM)	5.25E+12	0.00	-480.	[43]
254.	$CH_3 + CH_3 = C_2H_4 + H_2$ (WAR)	1.00E+16	0.00	32028.	[7]
255.	$CH_3 + CH_4 = C_2H_6 + H$ (TAB)	8.00E+13	0.00	40000.	[31]
256.	$CH_3 + OH = CH_2O + H_2$ (DEAN)	3.19E+12	-0.53	10810.	[24]
257.	$CH_3 + CO = CH_3CO$ (TSA)	1.44E+38	-7.56	10910.	[16]
258.	$CH_3 + CH_2 = C_2H_4 + H$ (TSA)	4.22E+13	0.00	0.	[16]
259.	$CH_3 = CH_2 + H$ (TSA)	1.00E+16	0.00	90580.	[16]
260.	$CH_3 + CHO = CH_4 + CO$ (TSA)	1.21E+14	0.00	0.	[16]
261.	$CH_2CHO = CH_2CO + H$	1.58E+13	0.00	47501.	[16]
262.	$CH_2CHO = CH_3CO$	1.00E+13	0.00	47001.	[44]
263.	$CH_2CHO + CH_3CHO = CH_3CHO + CH_2CO$	2.51E+07	0.00	0.	[45]

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3.4. Kinetic Mechanism and modeling

The reaction mechanism for the oxidation and pyrolysis of $CH_3Cl/H_2/O_2/Ar$ has been published [18]. This study is trying to develop and improve this chemical kinetic mechanism to model the results of thermal reaction system $CH_3Cl/CH_4/O_2/Ar$ (see page 86, Table 4). Thermochemical parameter for some C_2 Oxy-Carbon intermediates that have not been previously measured or calculated are also developed because these are important to the chemical kinetic rate constant evaluation.

The kinetic reaction mechanism used in this study (Table 4) includes 263 elementary reaction steps involving 76 radical and stable compounds. Important unimolecular reactions, addition and recombination reactions are analyzed by the DISSO and CHEMACT computer codes [16]. The rate constants for theimportant C_2 species abstraction reactions are evaluated.

A comparison of calculated and experimental data on CH_3Cl decay, important intermediate, and final product versus reaction times at 1173K and versus temperatures between 1098K-1223k at 1.0 sec are shown in Figures 145-160 respectively. For $CH_3Cl/H_2/O_2/Ar$ systems, the agreement between the model and experiment is quite good. The model slightly underpredicts the C_2H_2 concentration prior to 0.4 sec for the ratio $Ar:CH_3Cl:H_2:O_2$=97:1:1:1 (I) and prior to 0.8 sec for $Ar:CH_3Cl:H_2:O_2$=96:2::1:1 (II) and

somewhat overpredicts it after 0.4 sec for (I) and after 0.8 sec for (II) at 1173K (Figure 147, 148 and 155, 156). The model initially predicts higher conversion of CH_3Cl and higher yield of CO and HCl than those observed at 1098K-1148K. But at 1173K and above, the model has good fits to experiments of these three species for (I) and (II) (Figure 149, 150 and 153, 154). For CO_2 yield, model has underprediction. Figures 161-176 illustrate the fit of the model (Table 4) to data of experiment for $CH_3Cl/CH_4/O_2/Ar$ reaction. The comparison between model and experiment on CH_3Cl decay, CH_4, CO, HCl, and C_2H_3Cl formation with reaction time at 1173K or with reaction temperature at 1.0 sec is reasonably good over the general trend (Figures 161 to 176). The model underpredicts conversion of CH_3Cl and formation of CO, HCl, C_2H_2, and C_2H_4 for $Ar:CH_3Cl:CH_4:O_2=96:1:1:2$ (III) and $Ar:CH_3Cl:CH_4:O_2=95:2:1:2$ (IV) and overpredicts the production of CO2 for system (III) after 1.6 sec and for system (IV) after 1.8 sec at 1173K. Model prediction for CH4 and C2H3Cl formation is better for (III) than (IV) at 1173K. Experimental data are compared also with model prediction for CH_3Cl decay and other product distribution between 1173-1223K at 1.0 sec. Results show that the general reaction trend for CH_3Cl decay and the formation of CH_4, CO, CO_2, HCl, C_2H_2, C_2H_4, and C_2H_3Cl is agreement between modeling and observed data. However, the model underpre-

dicts the CH_3Cl decay and formation of CO, HCl, C_2H_2, and C_2H_4 and overpredicts the formation of CO_2 for systems (III and IV); the model prediction for CH4 is also better for system (III) than for (IV).

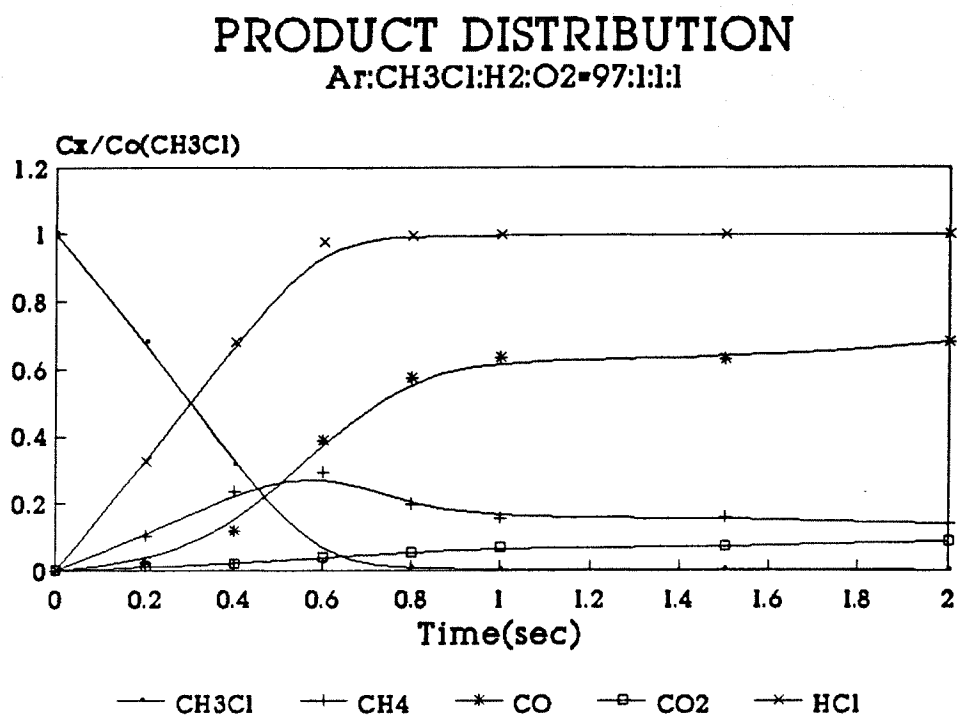


Fig. 145 1173K "10.5" Tube

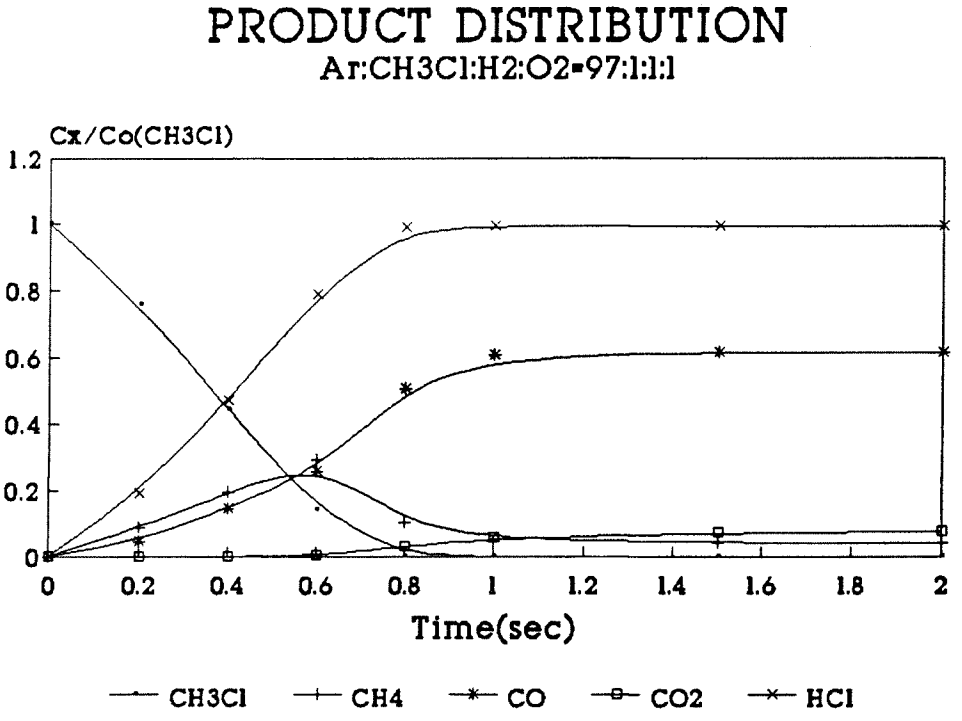


Fig. 146 1173K (M)

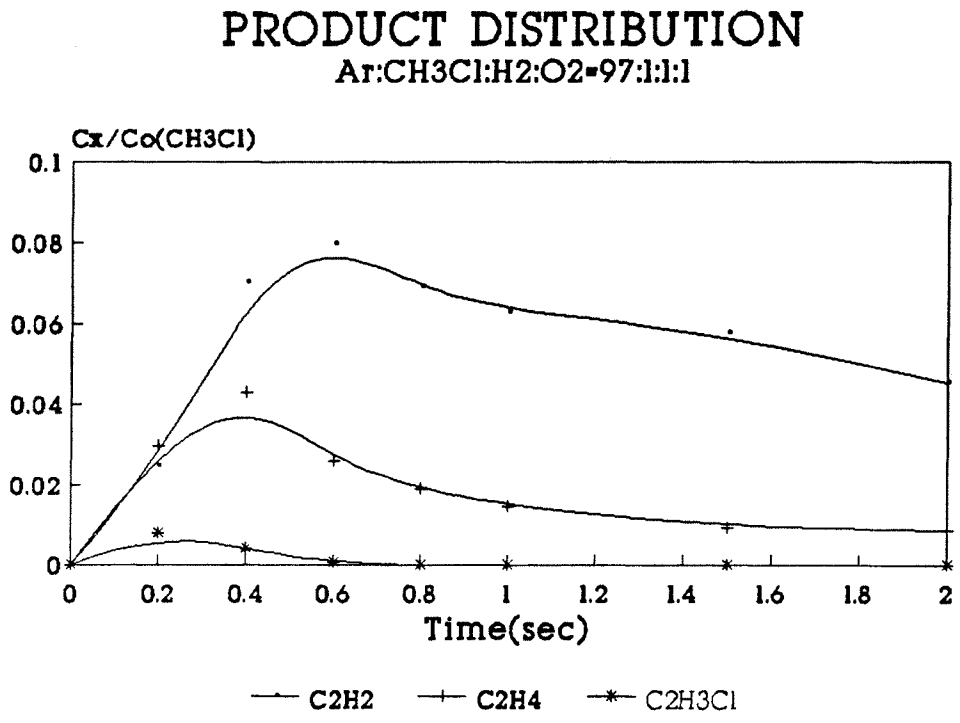


Fig. 147 1173K "10.5" Tube

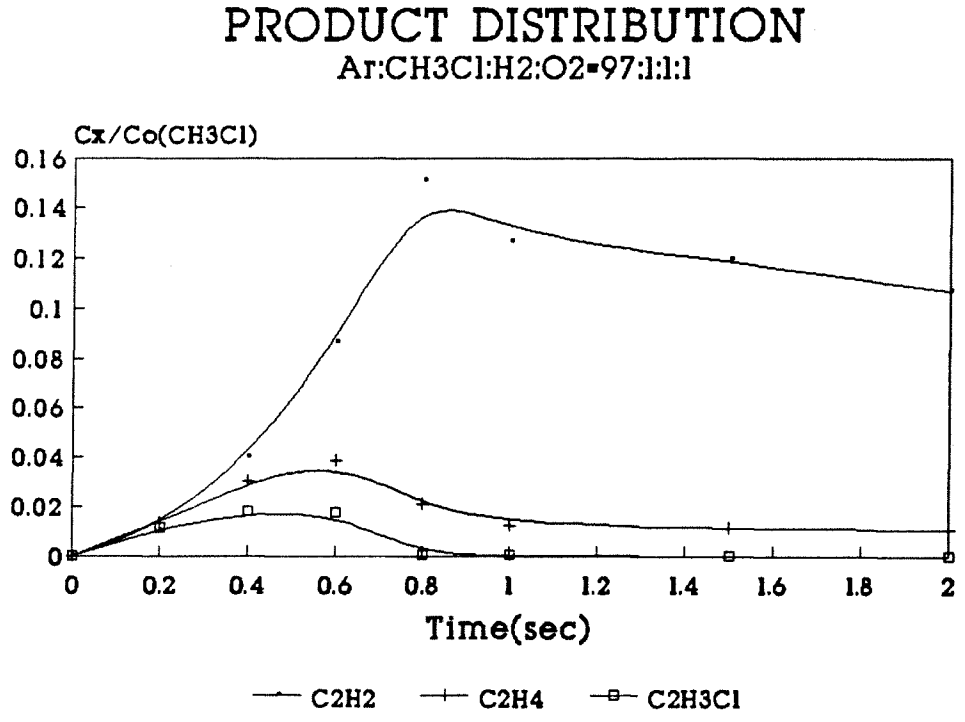


Fig. 148 1173K (M)

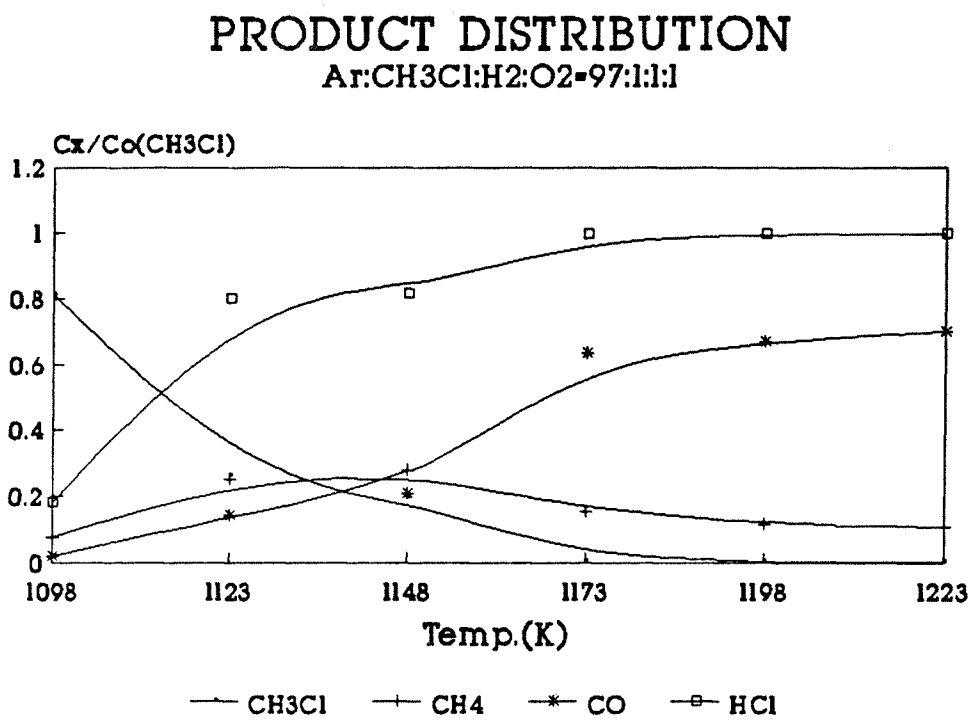
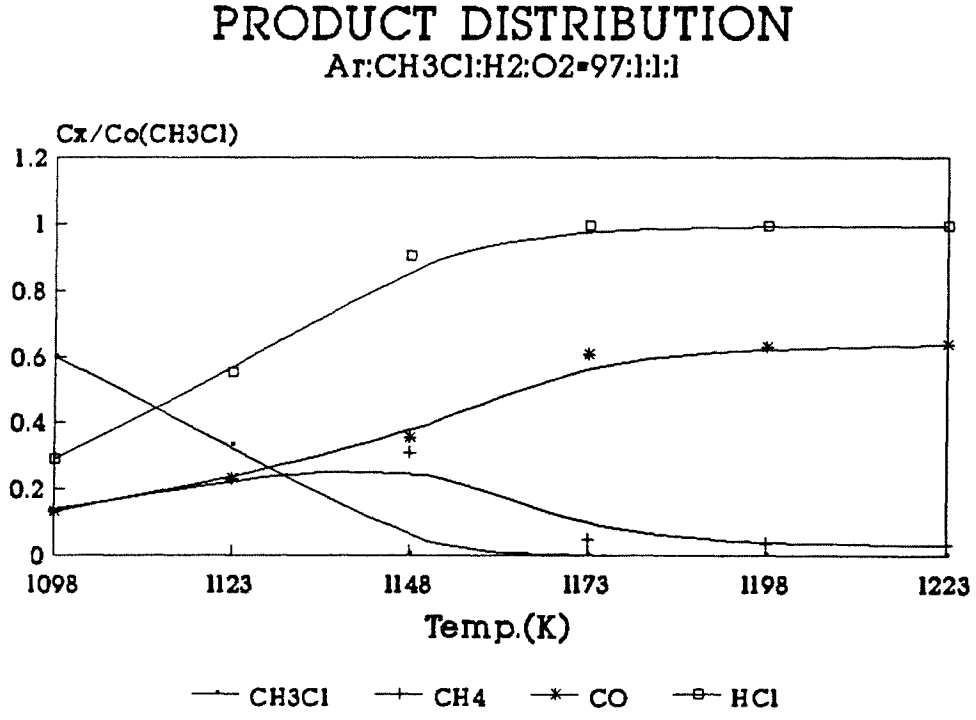


Fig. 149 1.0 sec "10.5" Tube



F150. 1.0 s 1098-1223K (M)

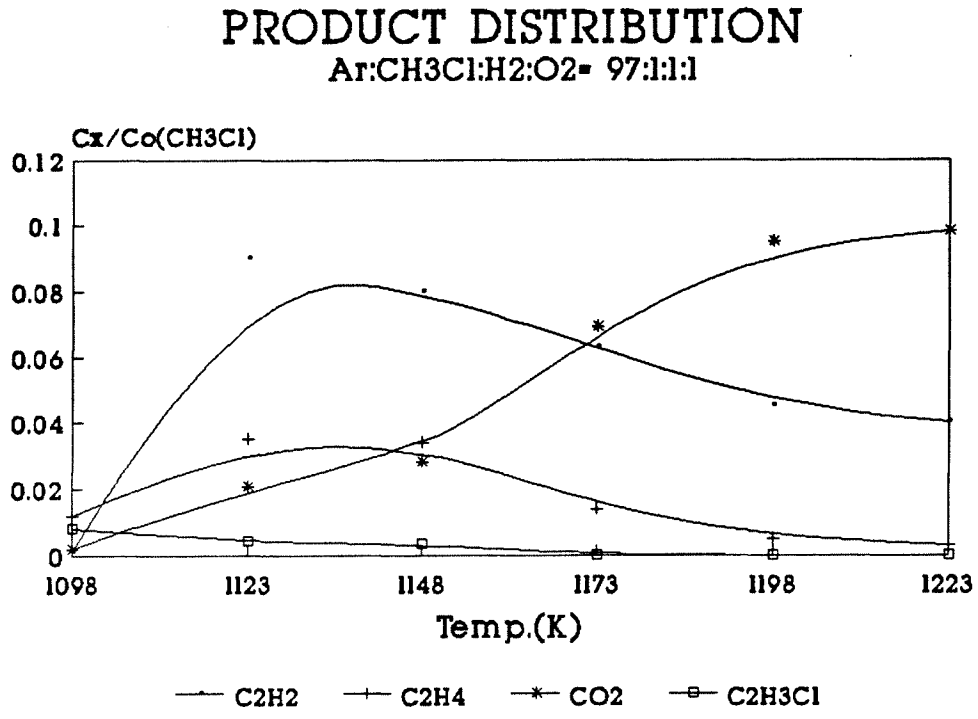
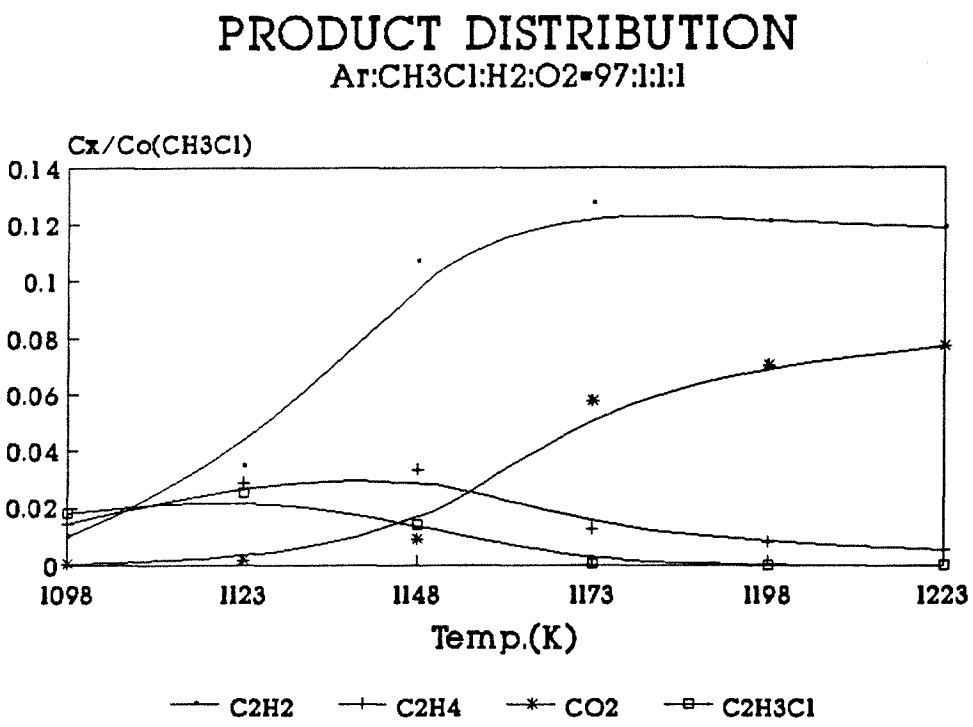


Fig. 151 1.0 sec "10.5" Tube



F152. 1.0 s 1098-1123K (M)

