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Thermodynamic and kinetic analysis on $Cl_2 + RCl$ -- $Cl_2 + R$.reactions, $CH_3C_jO + O_2 =$ products and $C_jCHO + O_2 =$ products

Jongwoo Lee

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ABSTRACT

THERMODYNAMIC AND KINETIC ANALYSIS ON Cl. + RCl \leftrightarrow Cl₂ + R. REACTIONS, CH₃C_jO + O₂ \Rightarrow PRODUCTS AND C_jCHO + O₂ \Rightarrow PRODUCTS

by
Jongwoo Lee

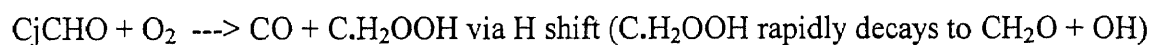
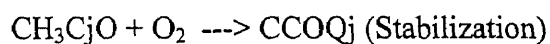
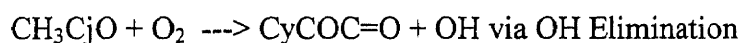
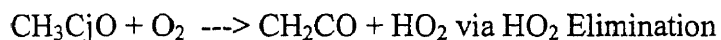
Thermodynamic Parameters, $\Delta H_{f(298)}^{\circ}$, $S_{(298)}^{\circ}$ and $C_p(T)$ are evaluated for C₁ and C₂ chlorocarbon molecules and radicals. These thermodynamic properties are used in evaluation and comparison of R. + Cl₂ \Rightarrow R-Cl + Cl. (defined forward direction) reaction rate constants from the kinetics literature. Data from some 20 reactions in the literature show linearity on a plot of $E_{a\text{fwd}}$ vs. $\Delta H_{\text{rxn},\text{fwd}}$, yielding a slope of (0.38 ± 0.04) and intercept of (10.10 ± 0.77) kcal/mole. Thermodynamic properties ($\Delta H_{f(298)}^{\circ}$, $S_{(298)}^{\circ}$ and $C_p(T)$ from 300 to 1500 K) for reactants, adducts, transition states, and products in reactions of CH₃ and C₂H₅ with Cl₂ are calculated using CBSQ//MP2/6-311G(d,p). Evaluated thermodynamic property data are presented for all isomers of the stable molecules CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄, C₂H₅Cl, C₂H₄Cl₂, C₂H₃Cl₃, C₂H₂Cl₄, C₂HCl₅, C₂Cl₆, C₂H₃Cl, C₂H₂Cl₂, C₂HCl₃, and C₂Cl₄. Evaluated thermodynamic property data are also presented for the alkyl radicals, (including isomers) C•H₂Cl, C•HCl₂, C•Cl₃, C₂H₄Cl•, C₂H₃Cl₂•, C₂H₂Cl₃•, C₂HCl₄•, and C₂Cl₅•, for the olefin radicals (including isomers) C₂H₂Cl•, C₂HCl₂•, and C₂Cl₃•.

Thermodynamic property and chemical kinetic analysis are performed on reactants, intermediates, transition states and products from reactions of the two radicals resulting

via H atom abstraction from acetaldehyde: $\text{CH}_3\text{C}_j\text{O}$ and C_jCHO with molecular oxygen.

Density functional and *ab initio* calculations are utilized to estimate thermodynamic properties: $\Delta H_f^\circ_{298}$, S°_{298} , and $C_p^\circ(T)$ 300 – 1500K. Rate constants are estimated as a function of temperature and pressure using QRRK analysis for $k(E)$ and modified strong collision analysis for fall-off for application to atmospheric and combustion kinetic modeling.

The important reaction paths are determined as:



**THERMODYNAMIC AND KINETIC ANALYSIS ON
Cl. + RCl \leftrightarrow Cl₂ + R. REACTIONS,
CH₃C_jO + O₂ \Rightarrow PRODUCTS AND C_jCHO + O₂ \Rightarrow PRODUCTS**

**by
Jongwoo Lee**

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Submitted to the Faculty of
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APPROVAL PAGE

**THERMODYNAMIC AND KINETIC ANALYSIS ON
Cl. + RCl \leftrightarrow Cl₂ + R. REACTIONS,
CH₃CjO + O₂ \Rightarrow PRODUCTS AND CjCHO + O₂ \Rightarrow PRODUCTS**

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To my beloved family

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PART I

**THERMODYNAMIC AND KINETIC ANALYSIS ON Cl ATOM
ABSTRACTIONS OF CHLORINE FROM HALOCARBONS AND REVERSE
ALKYL ABSTRACTIONS FROM Cl₂: Cl + RCl <--> Cl₂ + R.**

CHAPTER 1

ABSTRACT FOR PART ONE

Thermodynamic Parameters, $\Delta H_{f(298)}^{\circ}$, $S_{(298)}^{\circ}$ and $C_p(T)$ are evaluated for small, C_1 and C_2 chlorocarbon molecules and radicals. These thermodynamic properties are used in evaluation and comparison of $R + Cl_2 \Rightarrow R-Cl + Cl$. (defined forward direction) reaction rate constants from the kinetics literature. Data from some 20 reactions in the literature show linearity on a plot of $E_{a, fwd}$ vs. $\Delta H_{rxn, fwd}$, yielding a slope of (0.38 ± 0.04) and intercept of (10.10 ± 0.77) kcal/mole. A correlation of average Arrhenius pre-exponential factor for $RCl + Cl \Rightarrow R + Cl_2$ (reverse rxn) of $(4.44 \pm 1.58) \times 10^{13}$ cm³/mol-sec on a per chlorine basis is obtained with $E_{a, Rev} = (0.64 \pm 0.04) * \Delta H_{rxn, Rev} + (9.70 \pm 0.79)$, where $E_{a, Rev}$ is 0.0 if $\Delta H_{rxn, Rev}$ is more than 15.2 kcal/mole exothermic.