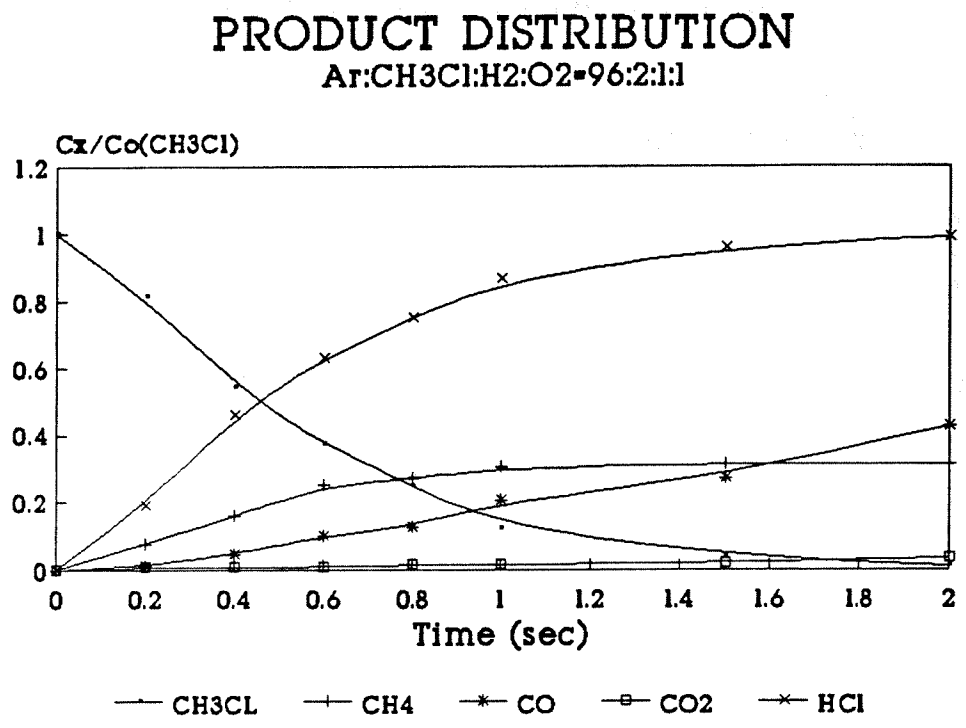


Fig. 153 1173K "10.5" Tube

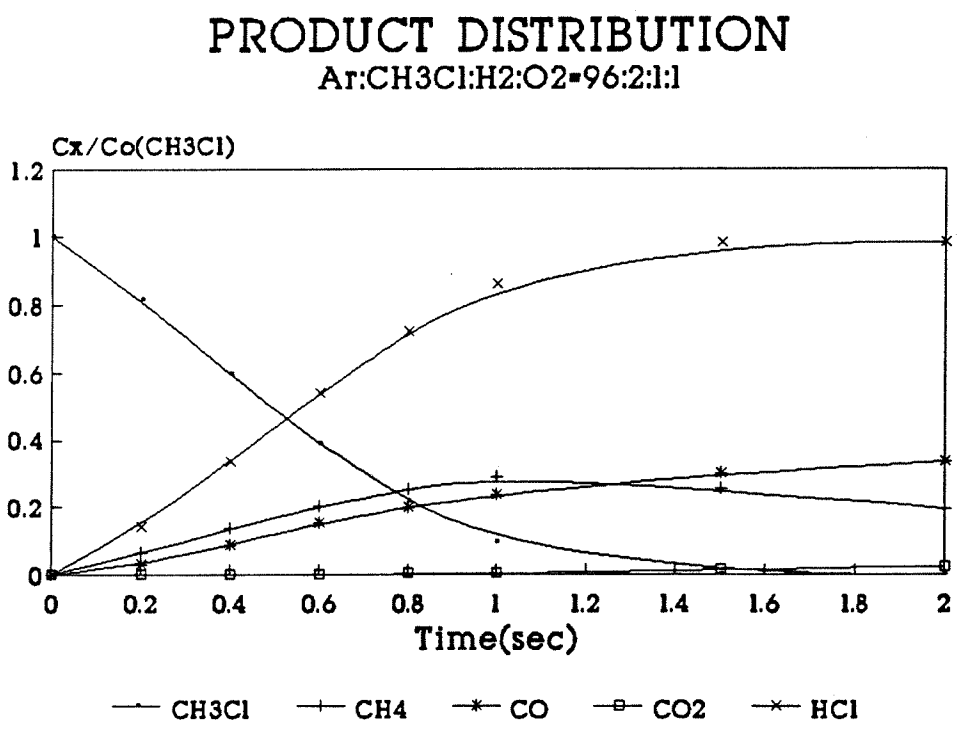


Fig. 154 1173K (M)

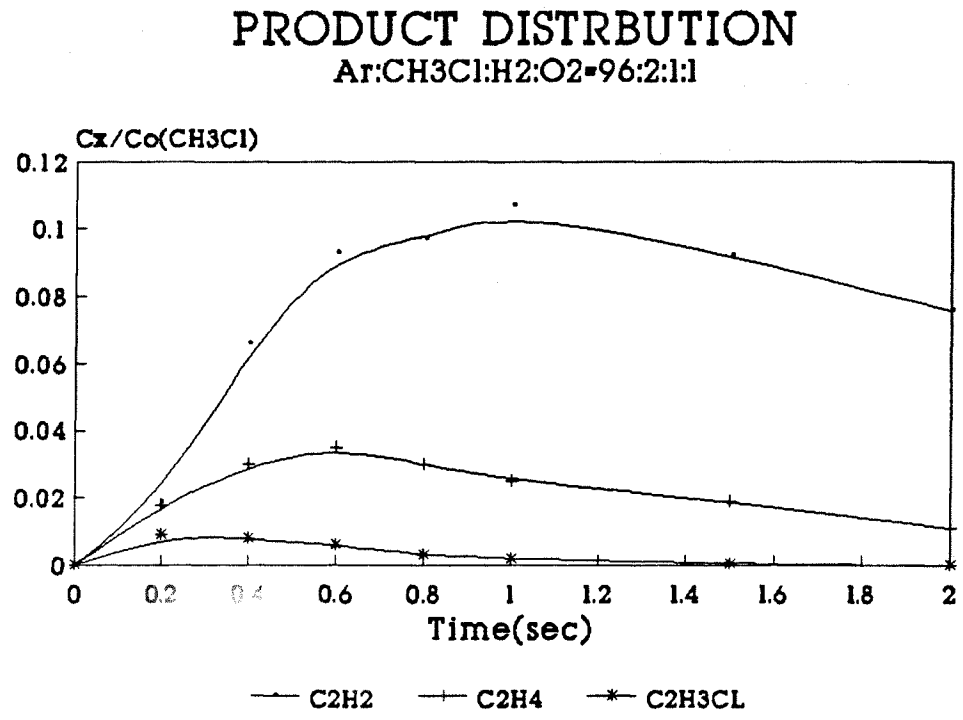


Fig. 155 1173K "10.5" Tube

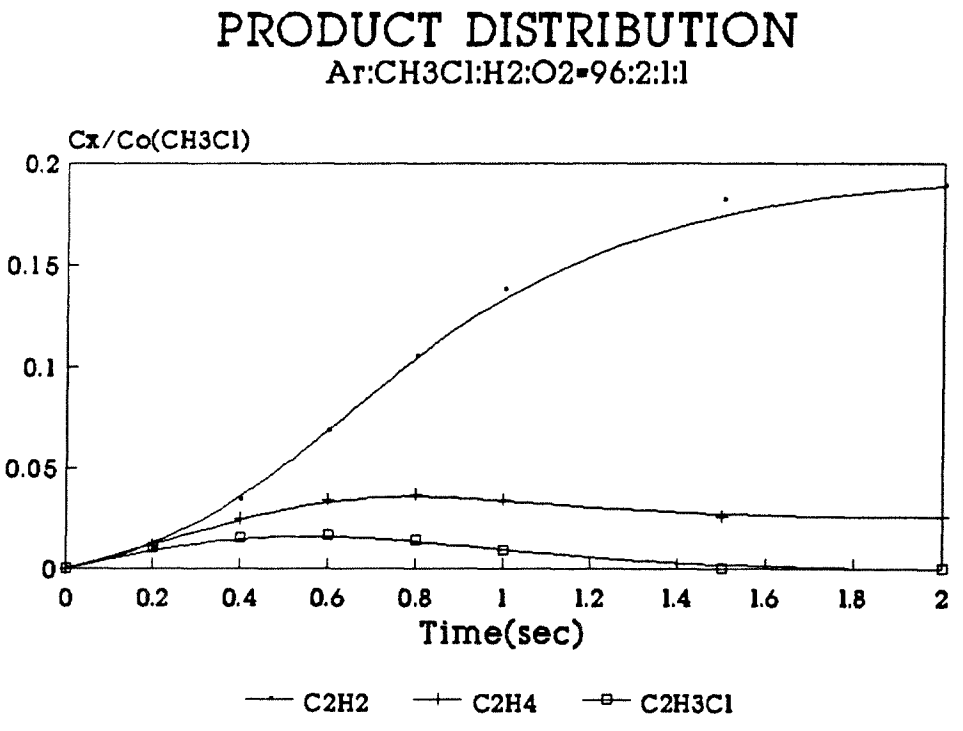


Fig. 156 900C (M)

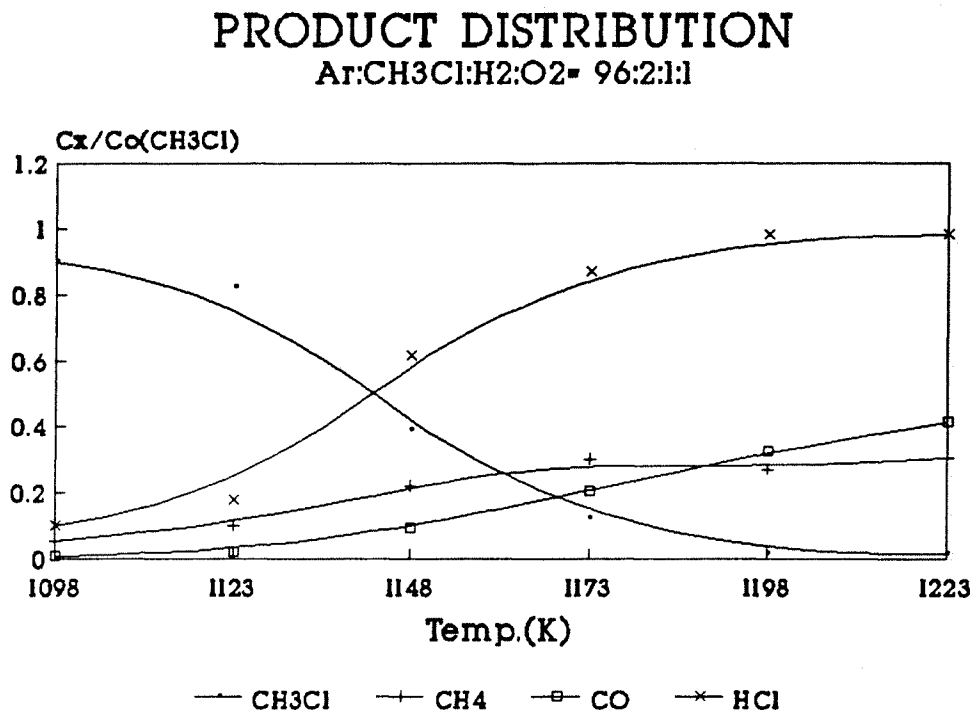


Fig. 157 1.0 sec "10.5" Tube

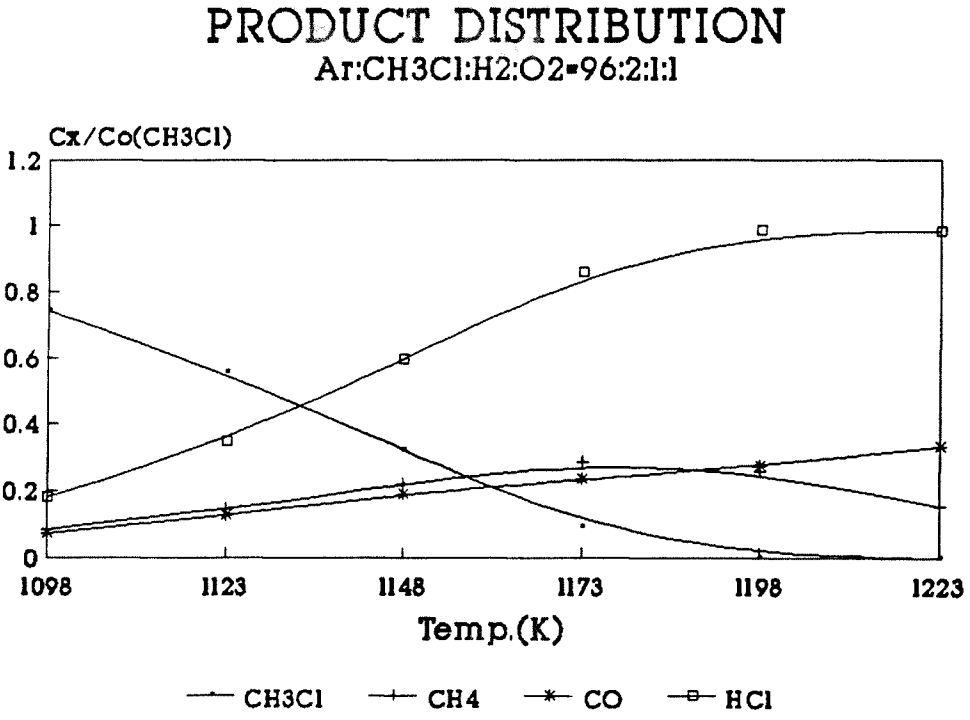


Fig. 158 1.0 s 1098-1223K (M)

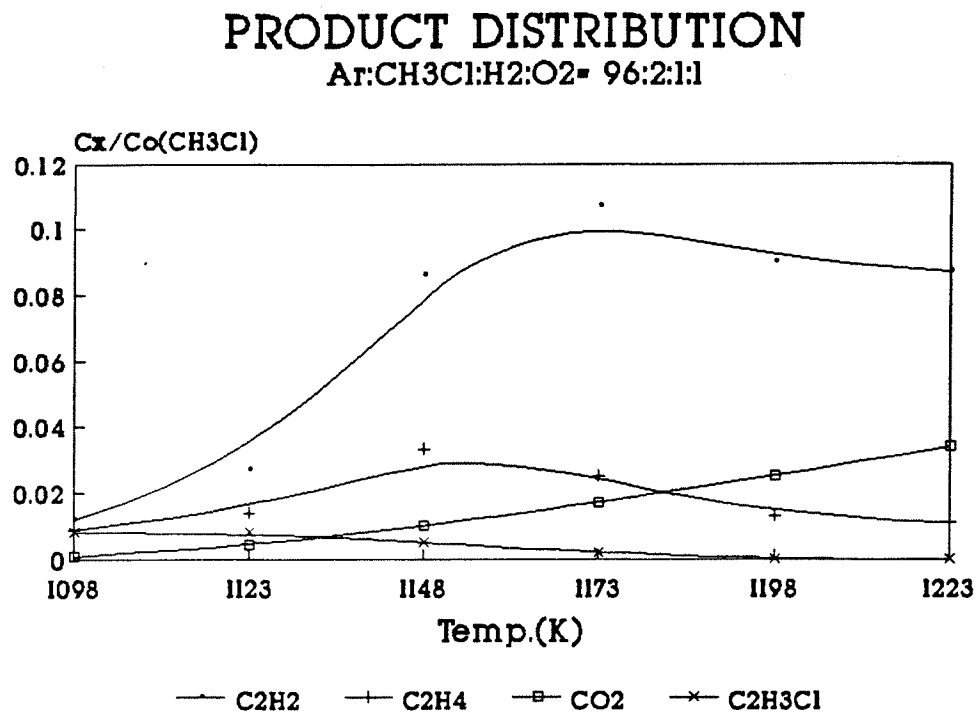


Fig. 159 1.0 sec "10.5" Tube

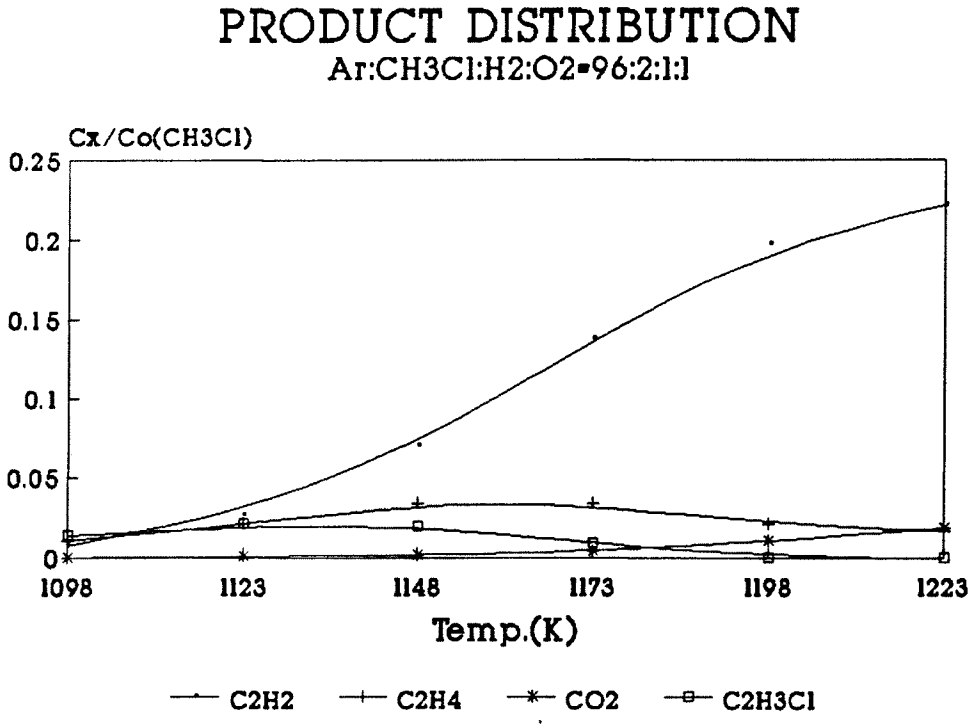


Fig. 160 1.0 s 1098-1123K (M)

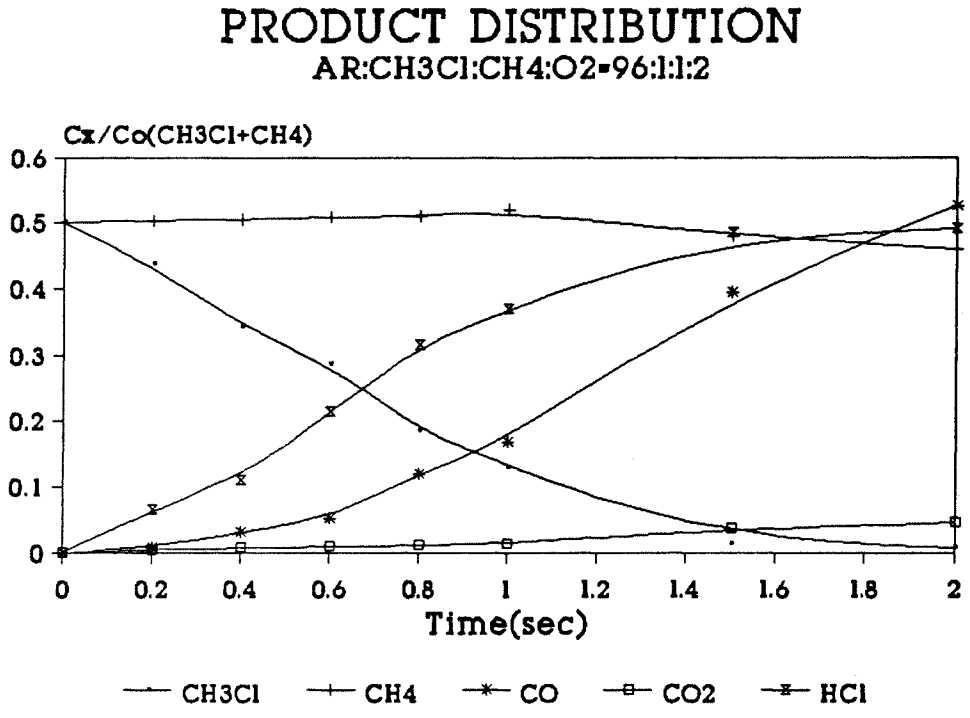


Fig. 161 1173K "10.5" Tube

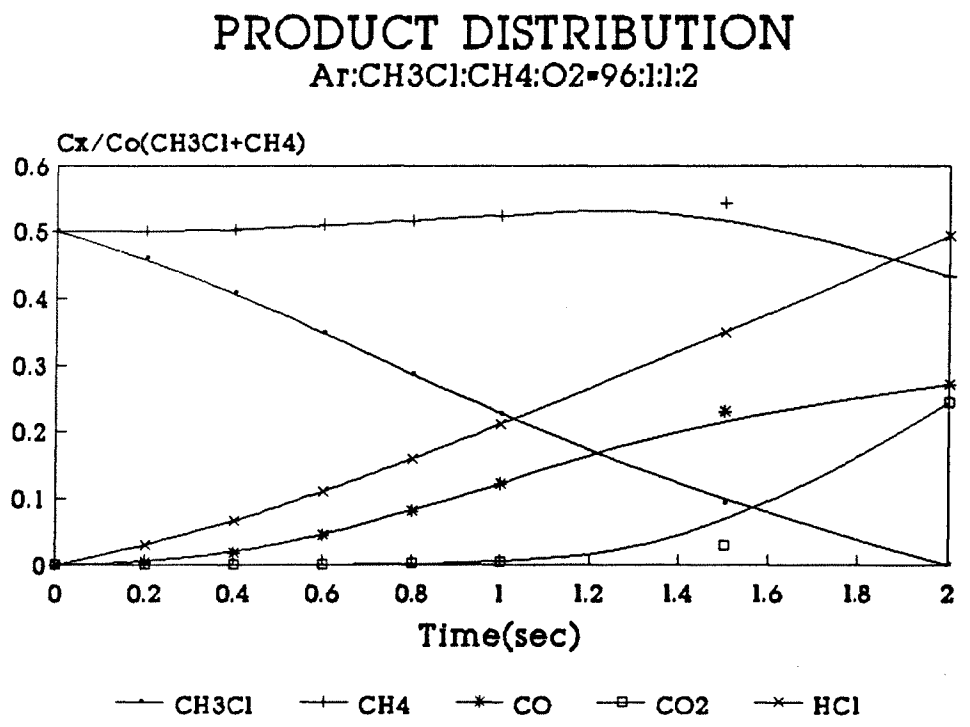


Fig.162 1173K (M)

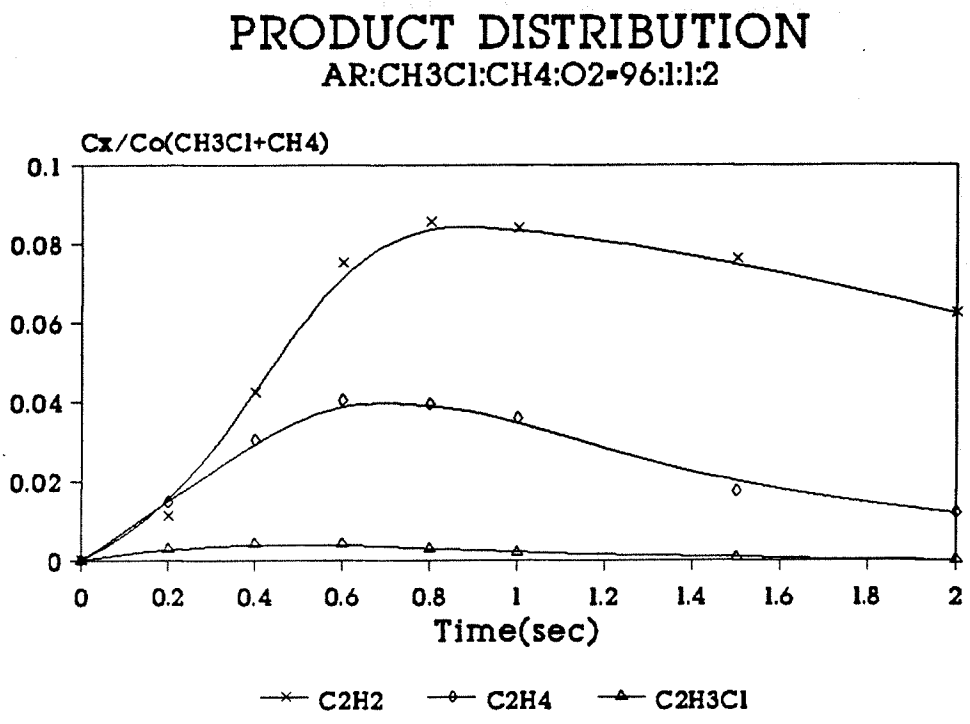


Fig. 163 1173K "10.5" Tube

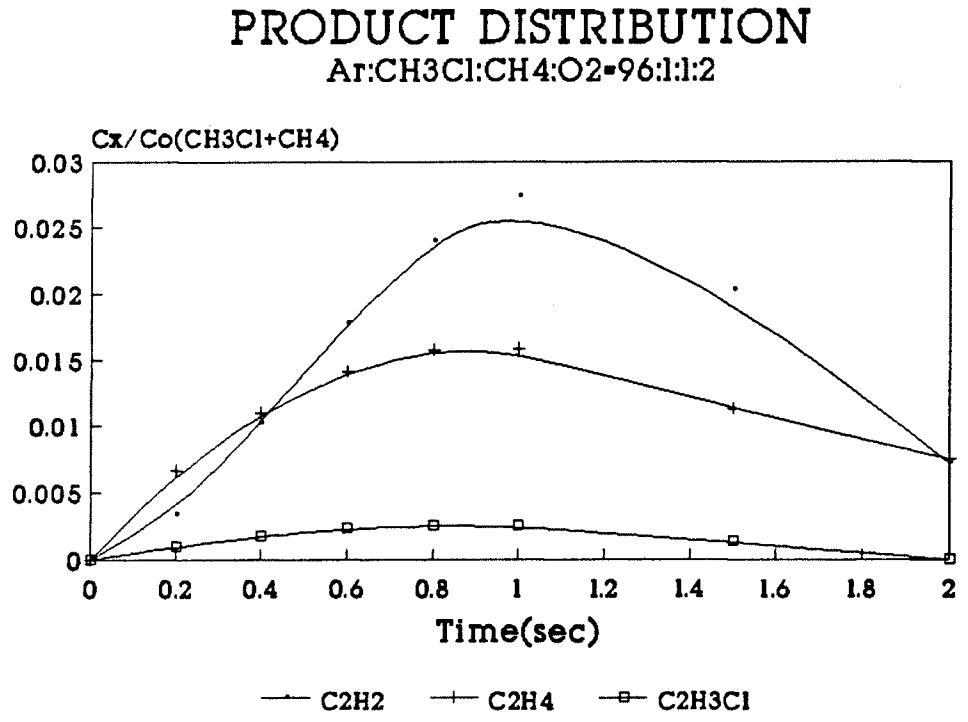


Fig.164 1173K (M)

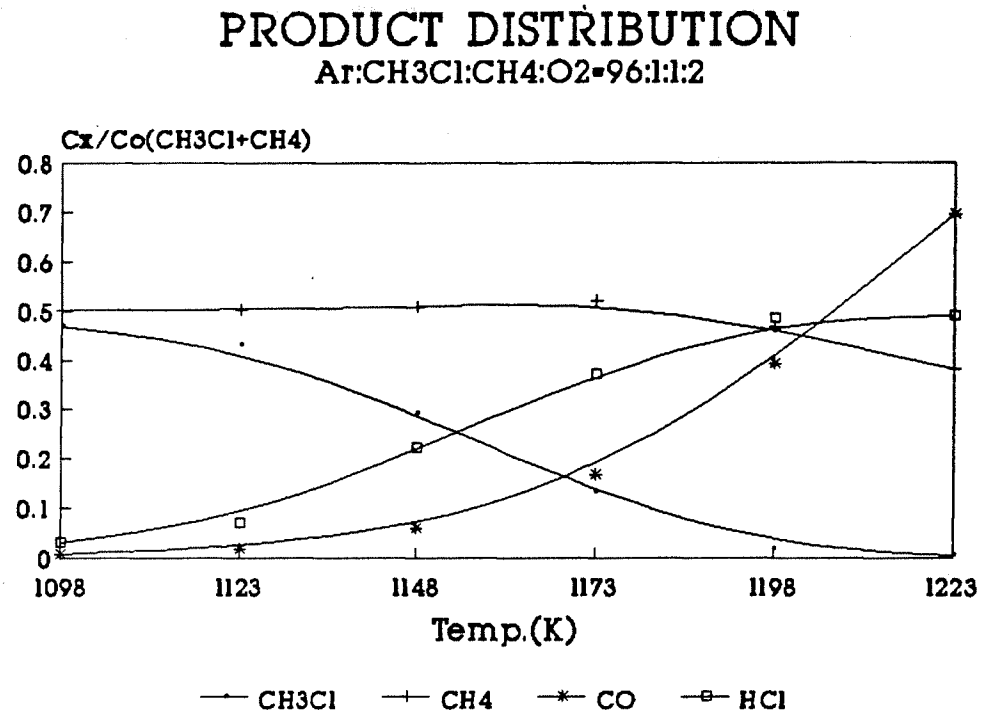


Fig. 165 1.0 sec "10.5" Tube

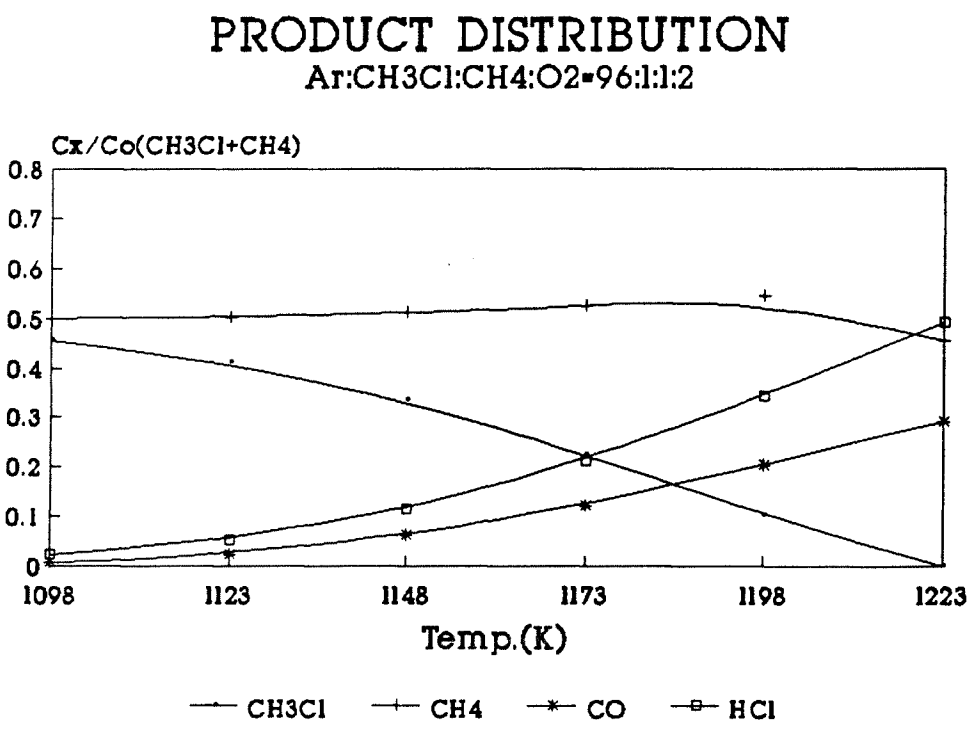


Fig.166 1.0 s 1098-1223K (M)

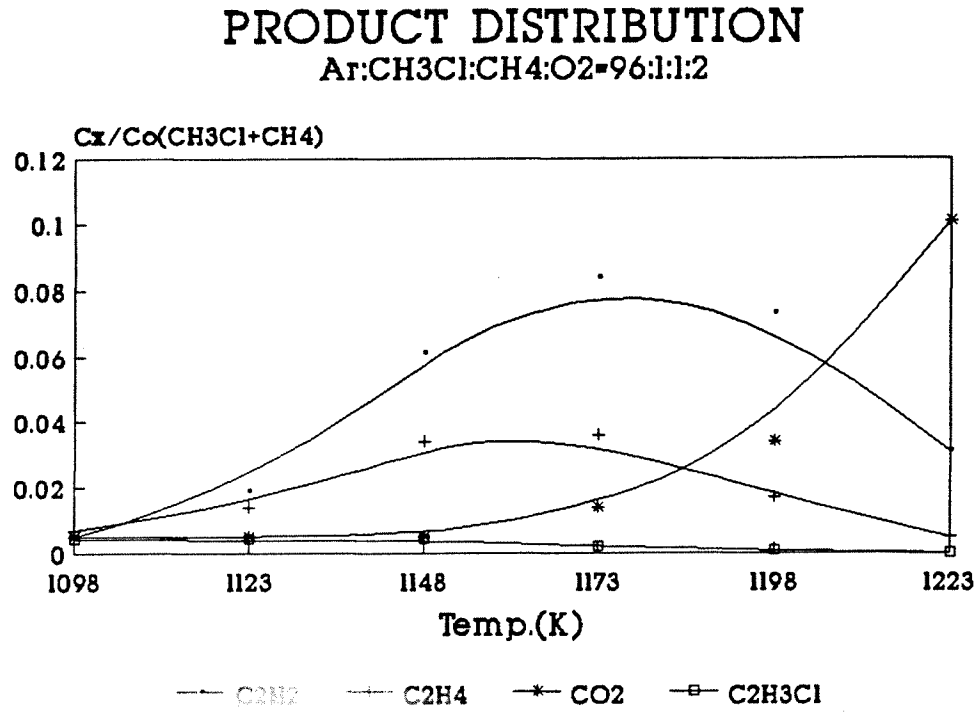


Fig. 167 1.0 sec "10.5" Tube

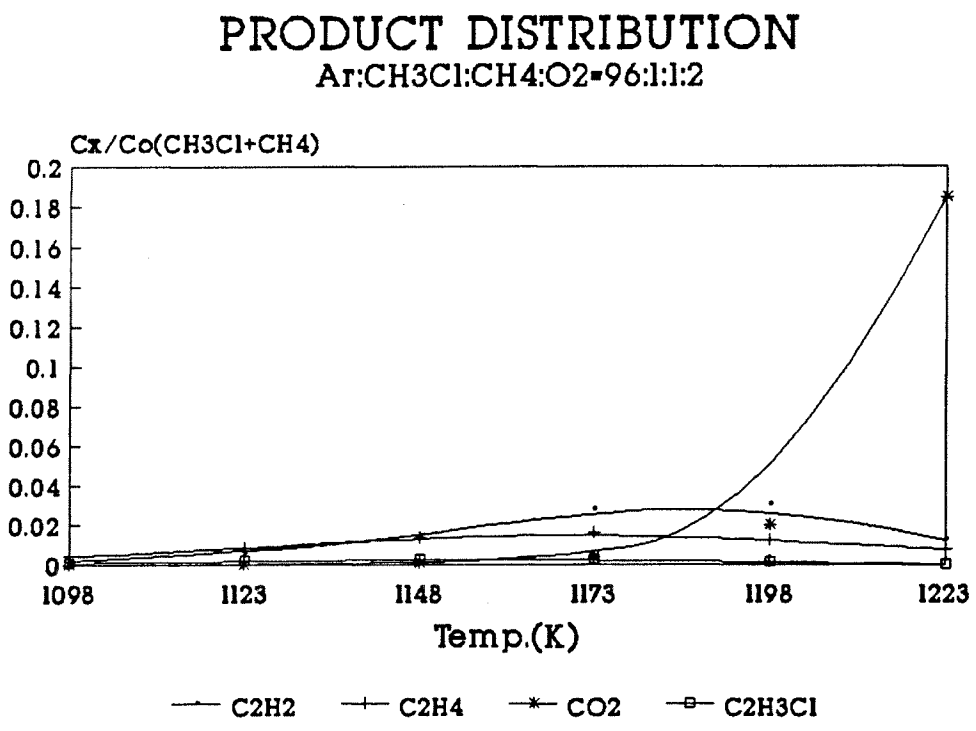


Fig.168 1.0 s 1098-1223K (M)

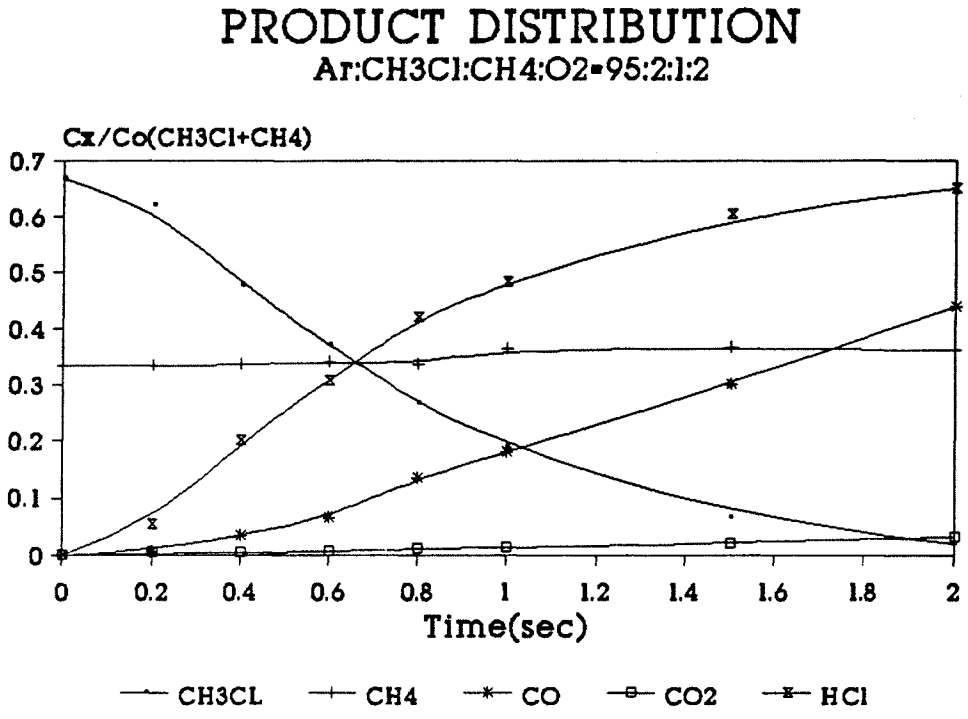


Fig. 169 1173K "10.5" Tube

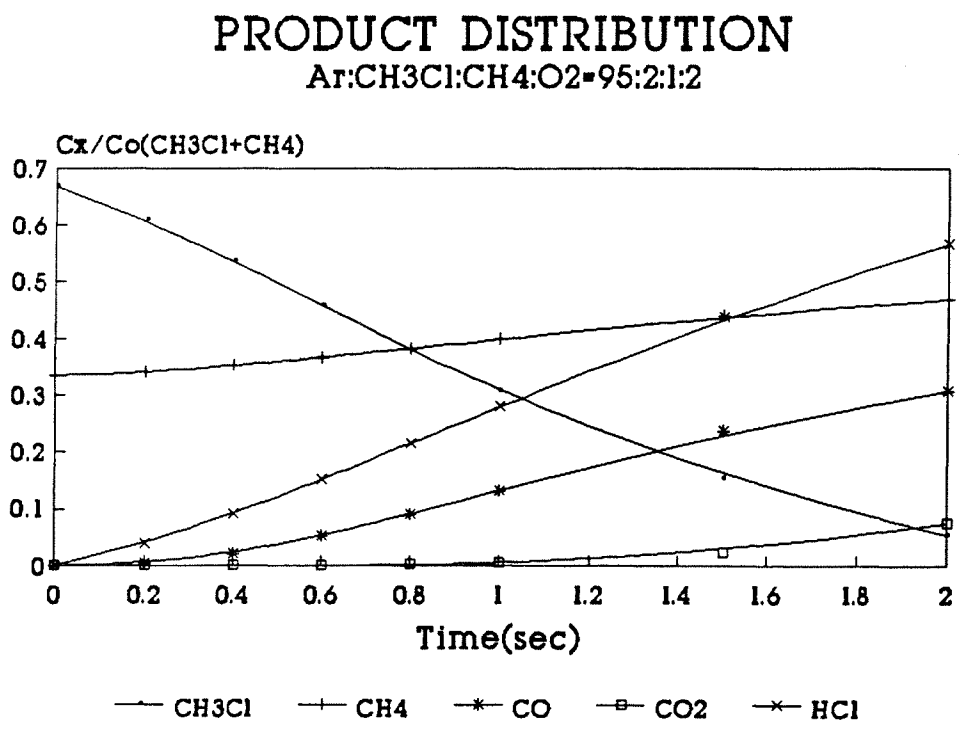


Fig. 170 1173K (M)

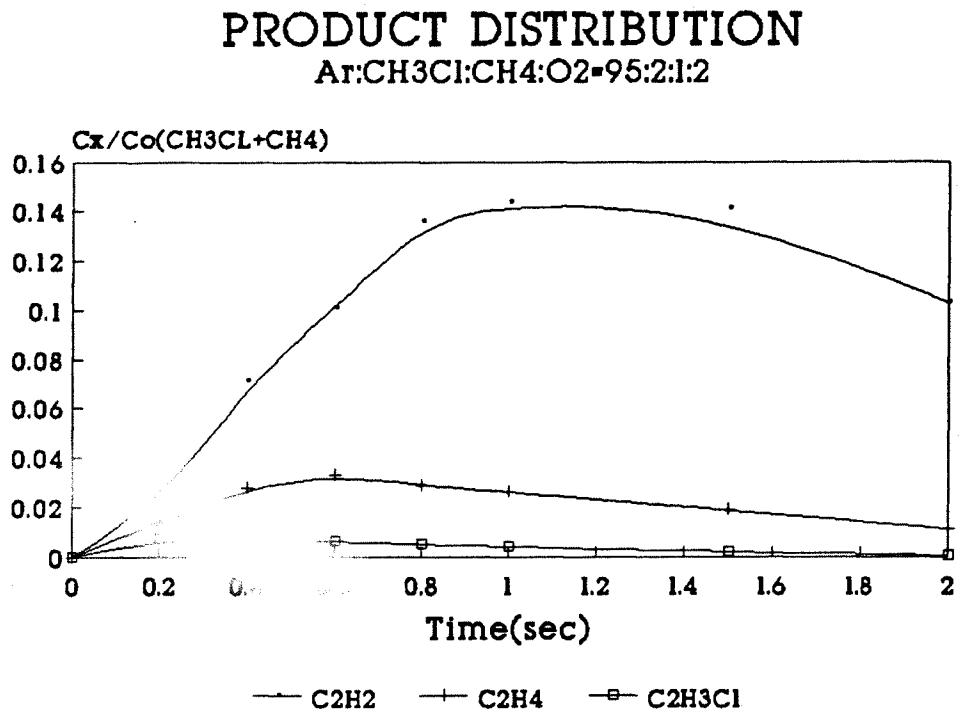


Fig. 171 1173K "10.5" Tube

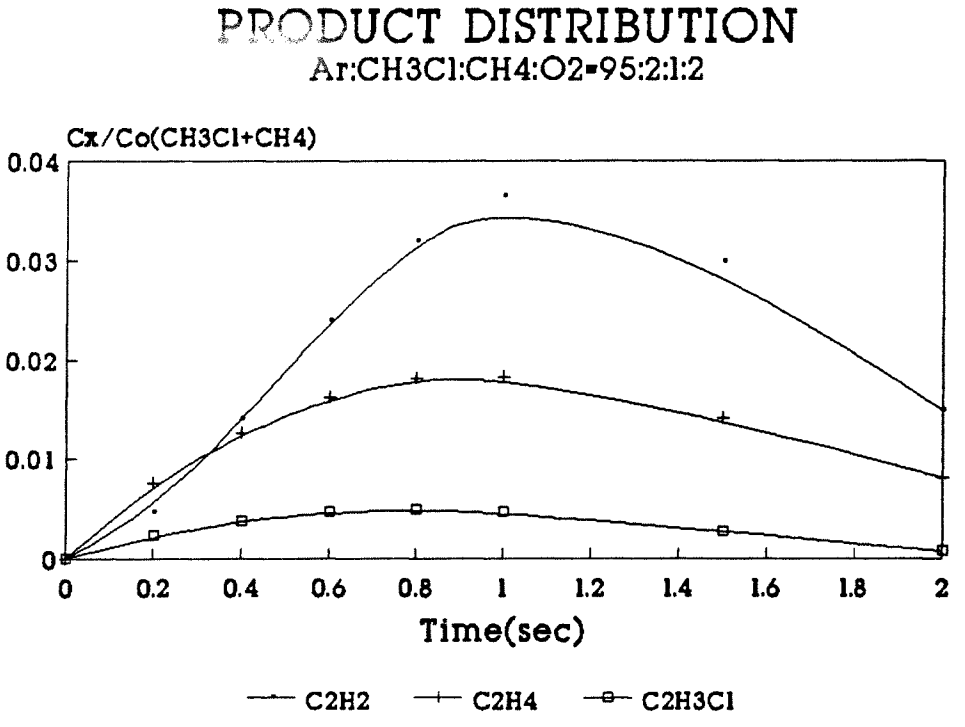


Fig. 172 1173K (M)

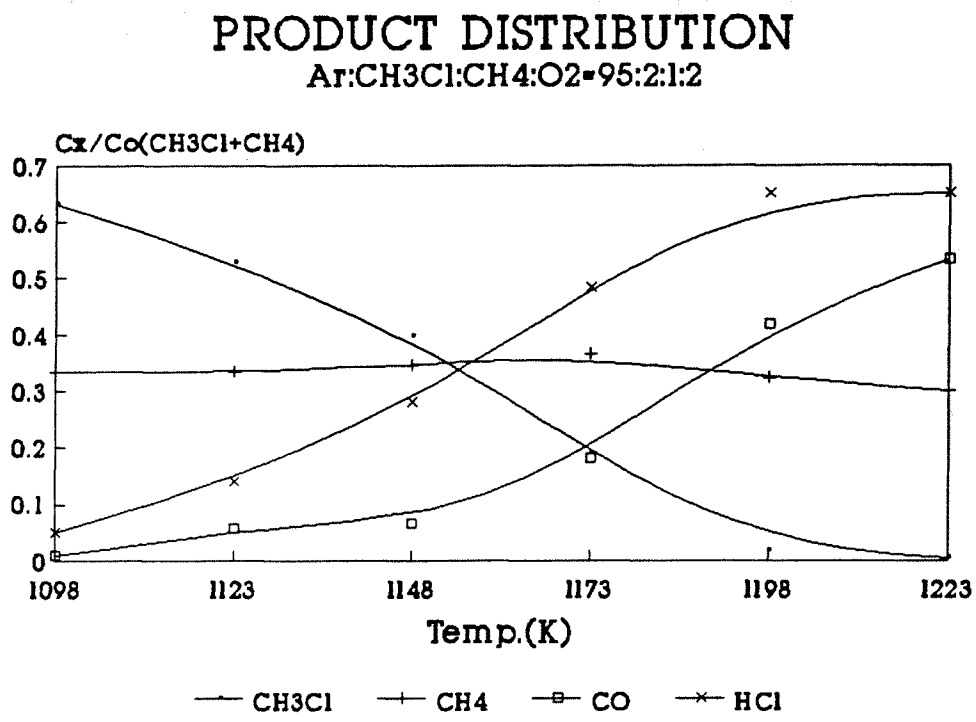


Fig. 173 1.0 sec "10.5" Tube

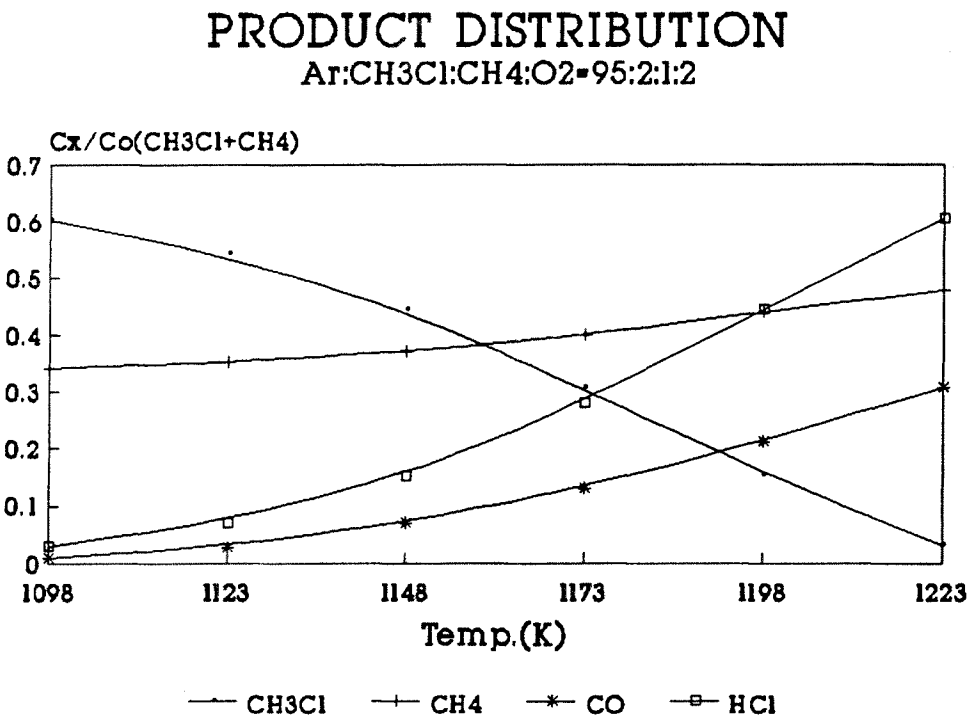


Fig.174 1.0 s 1098-1223K (M)

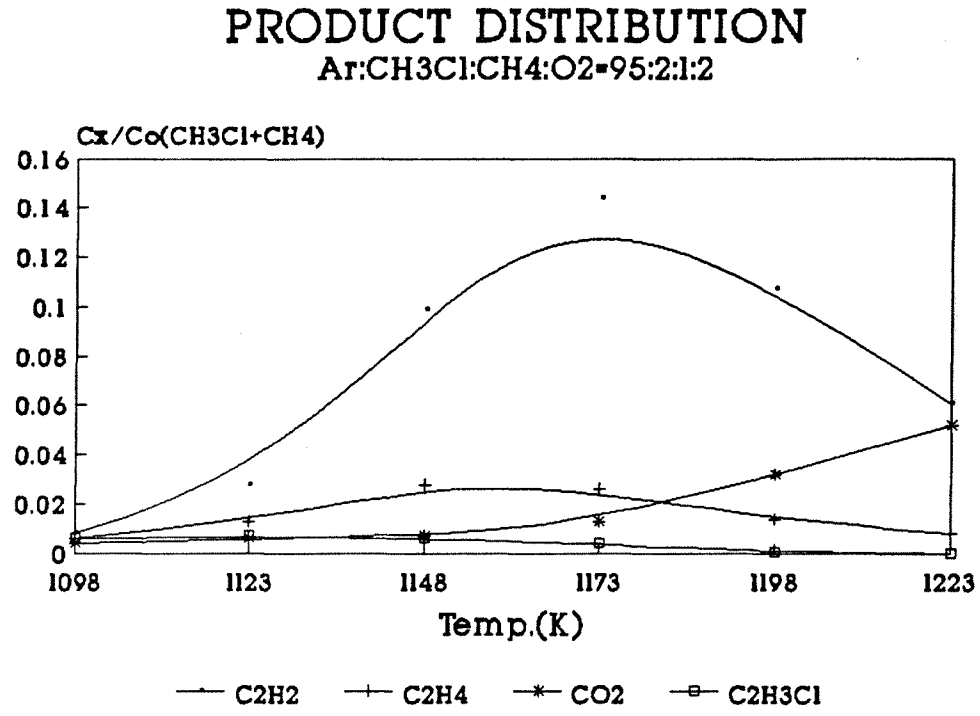


Fig. 175 1.0 sec "10.5" Tube

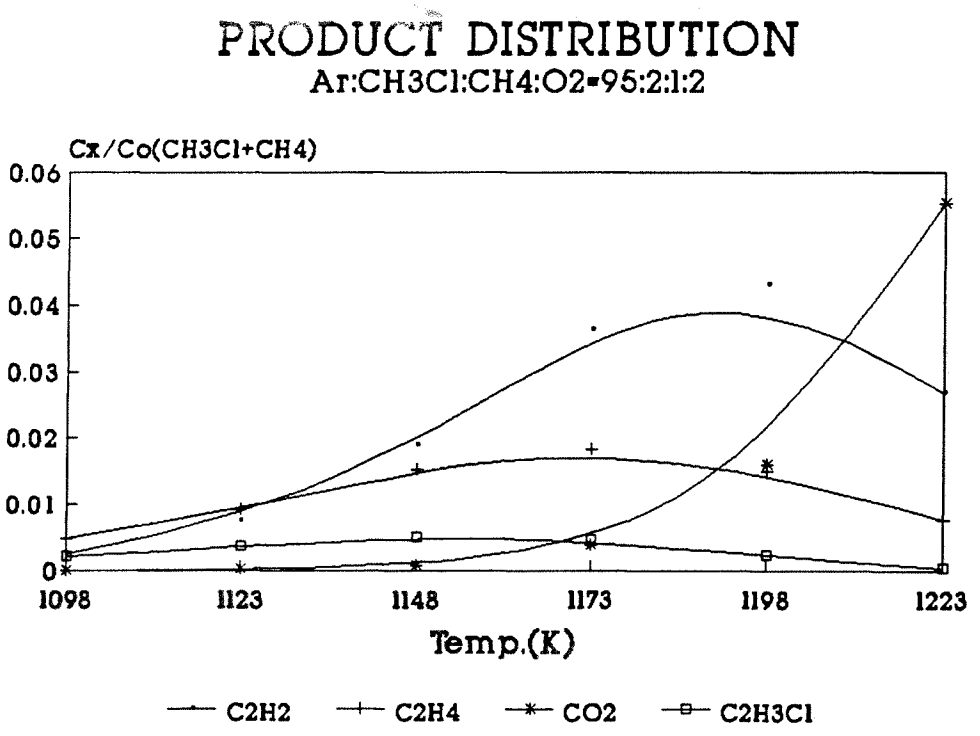


Fig.176 1.0 s 1098-1223K (M)

The sensitivity computer code SENS (Lutz et al. 1987, Won and Bozzelli 1991) was utilized to determine reactions exhibiting high sensitivity to various species in the given reaction system.

The dominant initiation step either in CH3Cl/H2/O2/Ar or in CH3Cl/CH4/O2/Ar reaction is unimolecular decomposition of CH_3Cl to CH_3 + Cl due to its relatively low Ea and higher A factor (Table 4). Reactions of O_2 with reactants also are very important at the beginning stage including H abstraction by O_2. A brief reaction rate comparison has been done as the following example is shown:

for $Ar:CH_3Cl:CH_4:O_2$=96:1:1:2, at 727C (1000K).

Reaction	Rate (mol/cm^3*s)
$CH_3Cl = CH_3 + Cl$	5.85E-11
$CH_3Cl = {}^1CH_2 + HCl$	2.00E-16
$CH_3Cl + O_2 = CH_2Cl + HO_2$	5.60E-14
$CH_4 = CH_3 + H$	1.50E-15
$CH_4 + O_2 = CH_3 + HO_2$	1.16E-14

It should be noted that the relative reaction rate between CH_3Cl unimolecular decomposition and H abstraction from $CH_3Cl/CH_4/H_2$ by O_2 molecule is dependent on not only their kinetic rate constant but also these species relative concentration. At the initial reaction stages, the above reactions contribute to initiation. At the stage for medium to high conversion of CH_3Cl, sensitivity analysis indicates that these reactions proceed in reverse.

Sensitivity analysis tells us that the most significant routes for formation of CH_3 radical in $Ar:CH_3Cl:CH_4:O_2$ = 96:2:2:1 system at 1.0 sec and 1173K are following reactions:

$CH_2Cl + HCl = CH_3Cl + Cl$

$CH_3Cl = CH_3 + Cl$

The production for CH_4 stems from the reactions:

$CH_3Cl + CH_2Cl = CH_2Cl_2 + CH_3$

$CH_3Cl = CH_3 + Cl$

Results from both model and experiment show that CH_4 production is close to or greater than its loss at the temperature below 1173K and 1.0 sec in $CH_3Cl/CH_4/O_2/Ar$ systems. These results from the important reaction $CH_3Cl = CH_3 + Cl$.

Sensitivity analysis also help us probe key reaction channel for the CO conversion to CO_2. The reaction $CO + OH = CO_2 + H_2O$ for formation of CO_2 is an important pathway. While when the concentration of HCl is comparable to that of CO, the reaction $HCl + OH = H_2O + Cl$ depletes OH and effectively inhibits CO conversion. As the rate for the latter is faster than that of the former (the latter k = 1.5E+12 cm3/mol * sec; the former k = 2.42E+11 cm3/mol*sec at 1000K). Model research results further indicate reactions of CO with HO_2 and ClO become more important for CO conversion to CO_2 under the conditions stated above:

$CO + HO_2 = CO_2 + OH$

$CO + ClO = CO_2 + Cl$

The channel $C_2H_3 + O_2 = CH_2CHO + O$ is an important reaction that is analyzed by Bozzelli and Dean. Input of this reaction into mechanism leads to increases of major species (CH_3Cl, CH_4, C_2H_2, C_2H_4, C_2H_3Cl, CO) conversion to CO2 with The reaction $CH_2CHO = CH_2CO + H$ is also important here. Model research found that C_2H_3 could liberate reactive O atom from less active O_2 molecule and CH_2CHO decomposition could release active H atom.

Another interesting species is $^1CH_2$. Model research indicated that it was not important for all reactions at below 1173K. Whereas at temperature above 1198K the following reactions accelerate conversion of CH_4, CH_3Cl, C_2H_2, C_2H_4, and C_2H_3Cl to CO and CO_2.

$^1CH_2 + H_2 = CH_3 + H$

$^1CH_2 + O_2 = CO + OH + H$

When temperature increases to above 1173K, the reaction rate for $CH_3Cl = {}^1CH_2 + HCl$ is increased because of its higher A factor. The reaction of $^1CH_2$ with O_2 and H_2 causes more active OH and H production, which leads to CH_4, CH_3Cl, C_2H_2, C_2H_4, and C_2H_3Cl further conversion.

Modeling research found formaldehyde is important product in our studied systems. It has yet to be experimentally monitored.

CHAPTER 4
CONCLUSIONS

Comparison between experimental data and detailed modeling is presented for the high temperature combustion systems involving $CH_3Cl/H_2/O_2/Ar$ and $CH_3Cl/CH_4/O_2/Ar$ reaction systems. Rate constants of important C_2 species reaction with O and OH are analyzed and reported.

Experimental and modeling results indicate:

1. The initiation step is unimolecular decomposition of CH_3Cl to CH_3 + Cl in all studied systems under all given conditions.

2. O_2 contributes to accelerated decay of CH_3Cl, CH_4, H_2 and C_2 intermediates (as C_2H_2, C_2H_4, and C_2H_3Cl) formation in fuel rich conditions and O_2 also serves to help CH_3Cl conversion to CO_2 in fuel lean conditions.

3. The reaction OH + HCl = H_2O + Cl is an important source of OH loss, which strongly effects the rate of conversion of CO to CO_2 in fuel rich conditions. Therefore, CO + HO_2 = CO_2 + OH, and CO + ClO = CO_2 + Cl both become more important for CO conversion to CO2.

4. CH_4 formation occurs in $CH_3Cl/H_2/O_2/Ar$ reaction systems from CH_3 reactions with H_2 an H_2O_2.

5. Conversion of C_1 to C_2 species results from combination reactions CH_3 + CH_3, CH_3 + CH_2Cl, and CH_2Cl + CH_2Cl.

6. $^1CH_2$ reactions with O_2, H_2, and contributes to

CH_4 and C_2H_2 conversion and CO and CO_2 formation at higher tempertures. This comes from above $^1CH_2$ reactions liberating more active OH, and H radicals.

7. $C_2H_3 + O_2 = CH_2CHO + O$ is very important. Its small rate changes drastically influences the CH_3Cl conversion due to production of significant O atoms from O_2.

8. Modeling research found that formaldehyde is an important product, which has yet to be experimentally monitored.

APPENDIX
GISOQRRK INPUT DATA and CALCULATION RESULTS

Table A-a

$$CH_2Cl + H \underset{}{\overset{1}{<=====>}} (CH_3Cl)^{\#} \overset{2}{====>} CH_3 + Cl$$
$$\overset{3}{====>} {}^1CH_2 + HCl$$

K	A	Ea	Source
1	1.00E + 14	0.00	a
-1	1.44E + 16	100.50	b
2	1.39E + 15	82.50	c
3	1.69E + 14	103.10	d

A = (cc/sec mol) or 1/sec. Ea = Kcal/mol below is same

<v> = 1565.26 1/cm e

LJ Parameters:

Sigma = 4.18 A e/k = 350 K f

Number of Oscillator for CH_3Cl = 9 Its Mass = 50.5

Third body is Ar.

Mass = 40 Sigma = 3.330 A e/K = 113.8 K

Energy Transferred = 630 cal/mol

a. A1 and Ea1 are taken as those for $1\text{-}C_3H_7+H=C_3H_8$. Allara and Shaw J. Phys. Chem. Ref. Data 9, 528, (1980)
b. k-1 is based on Thermodynamic Analysis for Reaction.
c. A=2E13, data of reference reaction, CH3 + C2H5 = C3H8 as A-2. A2 is based on thermrxn. Reference is same as that of a. Ea=ΔH-RT (data are from Thermorxn.).
d. A3 is based on Transition State Theory (TST), A=ekT/h, ΔS= (no rotor is lost), Ea3=ΔH+3.75. (K range between 800-1500K).
e. V is based on the cpfit.
f. Sigma and e/k are based on the equation from The Properties of Gases and Liquids by Robert, C. Reid et al. (McGRAW-HILL).

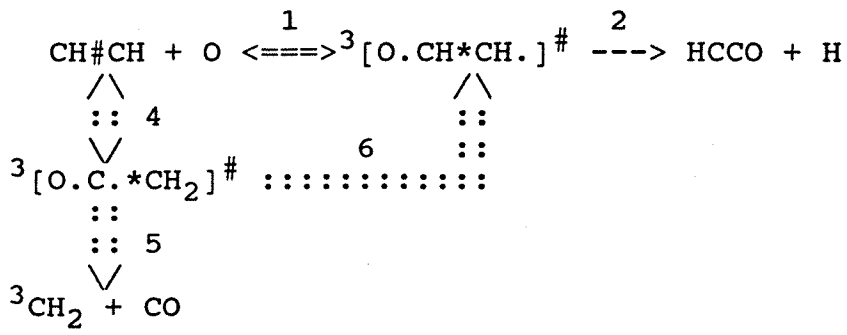
Table A-b

Calculated Apparent Reaction Rate Constants*

Reaction	P	A	N	E
$CH_2Cl+H=CH_3Cl$	76.0	1.560E+26	-4.94	4.27
	760.0	1.622E+27	-4.95	4.29
	7600.0	2.305E+28	-4.99	4.50
	76000.0	7.921E+29	-5.12	5.68
$CH_2Cl+H=CH_3+Cl$	76.0	3.267E+15	-0.46	0.69
	760.0	3.453E+15	-0.47	0.71
	7600.0	5.774E+15	-0.53	0.96
	76000.0	7.938E+16	-0.82	2.50
$CH_2Cl+H=^1CH_2+HCl$	76.0	2.420E+06	1.26	7.64
	760.0	2.460E+06	1.25	7.65
	7600.0	2.890E+06	1.24	7.72
	76000.0	1.089E+07	1.08	8.35

* P Unit is Torr; The below is same.
Bath gas is Ar; Temperatures range 800-1500K.

Table B-a



k	A	Ea	Source
1	7.00E12	1.00	a
-1	2.19E13	46.20	b
2	6.60E13	30.00	c
4	5.62E13	21.50	d
-4	1.12E14	38.00	e
5	2.55E13	19.20	f
6	1.07E14	46.20	g

Units: A = (cc/sec mol) or 1/sec Ea = Kcal/mol

<v> = 1091.3 1/cm h

LJ Parameters:

Sigma = 4.25 A e/k = 301.8 i

Number of Oscillator for OCHCH = 9 Mass = 42

Third body is Ar

Mass = 40 Sigma = 3.33 A e/k = 136.50

Energy Transferred = 630 cal/mol

a. A and Ea are estimated using for the kinetic data of acetylene reaction with hydroxyl radical.
b. Reverse reaction data are from thermrxn and thermodynamics.
c. A=3.98E12, Ea= 2.7 data of reference reaction, $H+CH_2*C*CH_2=CH_2CHC.H_2$ Dean A. M. J. Phys. Chem. 89,

4600, (1985) and based on thermrxn.

d. Based on TST: Ea4 = Rs+$\angle\!\!\!\backslash$H+Eab = 16+0+5.5 = 21.5.

$A_4=10^{13.75}$=5.62E13; degeneracy=1; Eab is obtained using for Eab=5.5 of reference reaction, $C_2H_3+CH_4=C_2H_4+CH_3$ Tsang, W. et al. J. Phys. Chem. Ref. Data 15, 1087, (1986).

e. Based on TST: degeneracy=2; Ea-4=16+16.5+5.5=38.0.

f. Reference reaction, CO + CH_3 = CH_3CO A=5.19E11 Ea=6.5 Anastasi, C. et al. J. Chem. Soc. Faraday I 78, 2423, (1982) and based on thermrxn.

g. CH2C.O. species β scisson forms HC#CO. + H. HC#CO. is easy to convert HCCO. Reference reaction $CH_3C\#CH$ + H = $CH_3C.*CH$.

k. <v> is based on cpfit.

l. LJ parameters are based on refernce species CH_2CO.

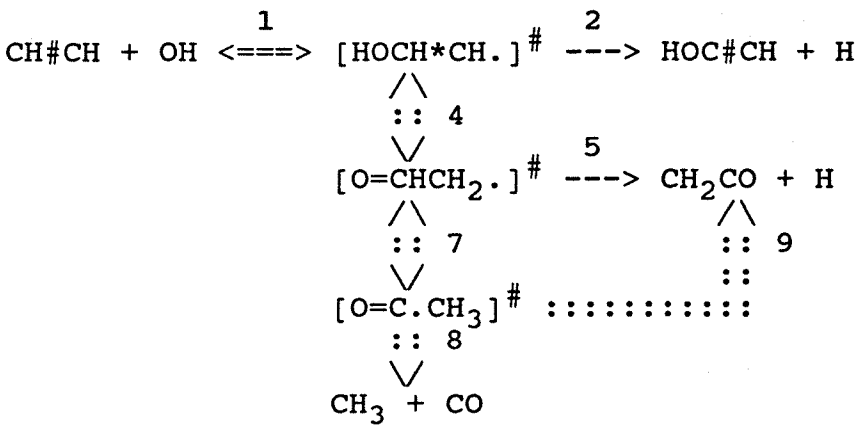
Table B-b

Calculated Apparent Reaction Rate Constants*

Reaction	P	A	n	Ea
C_2H_2+O=OCHCH	76.0	4.41E18	-3.27	2.79
	760.0	4.44E19	-3.27	2.79
	7600.0	4.72E20	-3.28	2.83
C_2H_2+O=HCCO+H	76.0	6.38E09	0.81	0.53
	760.0	7.04E09	0.76	0.59
	7600.0	7.55E09	0.75	0.62
C_2H_2+O=CH_2C.O	76.0	1.87E17	-2.96	2.65
	760.0	1.89E18	-2.96	2.65
	7600.0	2.04E19	-2.97	2.69
C_2H_2+O=$^3CH_2$+CO	76.0	7.06E14	-0.66	1.80
	760.0	7.11E14	-0.66	1.80
	7600.0	7.72E14	-0.67	1.84

* Bath gas is Ar; Temperatures range from 800-1500 K.

Table C-a



k	A	Ea	Source
1	5.12E12	1.40	a
-1	5.50E13	38.40	b
2	3.12E13	47.48	c
4	7.60E12	25.00	d
-4	1.52E13	49.50	e
5	8.23E12	42.71	f
7	7.59E12	33.60	g
-7	2.28E13	42.89	h
8	1.61E13	20.78	i
9	3.39E13	51.31	j

Units: A = (cc/sec mol) or 1/sec Ea = Kcal/mol

<v> = 1278.5 1/cm k
LJ Parameters: l
Sigma = 4.29 A e/k = 334.0
Number of Oscillator for HOCHCH. = 12 Mass = 43
Third body is Ar
Mass = 40 Sigma = 3.33 A e/k = 136.50
Energy Transferred = 630 cal/mol

a. A and Ea derived from Liu, A. et al. J. Chem. Phys., 92 3942, (1988).
b. Reverse reaction data are from thermrxn and thermodynamics.
c. A = 5.8E12, Ea = 2.414, data of reference reaction C_2H_3 <=> C_2H_2 + H (4 Refs. of NIST) to obtain A. Ea comes from thermrxn and thermodynamics.
d. Based on TST: loss of one rotor and degeneracy = 1

   $10^{13.75-4.0/4.6}$=7.6E12; Ea_4=Rs+ΔH+Eab=15+0+10=25.0
   Eab is obtained using for Eab=10 data of reference reaction: C_2H_3 + C_2H_6 = C_2H_4 + C_2H_5 Hidaka, Y. et al Int. J. Chem. Kinet. 17, 441, (1985).
e. Based on TST: degeneracy = 2; Ea-4 = 15+25.4+10 = 50.4
f. Use for reference reaction H+C*C*C=C*CCH_2. A=4.0E12 Ea=2.7 and on thermrxn and thermodynamics.
g. Based on TST: loss of 1 rotor and degeneracy = 1

   $10^{13.75-4.0/4.6}$=7.6E12; Ea_7=Rs+ΔH+Eab=27.6+0+6.0=33.6
   Eab is obtained using for that of reference reaction: CH_3 + CH_3CHO = CH_3CO + CH_4
h. Based on TST: degeneracy=3; Ea_{-7}=27.6+9.29+6.0=42.89
i. Based on A=6.2E11, Ea=6.7, data of reaction CH_3 + CO = CH_3CO and thermrxn. The above data are from the fit of that of two references from NIST.
j. Based on rate data of reaction CH_2CO + H = CH_3CO and thermrxn. Wagner, H. Gg. et al. Ber Bunsenges, Phys. Chem. 76, 667, (1972).
k. <v> is based on cpfit.
l. LJ parameters are based on arithmetic mean of that of CH_3CHO and CH_2CO.

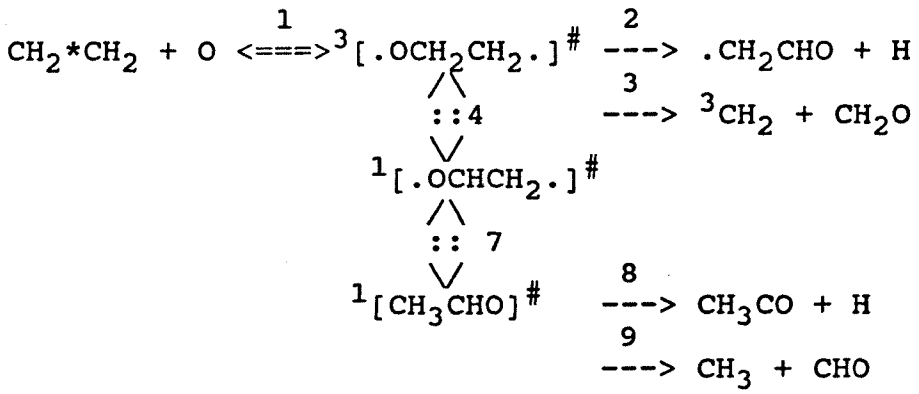
Table C-b

Calculated Apparent Reaction Rate Constants*

Reaction	P	A	n	Ea
	76.0	1.64E27	-5.38	5.58
C_2H_2+OH=HOCHCH.	760.0	3.37E28	-5.46	5.93
	7600.0	4,49E30	-5.75	7.71
	76.0	2.59E09	0.93	12.41
C_2H_2+OH=HOCCH+H	760.0	3.24E09	0.90	12.51
	7600.0	1.97E10	0.69	13.30
	76.0	1.74E25	-4.83	5.29
C_2H_2+OH=C.	760.0	5.07E26	-4.95	5.80
	0	7.02E29	-5.51	8.72
		1.33E12	-0.03	2.15
C_2H_2+OH=CH_2CO+H	760.0	1.22E13	-0.32	2.84
	7600.0	1.31E16	-1.13	6.15
	76.0	5.19E20	-3.87	4.40
C_2H_2+OH=CH_3CO	760.0	1.66E22	-4.00	4.93
	7600.0	5.47E25	-4.67	8.05
	76.0	7.89E16	-1.30	3.27
C_2H_2+OH=CH_3+CO	760.0	2.68E17	-1.44	3.81
	7600.0	1.56E20	-2.18	7.04

* Bath gas is Ar; Temperatures range from 800-1500 K.

Table D-a



k	A	Ea	Source
1	6.40E12	1.59	a
-1	1.87E13	21.23	b
2	2.46E13	5.70	c
3	7.70E13	20.40	d
4	1.00E13	15.00	e
-4	1.42E13	26.90	e
7	4.28E12	9.30	f
-7	6.42E12	89.63	f
8	2.85E16	83.90	g
9	8.30E13	85.39	h

Units: A = (cc/sec mol) or 1/sec Ea = Kcal/mol

<v> = 1328.7 1/cm i
LJ Parameters: j
Sigma = 4.64 A e/k = 396.4
Number of Oscillator for .OCH_2CH_2. = 15 Mass = 44
Third body is Ar
Mass = 40 Sigma = 3.33 A e/k = 136.50
Energy Transferred = 630 cal/mol

a. A and Ea are derived from Cvetanovic, R. J. et al. J. Chem. Phys. Ref. Data 16, 261, (1987).
b. Thermodynamic data for the reverse reaction are from Takayuki FUENO, et al. Chem Phys. Letter 167, 4, 291 (1990) and thermodynamics.
c. A=7.94E12; Ea=2.9, data of reference reaction as k_{-2} $CH_3CH^*CH_2 + H = CH_3CH_2CH_2$ Dean, A. M. J. Phys. Chem. 89, 4600, (1985) and based on thermodynamics.
d. A=5.19E11; Ea=6.6, data of reference reaction as k_{-3} $CH_3 + CO = CH_3C.O$ Anastasi, C. et al. J. Chem. Soc. Faraday Trans I, 78, 2423 (1982) and based on thermodynamics.
e. K_4 reference reaction CH + N2 = HCN + N spin forbidden Ea=15 as Ea_4 A_4 is estimated k_{-4} is based on thermodynamics and microreversibility.
f. $Ea_{7/-7}$ are from data of Takayuki FUENO. $A_{7/-7}$ are based on TST degeneracy = 2 for A_7; degeneracy = 3 for A_{-7}.
g. A=1.8E13; Ea=0, data of reference reaction $CH_3+CHO=CH_3CHO$, Tsang, W. J. Phys. Chem. Ref. data 15, 1087, (1987) and based on thermodynamics.
h. A=1E14, data of reaction $CH_2O = CHO + H$ and A_9 is adjusted to be $(30/44)^{1/2}*1E14 = 8.3E13$ and Ea is based on thermodynamics.
i. <v> is based on cpfit.
j. LJ parameters are used for that of $.CH_2CHOH$.

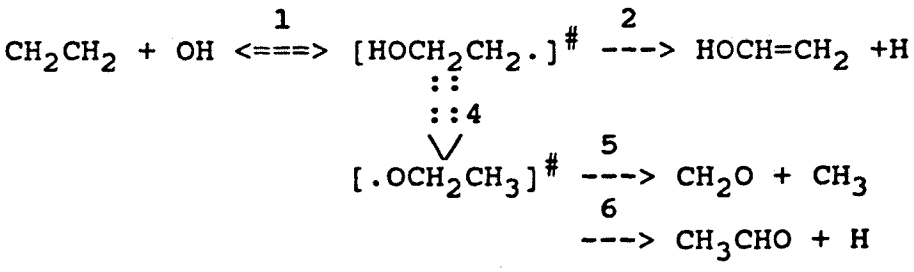
Table D-b

Calculated Apparent Reaction Rate Constants*

Reaction	P	A	n	Ea
$C_2H_4+{}^3O={}^3$[CH2CH2O]	76.0	5.67E16	-2.82	2.61
	760.0	5.69E17	-2.82	2.61
	7600.0	5.85E18	-2.82	2.63
$C_2H_4+{}^3O=.CH_2CHO+H$	76.0	2.69E13	-0.20	1.76
	760.0	2.70E13	-0.20	1.76
	7600.0	2.78E18	-0.21	1.78
$C_2H_4+{}^3O={}^3CH_2+CH_2O$	76.0	9.49E-02	3.91	-0.35
	760.0	9.53E-02	3.91	-0.35
	7600.0	9.93E-02	3.90	-0.33
$C_2H_4+{}^3O={}^1[CH_2CH_2O]$	[illegible]	3.99E08	-0.48	1.13
	760.0	3.05E09	-0.48	1.14
	7600.0	3.63E10	-0.50	1.24
$C_2H_4+{}^3O=CH_3CHO$	76.0	1.22E07	1.28	1.08
	760.0	1.50E06	1.57	0.81
	7600.0	4.06E05	1.75	0.71
$C_2H_4+{}^3O=CH_3CO+H$	76.0	2.03E33	-6.23	40.35
	760.0	1.11E27	-4.34	39.74
	7600.0	1.61E16	-1.17	36.82
$C_2H_4+{}^3O=CH_3+CHO$	76.0	3.32E37	-6.65	40.57
	760.0	2.70E30	-4.54	39.49
	7600.0	1.89E19	-1.29	36.32

* Bath gas is Ar; Temperatures range from 300-1500 K.

Table E-a



k	A	Ea	Source
1	5.42E12	0.00	a
-1	2.10E13	29.70	b
2	1.27E13	39.62	c
4	1.31E12	38.44	d
-4	2.28E13	35.00	e
5	5.40E13	20.72	f
6	2.00E14	23.30	g

Units: A = (cc/sec mol) or 1/sec Ea = Kcal/mol

<v> = 1404.72 1/cm h

LJ Parameters:

Sigma = 4.641 A e/k = 396.36 i

Number of Oscillator for $HOCH_2CH_2$. = 18 Mass = 45

Third body is Ar

Mass = 40 Sigma = 3.330 A e/k = 113.8

Energy Transferred = 630 cal/mol

a. A and Ea derived from Atkinson, R. et al. J. Chem. Phys., Ref. Data 18, 881, (1989).
b. Reverse reaction is from thermrxn and thermodynamics.
c. Reference reaction $CH_3C{*}C + H = CH_3CH_2CH_2$. A_{-2} = 7.94E12 Ea_{-2} = 2.9 and on thermrxn and thermodynamics.
d. Based on TST: loss of two rotors and degeneracy = 1

$10^{13.75-7.5/4.6}$=1.31E12; Ea_4=Rs+$\triangle$H+Eab=26+3.44+9=38.44

e. Based on TST: degeneracy = 3; Ea-4 = 26+0+9 = 35

f. Reference reaction CH_3 + C*C = $CH_3CH_2CH_2$
A = 3.16E11, Ea = 7.7 as k_{-5} and on thermrxn and thermodynemics.
g. A and Ea are from Heicklen, J. Advances in Photochem. 14, 177, (1988).
h. <v> is based on the cpfit.
i. Sigma and e/k of HOCH2CH2. are used for data of HOCHCH2 and based on the equation from Properties of Gaseand Liquids by Robert, C. Reid et al. (McGROW-HILL BOOK COMPANY).

Table E-b

Calculated Apparent Reaction Rate Constants*

Reaction	p	A	n	Ea
$C_2H_4+OH=HOCH_2CH_2$	76.0	2.95E48	-11.20	13.43
	760.0	5.71E45	-9.91	14.22
	7600.0	6.10E34	-6.59	10.81
$C_2H_4+OH=HOCHCH_2+H$	76.0	2.88E15	-0.84	12.04
	760.0	8.04E17	-1.50	14.32
	7600.0	3.93E20	-2.17	18.75
$C_2H_4+OH=CH_3CH_2O$	76.0	9.23E30	-7.16	17.43
	760.0	2.68E33	-7.54	19.27
	7600.0	7.93E32	-7.00	21.40
$C_2H_4+OH=CH_3+CH_2O$	76.0	1.11E17	-1.72	12.59
	760.0	2.17E19	-2.34	14.84
	7600.0	1.36E21	-2.74	18.90
$C_2H_4+OH=CH_3CHO+H$	76.0	1.77E15	-1.09	11.95
	760.0	4.63E17	-1.75	14.25
	7600.0	1.20E20	-2.33	18.64

* Bath gas is Ar; Temperatures range from 800-1500 K.

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PART II

CHAPTER 1
INTRODUCTION

Modeling research needs accurate thermodynamic properties, thermodynamic analysis, QRRK kinetic analysis, and reliable kinetic constant (rate data) from experimental measurement. This study is a survey of reaction rate data important in describing high-temperature combustion of C_2-species because oxidation of C_2-species plays an important role in hydrocarbon and chlorocarbon combustion. The preceding work (Warnatz [1] and Tsang [2]) did not include the rate data of chlorine radical reactions. This work concentrates on evaluation and development of the rate constants of C2H6, C2H4, and C2H2 reaction with OH, O, H, and Cl. These reactions are important to acetylene production, which is of special interest in rich fuel combustion due to it's role in the processes of soot formation [2].

The principle for this work is to evaluate the available data and select accurate kinetic data to included in the statistical analysis rather than be exhaustive. Results obtained with experimental methods capable of measuring isolated elementary reaction rate parameters directly are preferred. Results obtained using computer simulations of complex reacting systems are considered only when sensitivity to a particular elementary reaction was demonstrated in the literature or when direct measurement are not available.

The important thermochemical analysis in both forward and reverse directions is also considered. Reaction products are specified.

CHAPTER 2
REACTION OF C_2H_6 WITH OH, H, O, AND Cl

Ethane is found as a intermediate product during the oxidation and pyrolysis of methane and chloromethane. Ethane is also a precursor of C_2H_5, which is an active species whose further reaction may involve higher hydrocarbon formation. Therefore elementary reactions of C_2H_6 play an important role in soot formation chemistry, especially in fuel-rich combustion. Ethane is thought to be removed primarily by OH and H attack [3,4] in stoichiometric combustion. Nevertheless, the reaction with O atoms probably plays a significant role in fuel-lean and higher temperature systems. When a chlorocarbon, HCl, and Cl_2 are present Cl atoms can rapidly abstract H from ethane to accelerate C_2H_6 conversion.

In all cases above, there are sufficient data to evaluate and weight to obtain rate data covering a greater temperature range. Recommended values for OH, O, H, and Cl reactions with C_2H_6 are shown in Table and Figures 1-4.

Table 1. Rate data on C_2H_6 reactions*

A	n	Ea	Reference	T	Method
			$C_2H_6 + OH = C_2H_5 + H_2O$ (/\H=-18700)		
1.40E13	0.00	2660	[5] BAU/BOW (1986)	250-1200	Review
8.85E09	1.04	1810	[2] TSA/HAM (1986)	300-2500	Review
6.29E06	2.00	646	[1] WAR (1984)	300-2000	Review
6.62E12	0.00	2190	[6] DEM/GOL (1987)	200-300	Review
9.67E08	1.33	1460	Recommended	200-2500	
			$C_2H_6 + H = C_2H_5 + H_2$ (/\H=-3500)		
554	3.50	5167	[2] TSA/HAM (1986)	300-2500	Review
540	3.50	5210	[1] WAR (1984)	300-2500	Review
1.00E14	0.00	9600	[7] CAO/BAC2(1984)	300-2000	Review
3.24E05	2.63	6300	Recommended	300-2500	
			$C_2H_6 + O = C_2H_5 + OH$ (/\H=-1450)		
1.20E12	0.60	7313	[2] TSA/HAM(1986)	300-2500	Review
3.00E07	2.00	5115	[1] WAR (1984)	300-2000	Review
1.10E14	0.00	7850	[8] HER (1988)	400-1100	Review
2.70E06	2.40	5840	[8] HER (1988)	1100-2000	Review
3.56E06	2.40	5842	[9] COH/WES (1986)	300-2000	Review
1.15E07	6.50	270	[10] MAH/MAR (1988)	297-1270	Photo
0.0193	4.85	2030	[10] MAH/MAR (1988)	297-1270	Calcul
2.62E07	2.05	5400	Recommended	297-2500	
			$C_2H_6 + Cl = C_2H_5 + HCl$(/\H=-2410)		
7.29E13	0.00	460	[11] TSC/NIE (1989)	280-368	Photo
4.63E13	0.00	179	[6] DEM/GOL (1987)	200-300	Review
3.85E13	0.00	0	[12] 85ATK/ASC2(1985)	296	Photo
3.72E13	0.00	0	[13] 87ATK/ASC5(1987)	298	Photo
4.04E13	0.00	0	[14] DAV/BRA (1970)	298	Photo
3.67E13	0.00	0	[15] DOB/BEN (1990)	298	
4.63E13	0.00	179	[16] ATK/BAU (1989)	220-350	Review
5.43E13	0.00	260	[17] LEW/SAN (1980)	220-604	FT
5.43E13	0.00	246	Recommended	200-604	

in cm^3, mol, s, cal, K units ; Photo, Calcul, FT denote Photolysis, Calculation and Flow Tube respectively. The bellows are same.

CHAPTER 3
REACTION OF C_2H_4 WITH OH, O, H, and Cl

Under normal hydrocarbon combustion conditions, the reaction consuming the majority of the ethylene is C_2H_4 + OH = C_2H_3 + H_2O. Tully et al [18] have established that the net reaction between C_2H_4 and OH consists exclusively of H atom abstraction under high temperature condition (above 1000K), rather than an addition-rearrangement-decomposition channel. Our QRRK analysis results support their view, which indicates that sum of all addition-rearrangement-decomposition reactions only accounts for 0.85% of the total rate of the reaction C2H4 + OH at 1200K. Next in importance is the reaction C_2H_4 + ^3O, whose rate data will be treated separately below. The reaction of C_2H_4 with H atoms consumes only a small fraction of C_2H_4 especially under the oxygen-rich conditions [19]. The hydrogen atomic Resonance Adsorption Spectrophotometry can be used to investigate the kinetic behavior of the decay of C2H4 from reaction with H and to characterize the formation of H2 and C2H3 [20]. According to the work of Gay [21] and Just [22], the channel C2H4 + H = C2H3 + H2 can be responsible for the acceleration of C2H4 decay in fuel-rich conditions.The channel C_2H_4 + Cl = C_2H_3 + HCl could be important to not only C2H4 decay but also the formation of higher hydrocarbons and soot. Benson's group has reported the rate data of this channel, however, these data are scattered, which indicates the need for

additional kinetic studies.

In order to obtain reasonable rate data of this reaction, we correlate a reference reaction, C_6H_6 + Cl = C_6H_5 + HCl, with title reaction. This channel rate data (A=2.0E13, Ea=10 Kcal/mol) are recommended. The recommended rate constants of C2H6 reactions with OH, O, H, and Cl are showed in Table 2 and Figures 5-7.

Table 2. Rate Data on C_2H_4 Reactions

A	n	Ea	Reference		T	Method
			C_2H_4 + OH = C_2H_3 + H_2O (/\H=-9400)			
1.50E04	2.75	4000 [4]	TSA/HAM	(1986)	300-2500	Review
2.02E13	0.00	5940 [18]	TUL	(1988)	650-901	Photo
1.45E13	0.00	4180 [19]	LIU/MUL	(1987)	748-1173	EB
2.09E06	2.01	1160 [23]	LIU/MUL	(1988)	723-1173	Calcul
9.41E13	0.00	8330	Recommended		300-2500	
			C_2H_4 + H = C_2H_3 + H_2 (/\H=5760)			
1.33E06	2.53	12241 [2]	TSA/HAM	(1986)	300-2500	Review
8.99E10	0.00	0 [24]	JAY/PAC	(1988)	900	Therm
1.00E14	0.00	15010 [25]	MAN/LOU	(1988)	872-1085	Calcul
1.31E04	3.10	11400	Recommended		300-2500	
			C_2H_4 + Cl = C_2H_3 + HCl (/\H=6900)			
2.39E13	0.00	2600 [26]	PAR/BEN	(1988)	263-338	Therm
1.00E14	0.00	7000 [27]	WEI/BEN	(1984)	1260-1310	Calcul
3.00E11	0.00	0 [15]	DOB/BEN	(1990)	298	DC
2.00E13	0.00	10000	Recommended		1000-1500	

* EB, Therm, and DC denote Electrical Beam, Thermal, and Discharge respectively. the belows are same.

The products for the reaction of C_2H_4 with O are very complicated. The reaction paths have been reported [28-32 and 51] as follow:

$C_2H_4 + O = CH_2CHO + H$ ----------(1)

$C_2H_4 + O = CH_3 + CHO$ ----------(2)

$C_2H_4 + O = CH_2 + CH_2O$ ----------(3)

$C_2H_4 + O = CH_2CO + H_2$ ----------(4)

$C_2H_4 + O = CH_3CO + H$ ----------(5)

$C_2H_4 + O = CH_2CH_2O$ (Ethylene Oxide)----(6)

A number of experimental studies [28-32] have been carried out to elucidate the reaction of triplet oxygen atom with ethylene in gases. Cvetanovic [28] first reported that the primary process is a direct addition of ^3O to double bond of ethylene to form an energized $^3[CH_2CH_2O]^{\#}$, which further undergoes unimolecular reaction:

$^3[CH_2CH_2O]^{\#}$ -> $CH_2CHO + H$ ----------(1)

-> $CH_3 + CHO$ ----------(2)

-> $CH_2 + CH_2O$ ----------(3)

-> $CH_2CO + H_2$ ----------(4)

-> Ethylene Oxide ---------(6)

According to the product determinations by Cvetanovic [28,29], fragmentation $CH_3 + CHO$ is the most dominant process in the gas phase. By contrast, gas kinetic experiments using the flow technique [30,31] indicated that the fragmentation (1) and (2) are the two main processes. A recent study by microwave kinetic spectroscopy [32], however, has provided results similar to those of previous

flow experiments. Our QRRK analysis (see part I) of reaction C_2H_4 + ^3O showed that the energized $^3[CH_2CH_2O]^\#$ could convert to a energized $^1[CH_2CH_2O]^\#$, which further undergoes unimolecular decomposition reaction to CH_3 + CHO and CH_3CO + H; the major channels were (1), (2), and (3). Table 3 and Figures 8-10 illustrate these results.

Table 3. Calculated Apparent Rate Constants*

Reaction	A	n	Ea
$C_2H_4 + {}^3O = {}^3[.CH_2CH_2O.]$	1.77E18	-2.97	2770
$C_2H_4 + {}^3O = CH_2CHO + H$	7.77E13	-0.35	1910
$C_2H_4 + {}^3O = {}^3CH_2 + CH_2O$	6.50E06	1.61	3790
$C_2H_4 + {}^3O = {}^1[CH_2CH_2O.]$	1.84E11	-1.03	1720
$C_2H_4 + {}^3O = CH_3CHO$	1.12E43	-8.83	27310
$C_2H_4 + {}^3O = CH_3CO + H$	3.58E34	-6.53	43930
$C_2H_4 + {}^3O = CH_3 + CHO$	2.25E41	-7.67	46260

* P = 760 torr, Temperature range: 300-2400K.

CHAPTER 4
REACTION OF C_2H_2 WITH OH, O, H, AND Cl

Acetylene decay is usually thought to involve hydroxyl radicals or O atoms depending on equivalence ratios. Fenimore and Jones [33] measured the concentration profiles of stable species in acetylene-oxygen flames. Assuming the elementary reactions of the H_2/O_2 system practically reach equilibrium in burned gas zone, they computed the concentration of H, O, and OH radicals by means of the equilibrium constants in that region. From their data they concluded that acetylene is removed primarily by O atoms in lean mixtures and by OH radicals in very rich mixtures.

The reactions of H atoms with C_2H_2 do not play an important role as far as the acetylene consumption in the flame investigation is concerned, when one considers the low concentration of H atoms compared with the OH concentration.

4.1 Reaction of C_2H_2 with OH

As what was stated by Miller [37], "The reaction between hydroxyl and acetylene is problematic in combustion modeling research. No consistent set of rate data or a clear determination of the dominant product channel, has emerged from the experimental sector at temperatures of direct interest in combustion. Almost all high-temperature determinations are indirect, involving a complex analysis

of flame or shock tube data. Various sets of products have been proposed for the high-temperature reaction."

In order to determine the species resulting from the elementary processes concerning acetylene combustion, the earlier studies using different techniques have been compared at 300 K. Gehring [34] suggested the formation of methyl radical by $C_2H_2 + OH = CH_3 + CO$; While Porter [35] supported the formation of ethynyl radical via $C_2H_2 + OH = C_2H + H_2O$ (1); Konofsky [36] using a similar technique detected ketene and proposed the elementary steps should cover the reaction $C_2H_2 + OH = CH_2CO + H$. The earlier studies have shown that the $CH_2CO + H$, $CH_3 + CO$ and $C_2H + H_2O$ are prevalent.

In the recent years, the investigations from Miller et al. [37] and Bozzelli et al. showed the path $C_2H_2 + OH = HOCCH + H$ might need to be considered although other channels are more prevalent for the high-temperature reaction (see Table 4 and Figures 11-14).

Table 4-1. Rate Data on C_2H_2 Reaction with OH*

A	n	Ea	Reference	T	Method
			C_2H_2 + OH = C_2H + H_2O (/\H=10520)		
3.37E07	2.00	14000	[38] MIL/BOW (1989)	1000-2500	Review
1.45E04	2.68	12040	[4] TSA/HAM (1986)	300-2500	Review
2.71E13	0.00	10500	[39] LIU/MUL (1988)	1073-1273	Review
3.37E07	2.00	14000	Recommended	300-2500	

* Via abstraction reaction path.

Table 4-2 Rate Data on C_2H_2 Reaction with OH*

A	n	Ea	Reference	T	Method
			C_2H_2 + OH = HOC#CH + H (/\H=8730)		
5.04E05	2.30	13500	[38] MIL/BOW (1989)	500-2500	Calcul
9.31E08	1.04	11910	YU/BOZ (1992)	300-2400	Calcul
9.31e08	1.04	11910	Recommended	300-2500	
			C_2H_2 + OH = CH_2CO + H (/\H=-23090)		
1.75E12	-0.09	2090	YU/BOZ (1992)	300-2400	Calcul
2.18E-04	4.00	-1000	[38] MIL/BOW (1989)	500-2500	Calcul
9.20E11	0.00	0	[40] KAI (1990)	1700	Est
3.20E11	0.00	200	[41] VAN/VAN (1977)	570-850	Therm
1.75E12	-0.09	2090	Recommended	300-2500	
			C_2H_2 + OH = CH_3 + CO (/\H=-55000)		
1.73E16	-1.12	2830	YU/BOZ (1992)	300-2400	Calcul
4.83E-04	4.00	-2000	[38] MIL/BOW (1989)	500-2500	Calcul
5.50E13	0.001	3700	[41] VAN/VAN (1977)	650-1110	Therm
1.73E16	-1.12	2830	Recommended	300-2500	

* Via addition reaction followed by other reaction channels.

In this study, other intermediate products of C2H2 reaction with OH can occur in low temperatures by our QRRK analysis (See Table 5).

Table 5. Calculated Apparent Rate Constants*

Reaction	A	n	Ea
C2H2 + OH = HOCHCH.	2.12E26	-4.85	4.36
C2H2 + OH = .CH2CHO	1.25E27	-5.08	5.87
C2H2 + OH = CH3C.O	3.41E20	-3.54	3.59

* P = 760 Torr, Temperature range: 300-2400K.

4.2 Reaction of C_2H_2 with O Atoms

We still do not have an exact answer of the nature of primary products of the reaction of C_2H_2 with O atoms:

$$C_2H_2 + O \Rightarrow CH_2 + CO \qquad /\backslash H = -47 \text{ Kcal/mol} \qquad (I)$$

$$C_2H_2 + O \Rightarrow HCCO + H \qquad /\backslash H = -19.4 \text{ Kcal/mol} \qquad (II)$$

Fenimore [33] suggested reaction (I) as a dominant reaction path at high temperatures (flame temperatures). The view that CH2 is the major product while HCCO formation -- at least at low to moderate temperatures -- is negligible, was supported by the cross molecular beam experiments of Blumenberg et al. [42], by the modeling of stable product formation of Homann et al. [43], and the H-Production analysis of Lohr at al. [44] in shock tubes.

On the other hand, (I) and (II) ab initio calculations by Harding [45] showed that H-Displacement path (II)

was energetically favored; also the HCCO radical was detected in crossed molecular beam experiments by Clem [46]. The occurrence of both reaction paths simultaneously is also proposed by several groups: Bayes [47] found 12% to probably 25% methylene formation; Williamson [48] concluded that route (I) accounts for about 40% of the total product formation. Both CH_2 and HCCO were detected as major products in a crossed molecular beam experiment by Kanofsky et al. [36]. From an appropriate calibration of the CH_2 concentration, Vinckier [49] deduced that reaction channel (I) accounts for about 50% of the primary C_2H_2 destruction rate. According to Aleksandrov [50], the production of hydrogen atoms shows that at room temperature 5% and at 600 K 16% of the primary reaction proceeds via HCCO. Our QRRK analysis indicates that the reaction channel (I) accounts for 34% of total C_2H_2 reaction rate and the channel (II) accounts for close to 66% at 1200K. A small amount of products, OCH*CH. and ^{3}[CH2C.O.]^o amount to less than 1% of the reaction (see Table 6 and Figures 15-16).

Table 6. Rate Data on C_2H_2 Reaction with O

A	n	Ea		Reference		T	Method
				$C_2H_2 + O = CH_2 + CO$ (/\H= -47000)			
2.70E14	-0.55	1460		YU/BOZ	(1992)	300-2400	Calcul
5.20E13	0.00	3700	[51]	PEE/MAH2	(1973)	1200-1700	Est
1.21E14	0.00	6560	[52]	ROT/LOE2	(1982)	1500-2600	ST
4.08E08	1.50	1690	[53]	CVE	(1987)	300-2500	Review
4.10E08	1.50	1700	[1]	WAR	(1984)	300-2500	Review
1.21E14	0.00	6560	[44]	LOH/ROT	(1981)	1500-2570	ST
1.60E14	0.00	8100	[54]	FRA/BHA	(1988)	1500-2500	ST
1.61E10	0.98	1720		Recommended		300-2600	
				$C_2H_2 + O = HCCO + H$ (/\H=-19440)			
7.95E09	0.74	550		YU/BOZ	(1992)	300-2400	Calcul
9.04E12	0.00	4540	[50]	ALE/ARV	(1981)	298-608	DC
4.34E14	0.00	12120	[52]	ROT/LOE2	(1982)	1500-2600	ST
4.30E14	0.00	12120	[53]	CVE	(1987)	1000-2500	Review
9.04E12	0.00	4540	[2]	TSA/HAM	(1986)	300-2500	Review
4.30E14	0.00	12120	[1]	WAR	(1984)	1000-2500	Review
4.00E14	0.00	10660	[54]	FRA/BHA	(1988)	1500-2500	ST
7.95E09	0.74	550		Recommended		300-2600	

4.3 Reaction of C_2H_2 with H Atoms

Due to the endothermicity, this reaction needs to be considered only at high temperatures. Warnatz, and Tsang, et al. have made extensive literature reviews. We have compared their data and did not find any obvious inconsistency. The weighted data have been chosen (see Table 7 and Figure 17).

Table 7. Rate Data on C_2H_2 Reaction with H

A	n	Ea	Reference		T	Method
			$C_2H_2 + H = C_2H + H_2$ (/\H=24000)			
6.03E13	0.00	23660	[55] GAR/TAU	(1985)	1800-2500	Review
6.03E13	0.00	22260	[2] TSA/HAM	(1986)	300-2500	Review
6.00E13	0.00	23660	[1] WAR	(1984)	300-2500	Review

4.4 Reaction of C_2H_2 with Cl Atoms

The only mention of this reaction in the literatures is an estimate of its rate data used in modeling research and theoretical consideration. The basis of recommendation given here is the fact that Ea of H-abstraction reaction is always greater than /\H. The rate data from Benson's group has been chosen (see Table 8 and Figure 17).

Table 8. Rate Data on C_2H_2 Reaction with Cl

A	n	Ea	Reference		T	Method
			$C_2H_2 + Cl = C_2H + H_2$ (/\H=26700)			
1.58E14	0.00	16900	[27] WEI/BEN	(1984)	1260-1310	Calcul
1.00E14	0.00	27700	[56] BEN	(1989)	500-1500	Est
1.00E13	0.00	28800	[57] BBB	(1990)	300-1500	Calcul
1.00E14	0.00	27700	Recommended		300-1500	

CHAPTER 5
CONCLUSIONS

This study evaluated and analyzed theoretically the rate constants of C_2H_6, C_2H_4, and C_2H_2 reactions with OH, O, H, and Cl important to incineration based on detailed selection of accurate experimental measurement data and QRRK analysis.

(1). Hydrogen abstraction reactions from C_2H_6 by OH, O, H, and Cl are important to decay of the C_2H_6.

(2). Under normal Hydrocarbon combustion conditions, the reaction consuming the majority of C_2H_4 is H abstraction by OH. Addition-rearrangement-decomposition channels are not important. The reactions where O, H, and Cl abstract H from C_2H_4 contribute C_2H_4 consumption.

(3). Addition-rearrangement-decomposition channels are very important for OH and O reactions with C_2H_2.

(4). Recommended rate constants can be applied to model research.

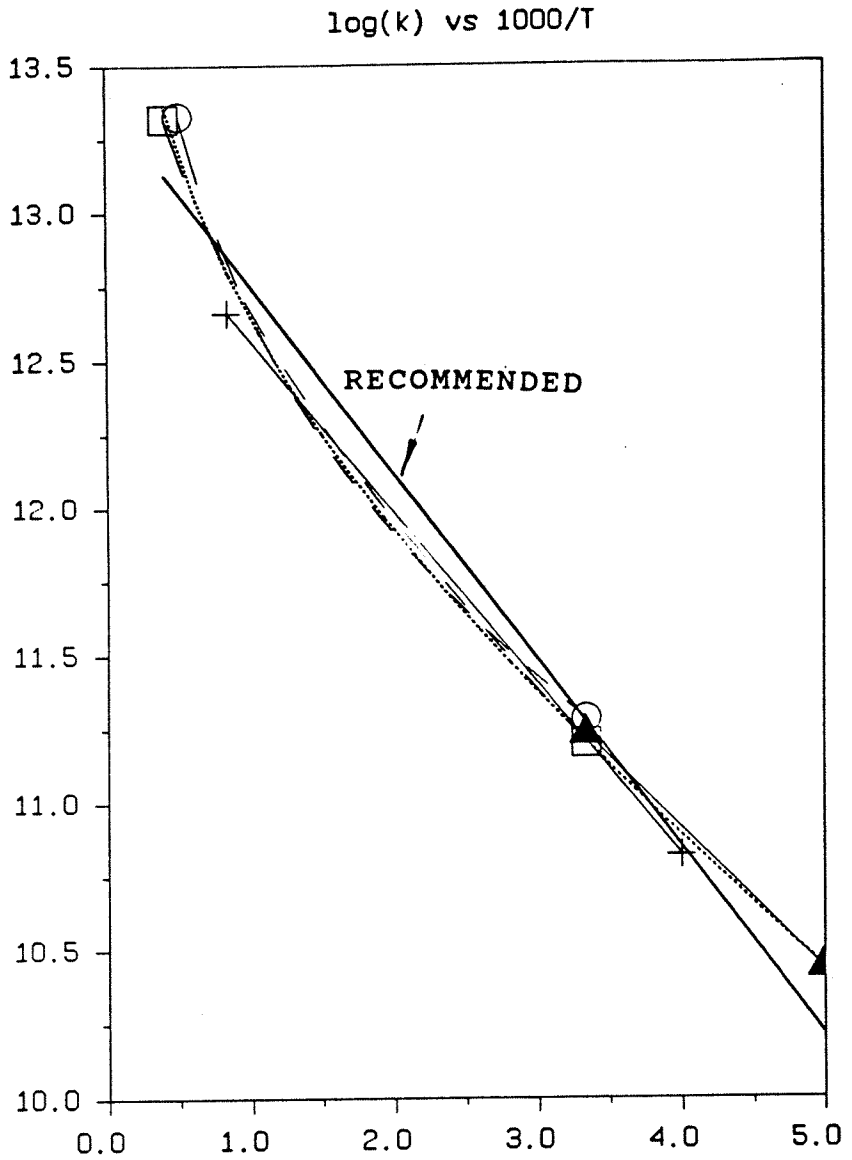

Figure 1. Rate data on OH + C2H6 => H2O + C2H5

+ 86BAU/BOW □ 86TSA/HAM
○ 84WAR ▲ 87DEM/GOL

RECOMMENDED DATA:

Temperature range: 200-2500

Linear fit:
A = 2.41e+13 $cm^3/(mol \cdot s)$
E_a= 2.90 kcal

Nonlinear fit:
A = 9.67e+08 $cm^3/(mol \cdot s)$
n = 1.33 E_a= 1.46 kcal

$k=AT^n exp(-E_a/RT)$

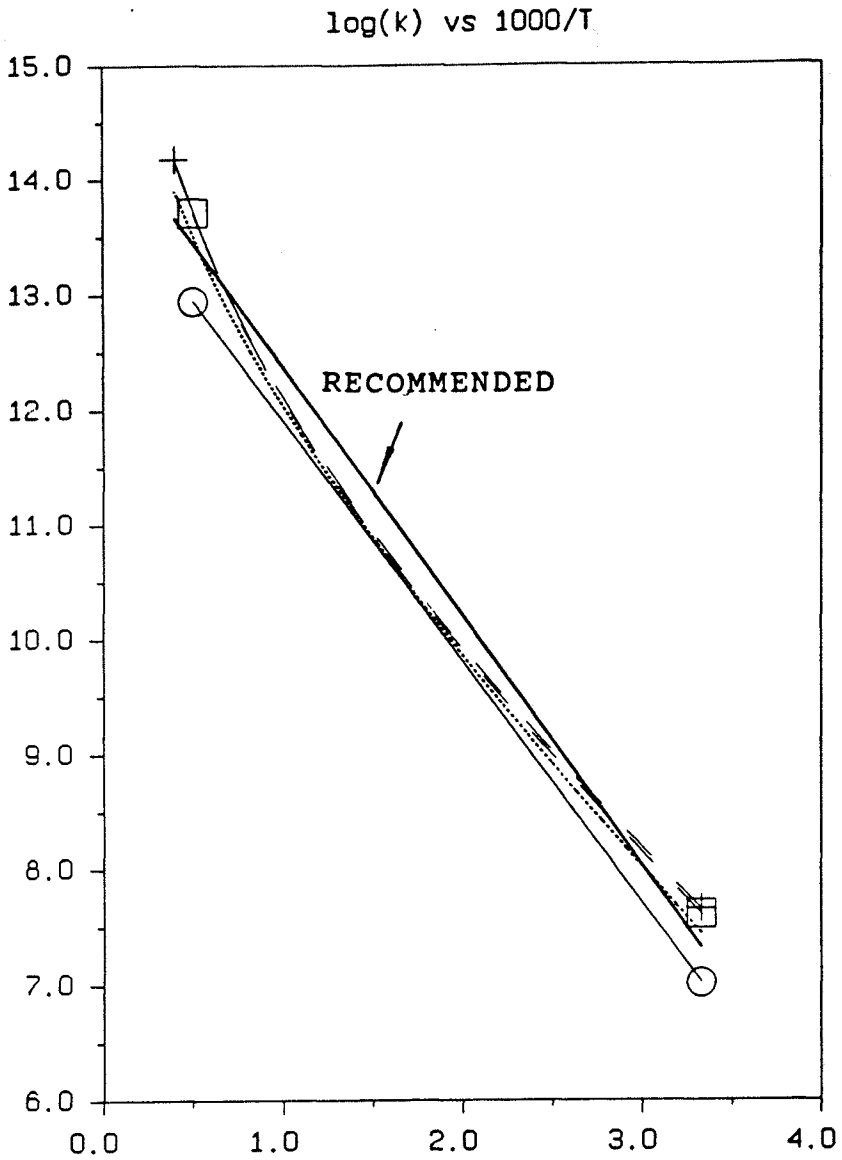

Figure 2. Rate data on H + C2H6 => H2 + C2H5

RECOMMENDED DATA:

Temperature range: 300-2500

Linear fit:

A = 3.46e+14 $cm^3/(mol \cdot s)$

E_a= 9.92 kcal

Nonlinear fit:

A = 3.24e+05 $cm^3/(mol \cdot s)$

n = 2.63 E_a= 6.30 kcal

$k=AT^n exp(-E_a/RT)$

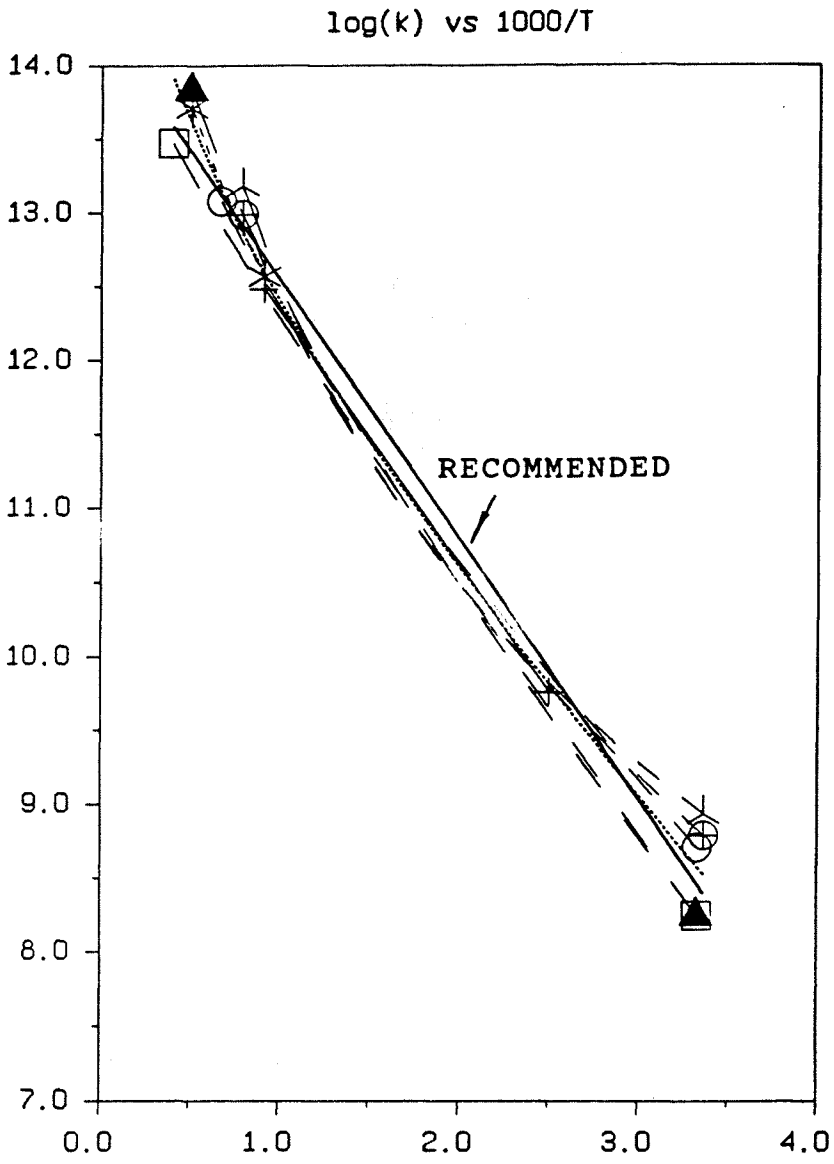

Figure 3. Rate data on O + C2H6 => OH + C2H5

+	88HER	□	86TSA/HAM
○	84WAR	▲	86COH/WES
✳	88HER	⅄	88MAH/MAR
⊕	88MAH/MAR		

RECOMMENDED DATA:
Temperature range: 297-2500

Linear fit:
A = 1.96e+14 $cm^3/(mol \cdot s)$
E_a= 8.02 kcal

Nonlinear fit:
A = 2.62e+07 $cm^3/(mol \cdot s)$
n = 2.05 E_a= 5.40 kcal

$k=AT^n exp(-E_a/RT)$

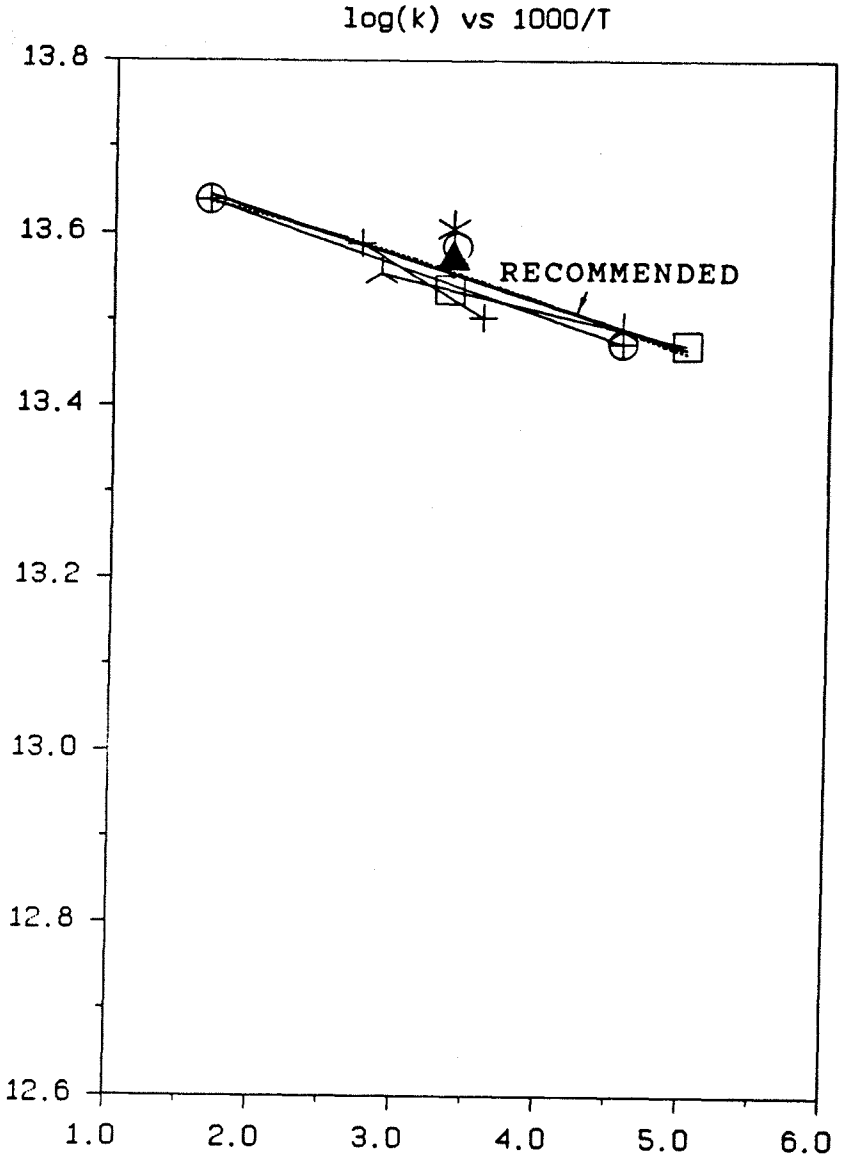

Figure 4. Rata data on Cl + C2H6 => HCl + C2H5

+	85TSC/NIE	□	87DEM/GOL
○	85ATK/ASC2	▲	87ATK/ASC5
✳	70DAV/BRA	⅄	89ATK/BAU
⊕	80LEW/SAN	◇	90DOB/BEN

RECOMMENDED DATA:
Temperature range: 200-604

Linear fit:
$A = 5.43e+13\ cm^3/(mol \cdot s)$
$E_a = 0.25\ kcal$

Nonlinear fit:
$A = 1.48e+14\ cm^3/(mol \cdot s)$
$n = -0.148\quad E_a = 0.34\ kcal$

$k = AT^n exp(-E_a/RT)$

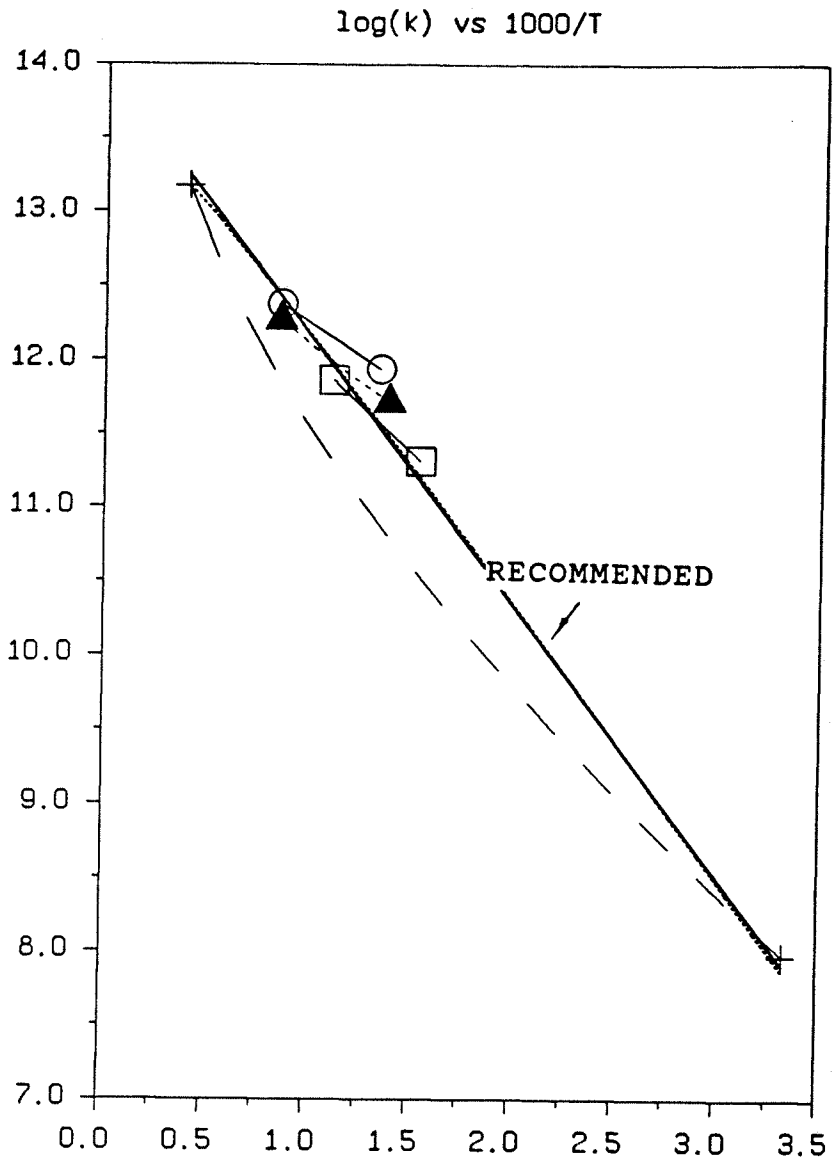

Figure 5. Rate data on OH + C2H4 => H2O + C2H3

RECOMMENDED DATA:

Temperature range: 300-2500

Linear fit:
$A = 9.41e+13$ $cm^3/(mol \cdot s)$
$E_a =$ 8.33 kcal

Nonlinear fit:
$A = 1.49e+15$ $cm^3/(mol \cdot s)$
$n = -0.363$ $E_a =$ 8.80 kcal

$k = AT^n exp(-E_a/RT)$

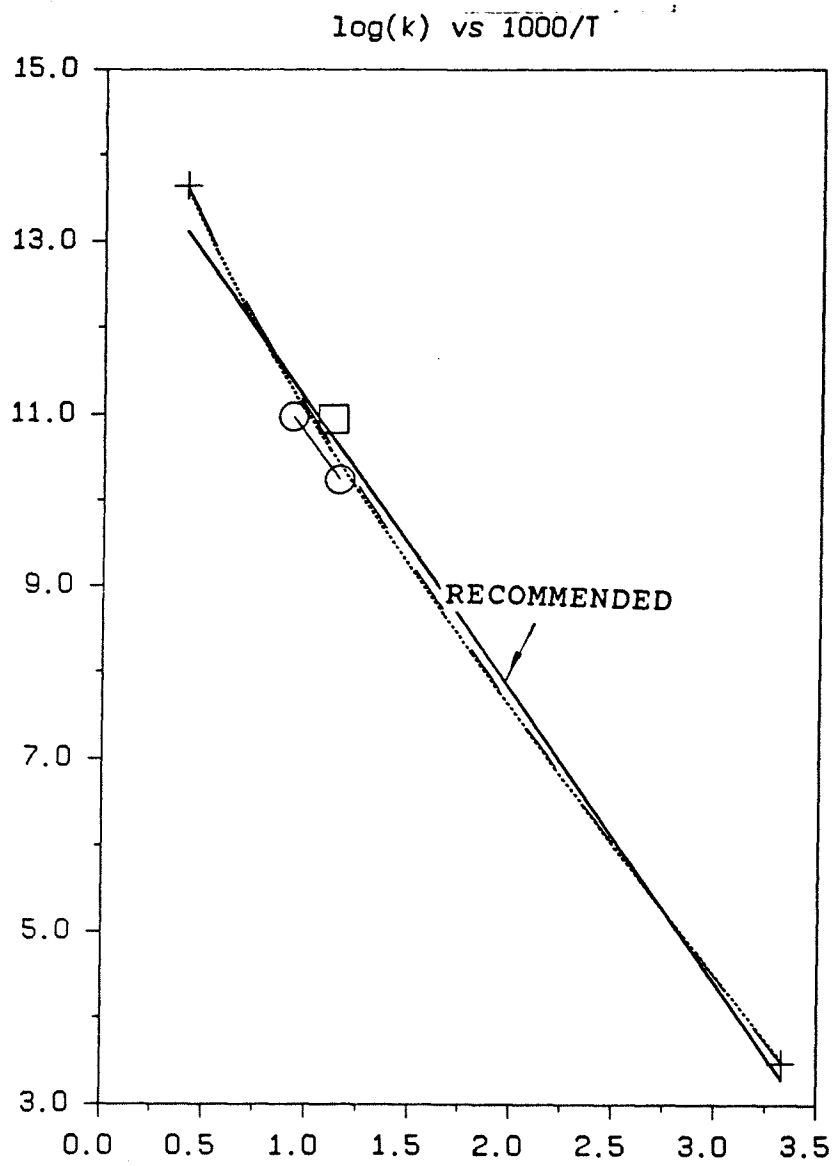

Figure 6. Rate data on H + C2H4 => H2 + C2H3

10 86TSA/HAM 12 88JAY/PAC

13 88MAN/LOU

RECOMMENDED DATA:

Temperature range: 300-2500

Linear fit:

$A = 2.95e+14$ $cm^3/(mol \cdot s)$

$E_a = 15.4$ kcal

Nonlinear fit:

$A = 2.48e+05$ $cm^3/(mol \cdot s)$

$n = 2.72$ $E_a = 11.9$ kcal

$k = AT^n exp(-E_a/RT)$

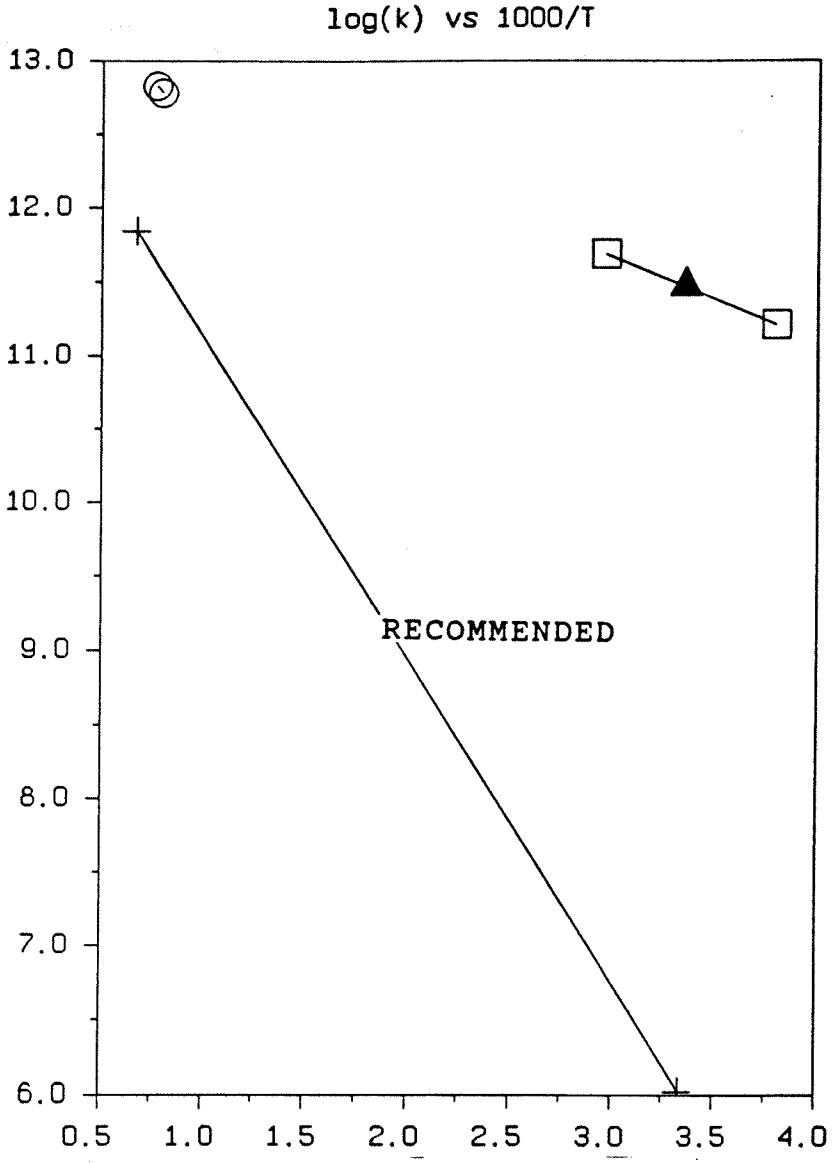

Figure 7. Rate data on Cl + C2H4 => HCl + C2H3

RECOMMENDED DATA:

Temperature range: 300-1500

Linear fit:

A = 2e+13 $cm^3/(mol \cdot s)$

E_a= 10.00 kcal

$k=AT^n exp(-E_a/RT)$

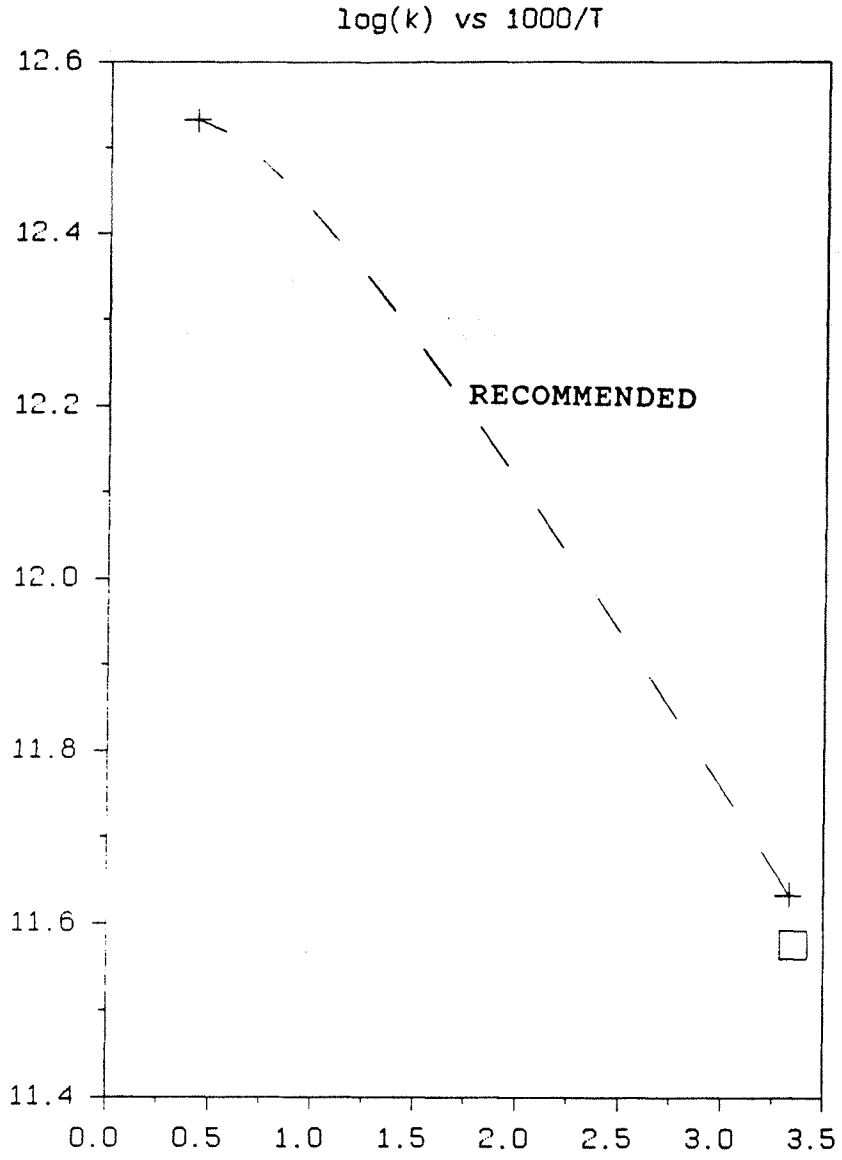

Figure 8. Rate date on O + C2H4 => CH2CHO + H

+ 92YU/BOZ □ 83SRI/KAU

RECOMMENDED DATA:

Temperature range: 300-2400

Linear fit:
A = 4.83e+12 $cm^3/(mol \cdot s)$
E_a= 1.41 kcal

Nonlinear fit:
A = 7.77e+13 $cm^3/(mol \cdot s)$
n = -0.35 E_a= 1.91 kcal

$k=AT^n exp(-E_a/RT)$

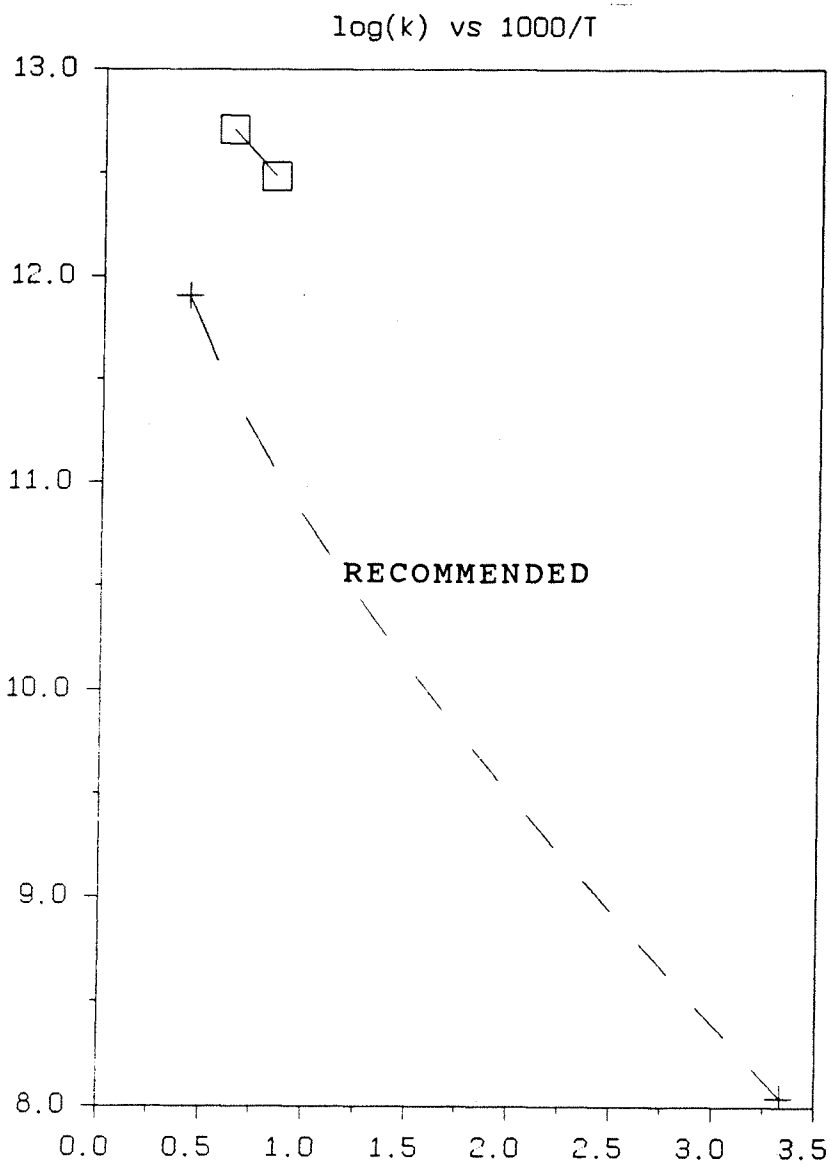

Figure 9. Rate data on O + C2H4 => CH2 + CH2O

+ 92YU/BOZ □ 73PEE/MAH2

RECOMMENDED DATA:

Temperature range: 300-2400

Linear fit:
A = 2.31e+12 $cm^3/(mol \cdot s)$
E_a= 6.09 kcal

Nonlinear fit:
A = 6.5e+06 $cm^3/(mol \cdot s)$
n = 1.61 E_a= 3.79 kcal

$k=AT^n exp(-E_a/RT)$

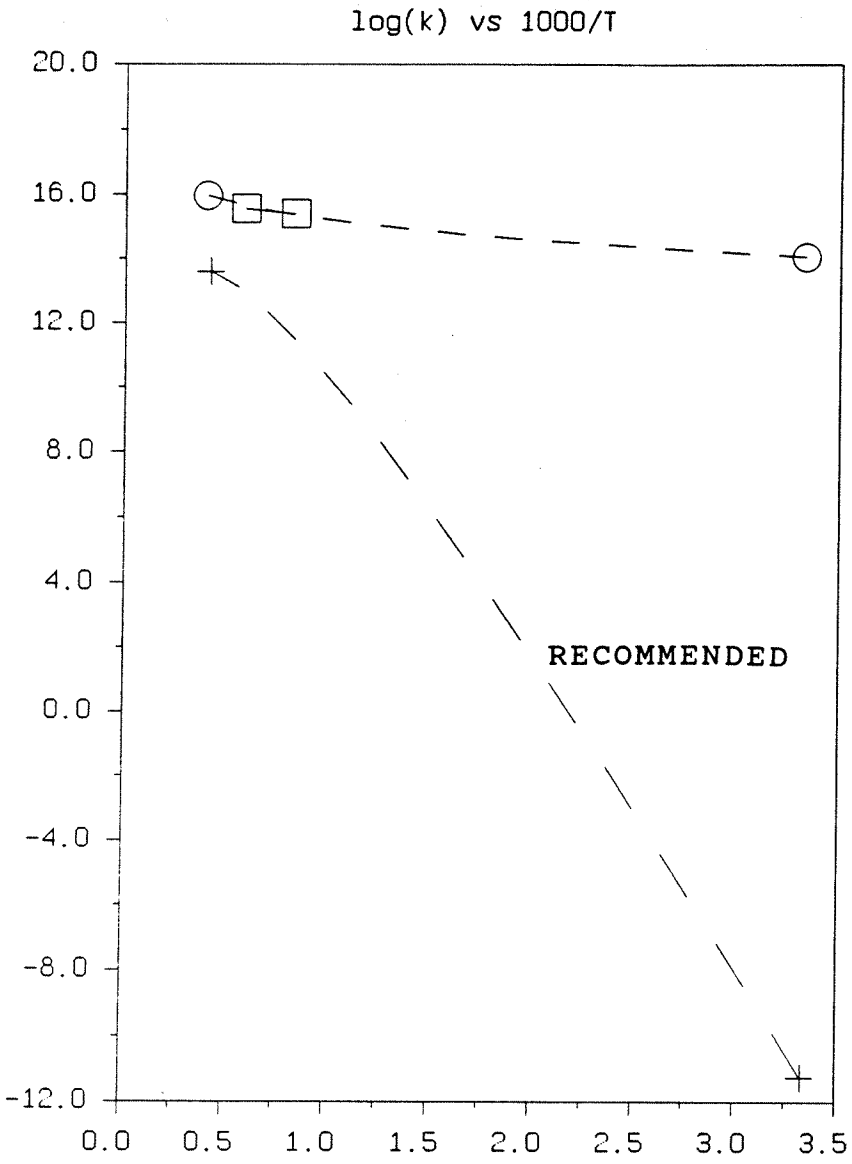

Figure 10. Rate data on O + C2H4 => CH3 + CHO

+ 92YU/BOZ □ 73PEE/MAH2
○ 86TSA/HAM

RECOMMENDED DATA:

Temperature range: 300-2400

Linear fit:
A = 8.06e+14 $cm^3/(mol \cdot s)$
E_a= 35.3 kcal

Nonlinear fit:
A = 2.25e+41 $cm^3/(mol \cdot s)$
n = -7.67 E_a= 46.3 kcal

$k=AT^n exp(-E_a/RT)$

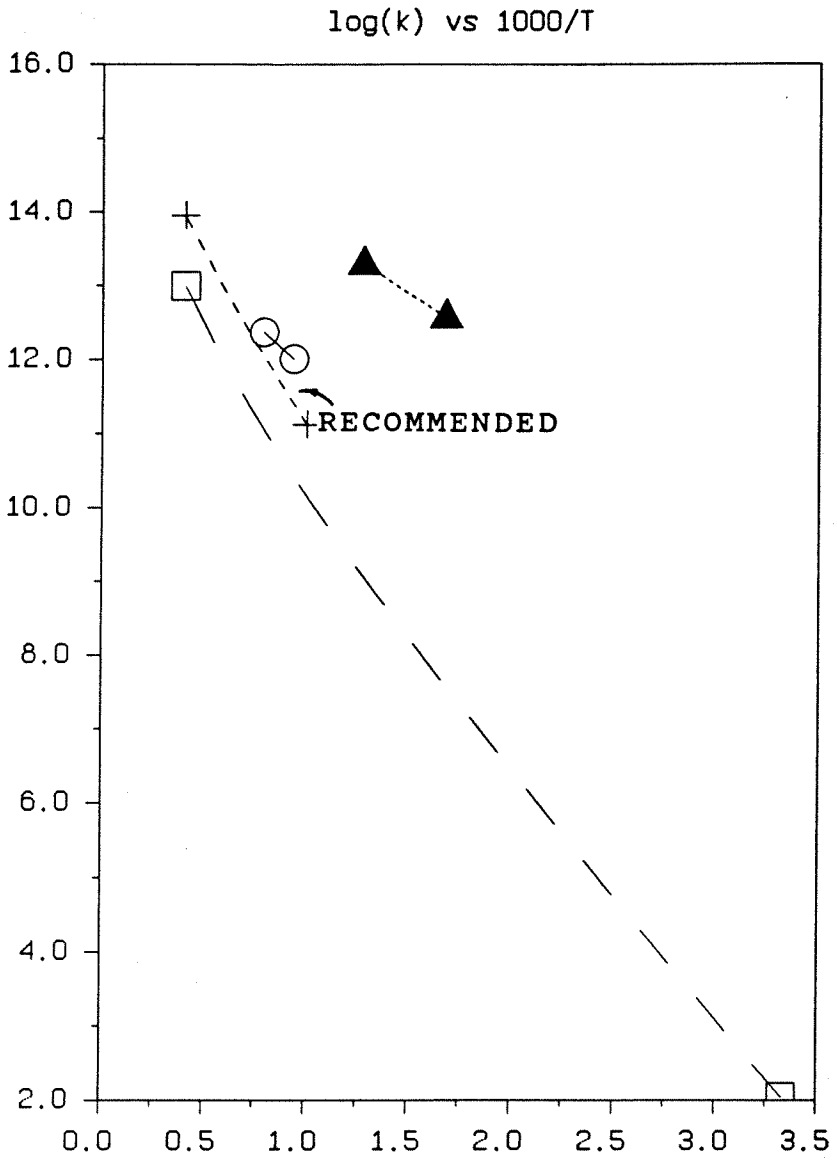

Figure 11. Rate data on OH + C2H2 => C2H + H2O

+ 89MIL/BOW □ 86TSA/HAM
○ 88LIU/MUL2 ▲ 49AVR/LOR

RECOMMENDED DATA:

Temperature range: 1000-2500

Linear fit:
A = 6.74e+14 $cm^3/(mol \cdot s)$
E_a= 20.1 kcal

Nonlinear fit:
A = 3.37e+07 $cm^3/(mol \cdot s)$
n = 2 E_a= 14.0 kcal

$k=AT^n exp(-E_a/RT)$

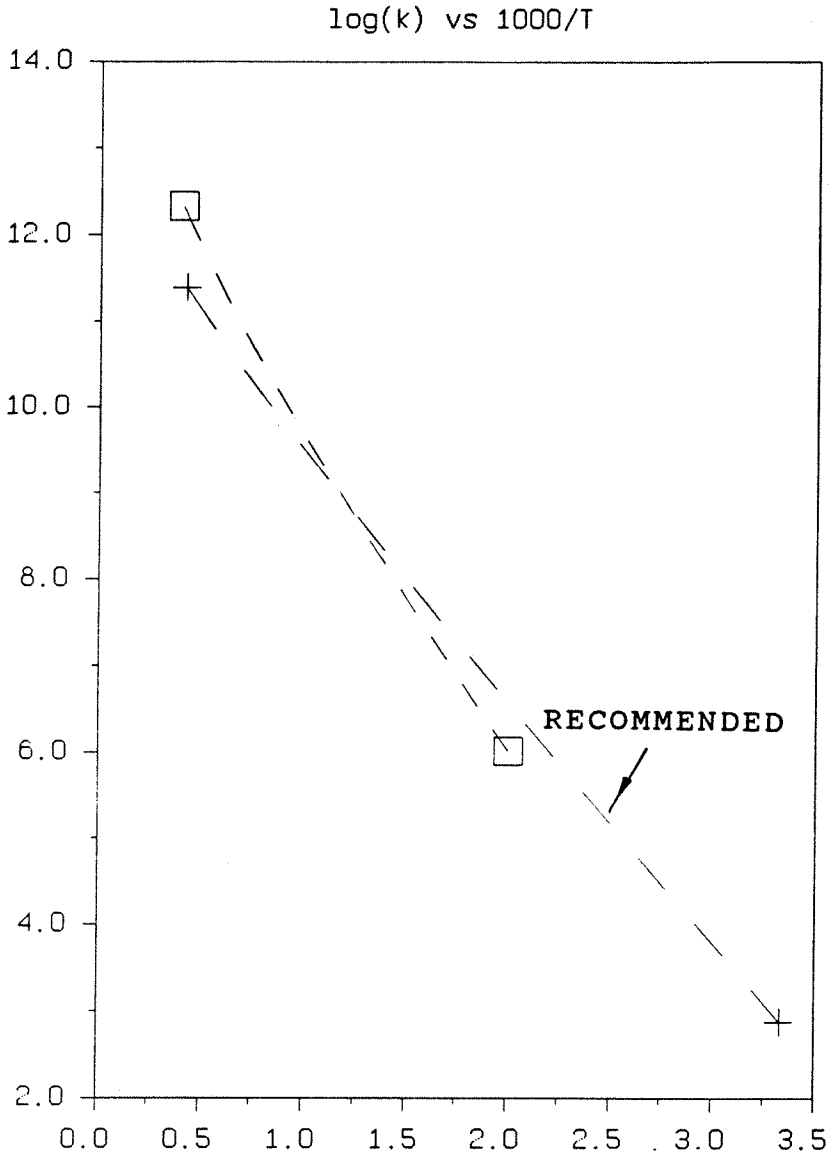

Figure 12. Rate data on OH + C2H2 => HOCCH + H

RECOMMENDED DATA:

Temperature range: 300-2400

Linear fit:
A = 3.59e+12 $cm^3/(mol \cdot s)$
E_a= 13.4 kcal

Nonlinear fit:
A = 9.31e+08 $cm^3/(mol \cdot s)$
n = 1.04 E_a= 11.9 kcal

$k=AT^n exp(-E_a/RT)$

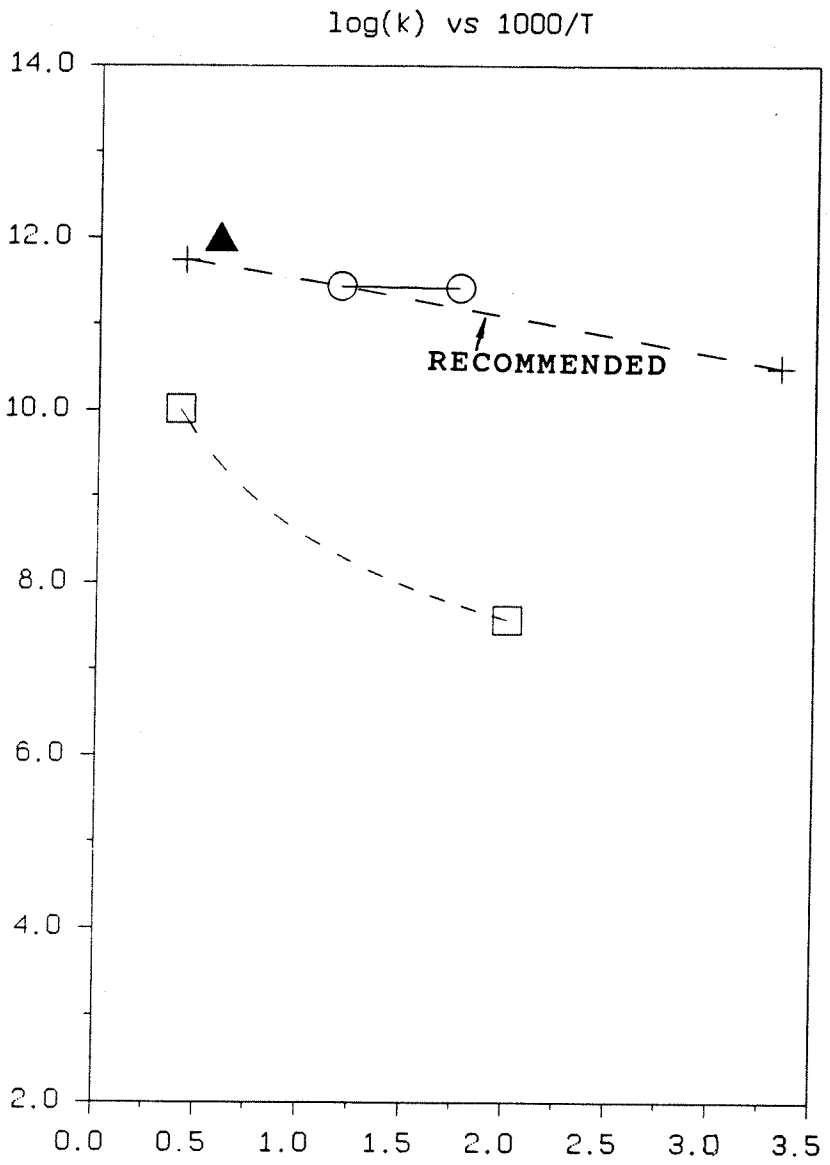

Figure 13. Rate data on OH + C2H2 => CH2CO + H

+ 92YU/BOZ □ 89MIL/BOW

○ 77VAN/VAN ▲ 90KAI

RECOMMENDED DATA:

Temperature range: 300-2400

Linear fit:

$A = 8.56e+11$ $cm^3/(mol \cdot s)$

$E_a = 1.96$ kcal

Nonlinear fit:

$A = 1.75e+12$ $cm^3/(mol \cdot s)$

$n = -0.09$ $E_a = 2.09$ kcal

$k = AT^n exp(-E_a/RT)$

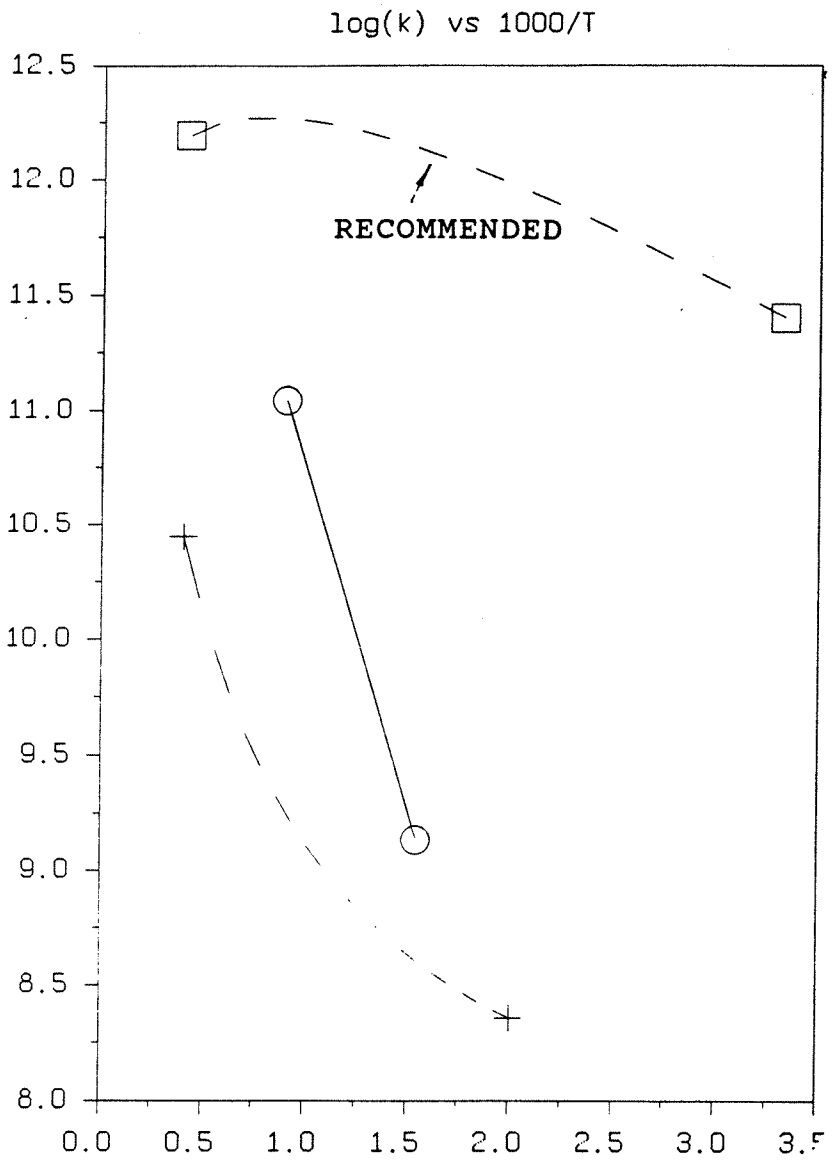

Figure 14. Rate data on OH + C2H2 => CH3 + CO

RECOMMENDED DATA:

Temperature range: 300-2400

Linear fit:

$A = 2.38e+12$ $cm^3/(mol \cdot s)$

$E_a =$ 1.23 kcal

Nonlinear fit:

$A = 1.73e+16$ $cm^3/(mol \cdot s)$

$n = -1.12$ $E_a =$ 2.83 kcal

$k = AT^n exp(-E_a/RT)$

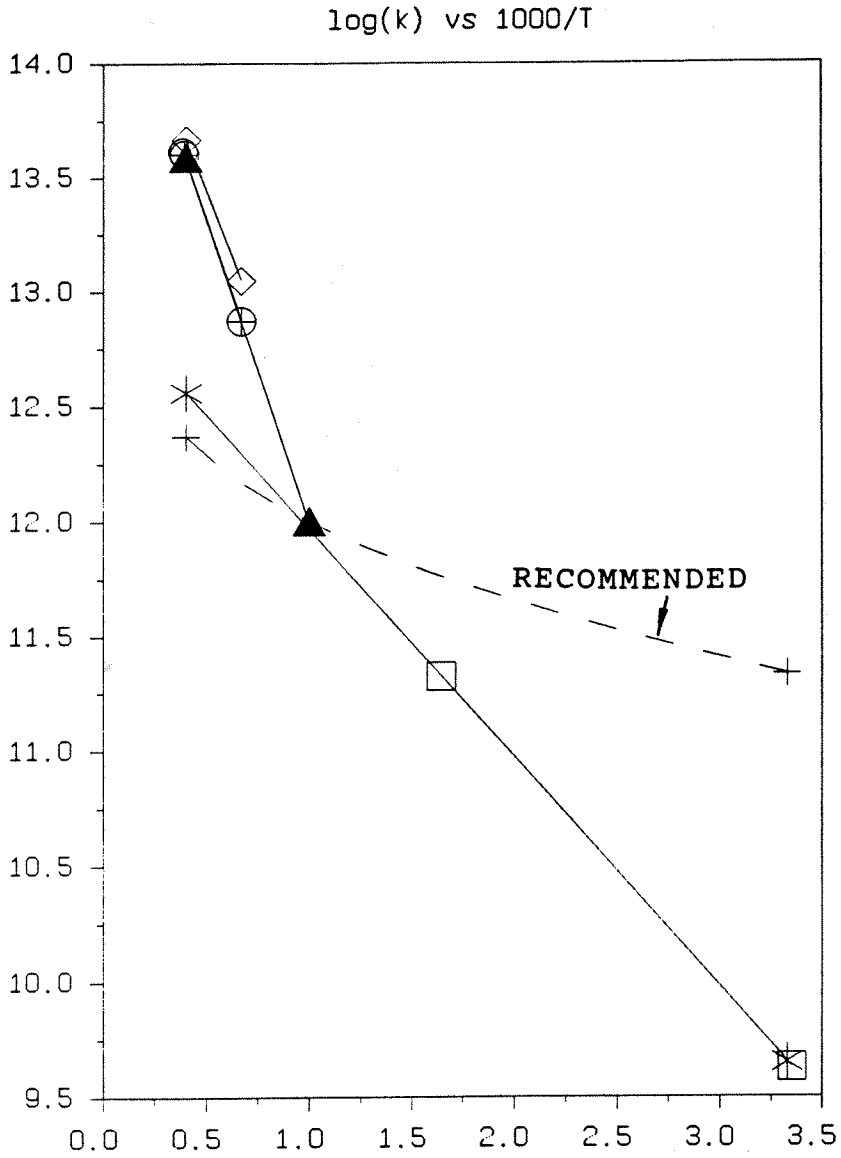

Figure 15. Rate data on O + C2H2 => HCCO + H

+	92YU/BOZ	□	81ALE/ARU
○	82ROT/LOE2	▲	87CVE
✳	86TSA/HAM	⅄	84WAR
⊕	81LOH/ROT	◇	88FRA/BHA

RECOMMENDED DATA:

Temperature range: 300-2500

Linear fit:

$A = 2.89e+12\ cm^3/(mol \cdot s)$

$E_a = 1.62$ kcal

Nonlinear fit:

$A = 7.95e+09\ cm^3/(mol \cdot s)$

$n = 0.74$ $E_a = 0.55$ kcal

$k = AT^n exp(-E_a/RT)$

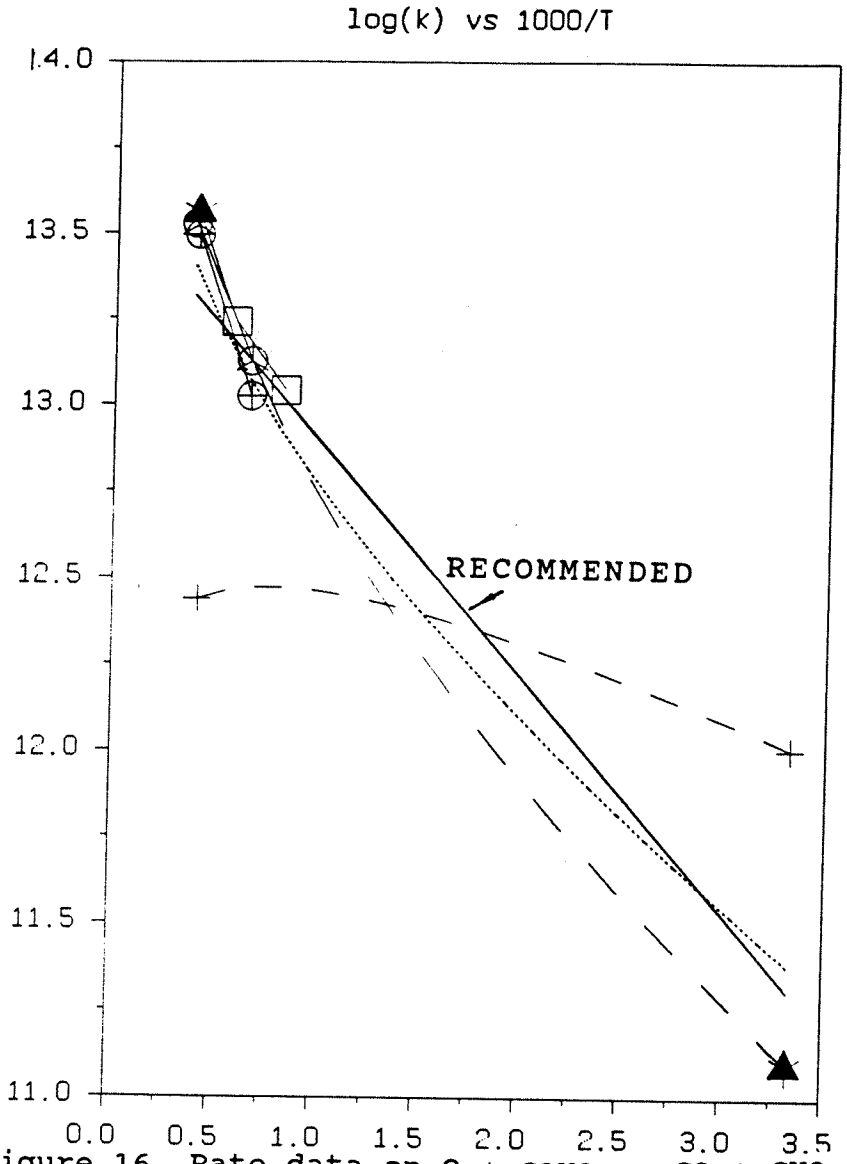

Figure 16. Rate data on O + C2H2 => CO + CH2

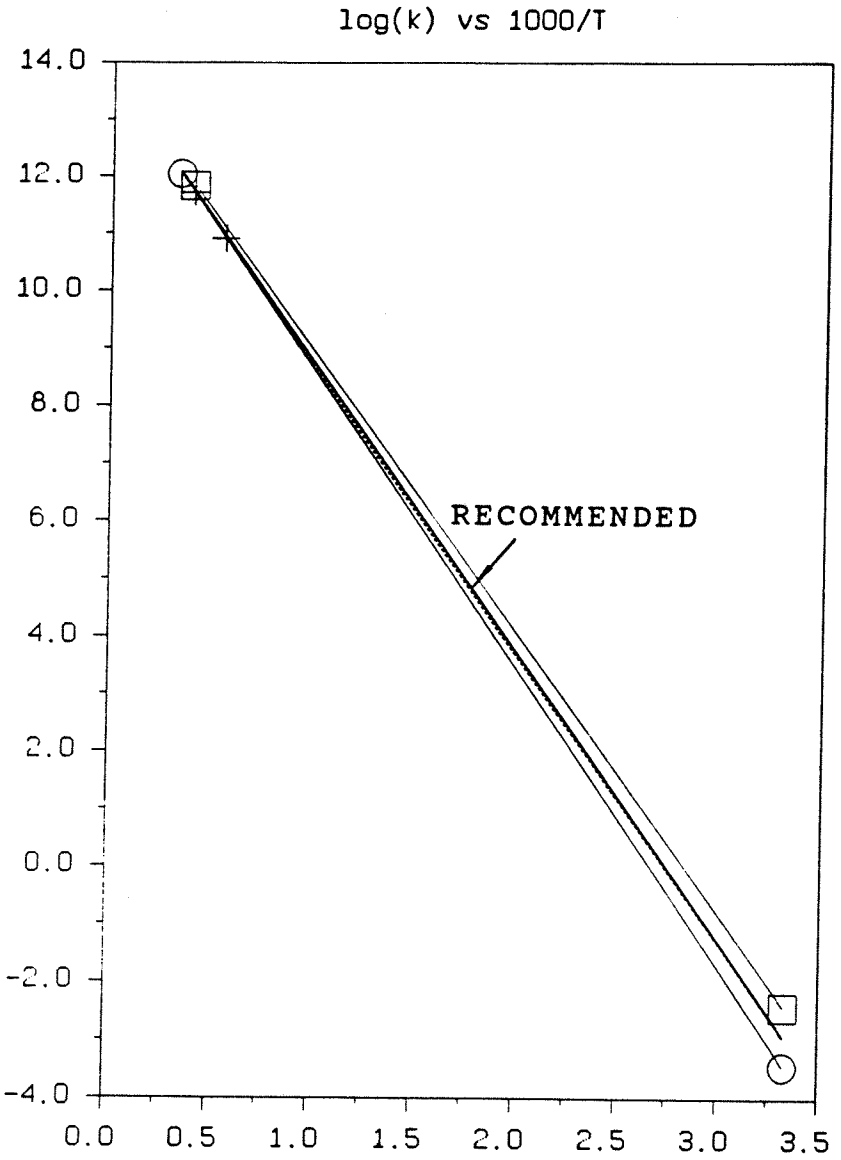

Figure 17. Rate data on H + C2H2 => H2 + C2H

\+ 85GAR/TAN □ 86TSA/HAM

○ 84WAR

RECOMMENDED DATA:

Temperature range: 300-3000

Linear fit:

A = 5.51e+13 $cm^3/(mol \cdot s)$

E_a= 22.9 kcal

Nonlinear fit:

A = 3.91e+12 $cm^3/(mol \cdot s)$

n = 0.327 E_a= 22.4 kcal

$k=AT^n exp(-E_a/RT)$

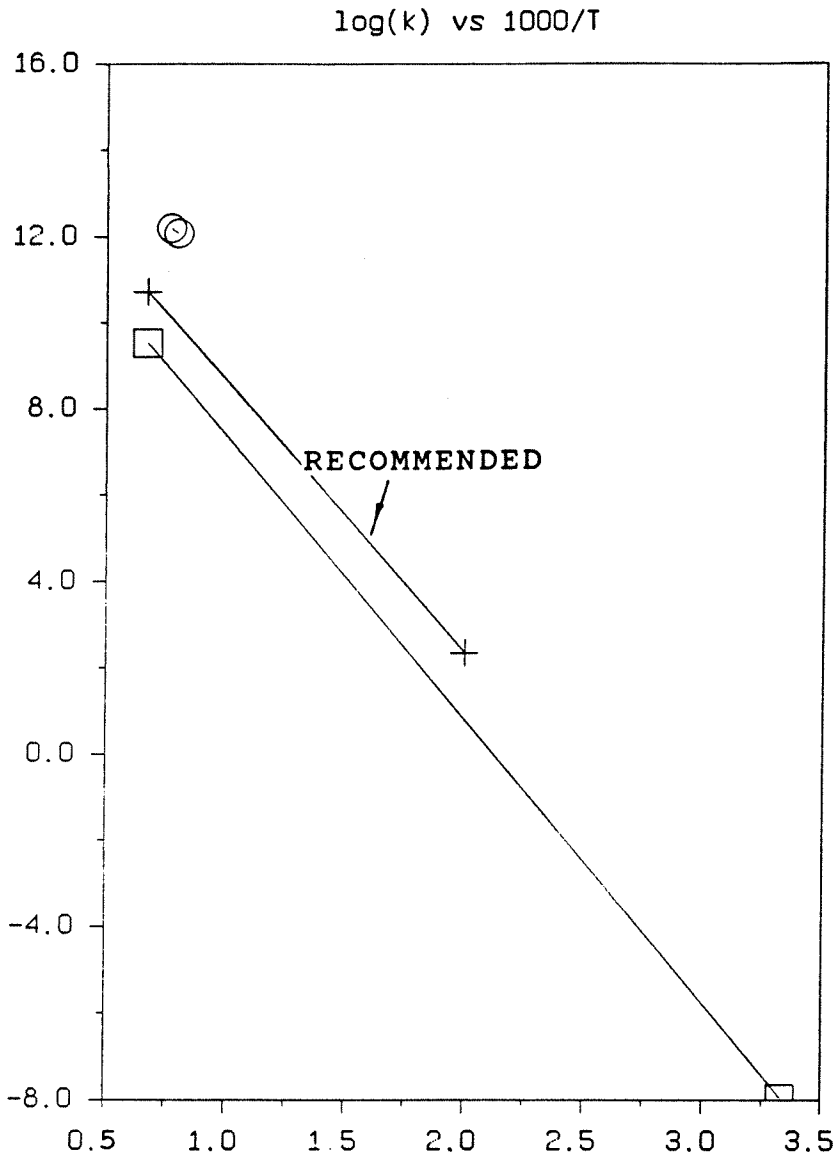

Figure 18. Rate data on Cl + C2H2 => HCl + C2H

RECOMMENDED DATA:

Temperature range: 500-1500

Linear fit:

A = 1e+14 $cm^3/(mol \cdot s)$

E_a = 27.7 kcal

$k = AT^n exp(-E_a/RT)$

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