Thermodynamic properties ($\Delta H_{f(298)}^{\circ}$, $S_{(298)}^{\circ}$ and $C_p(T)$ from 300 to 1500 K) for reactants, adducts, transition states, and products in reactions of CH_3 and C_2H_5 with Cl_2 are calculated using CBSQ//MP2/6-311G(d,p). Molecular structures and vibration frequencies are determined at the MP2/6-311G(d,p), with single point calculations for energy at QCISD(T)/6-311+G(d,p), MP4(SDQ)/CbsB4 and MP2/CBSB3 levels of calculation. Vibration frequencies are scaled by 0.9748 for zero point energies. Contributions of rotational frequencies for $S_{(298)}^{\circ}$ and $C_p(T)$'s are calculated based on rotational barrier heights and moments of inertia using the method of Pitzer and Gwinn's¹.

CHAPTER 2

INTRODUCTION FOR PART ONE

High chlorinated solvents such as CH_2Cl_2 , CHCl_3 , CCl_4 , C_2Cl_4 , C_2HCl_3 , $\text{C}_2\text{H}_3\text{Cl}_3$'s and fluoro chloro-carbon solvents or chemicals are in widespread use in the chemical, pharmaceutical and cleaning industries. The monomers are also present in a number of valuable and versatile polymers. The combustion, incineration or high temperature pyrolysis of these chlorocarbons includes reactions at or near surfaces and in liquids or polymers where oxygen is not present or is low in concentration. Chlorine atom abstraction of chlorine from the chlorocarbon is often the important chain propagation process in these systems; yet there is limited or almost no direct experimental kinetic information on these chlorine atom abstraction reactions. This is due to the Cl abstraction of Cl from R-Cl being endothermic, as the Cl-Cl bond is 57.8 kcal/mole, while a typical R-Cl bond energy ranges from 71 kcal/mole in CCl_4 to 95 or 98 in vinyl chloride and chlorobenzene, respectively. Most chlorocarbons also have a hydrogen which is readily abstracted by Cl atoms, where the rate constants have high Arrhenius pre-exponential factors ($> 10^{13}$) and little or no energies of activation. (ca 1.0 kcal/mole if thermo neutral or exothermic) Cl abstraction of halogens is also important in designed pyrolysis and oxidation experiments, where hydrogen is limited or not present. These chlorocarbon oxidation or pyrolysis with no hydrogen source, are not practical for incineration; but have value in modeling because the presence of hydrogen adds an order of magnitude complexity to the models (number of species, and reaction product

permutations). Pyrolysis of trichloroethylene, for example, shows extensive molecular weight growth products such as hexachloro-benzene, pentachloro-butadiene, etc which likely result from radical processes.² The radical intermediates present in oxidation and pyrolysis of high chlorine to hydrogen ratio thermal processes result from Cl atom elimination, beta scission and from Cl atom abstraction of Cl reactions.

We estimate kinetic data for these $\text{Cl} + \text{RCl} \Rightarrow \text{Cl}_2 + \text{R}$. reactions in this study by assembling and evaluating thermodynamic property data : $\Delta H_{f(298)}^\circ$, $S_{(298)}^\circ$, and $\text{Cp}(T)$ on chlorocarbon and several fluoro chlorocarbon molecules and radicals. We use the thermochemical properties with available literature data on the abstractions of Cl from Cl_2 by alkyl radicals and microscopic reversibility to evaluate trends in the forward and reverse rate constants.

Thermodynamic properties ($\Delta H_{f(298)}^\circ$, $S_{(298)}^\circ$) and $\text{Cp}(T)$ from 300 to 1500 K) for reactants, adducts, transition states, and products in reactions of CH_3 and C_2H_5 with Cl_2 , are determined using CBSQ//MP2/6-311G(d,p) *ab initio* calculations and kinetic predictions compared with evaluated data.

CHAPTER 3

METHOD FOR PART ONE

3.1 Thermodynamic Properties

Evaluated thermodynamic parameters : $\Delta H^\circ_{f(298)}$, $S^\circ_{(298)}$, and $C_p(300)$ to $C_p(1500)$ for species in the reaction schemes are listed in Table 1.2 along with literature references. Some enthalpies of chlorocarbon (C_1 and C_2) radicals are from literature data and calculations using isodesmic reactions: for example $C.H_2CH_2Cl$ is from a calculated ΔH_{rxn} for $(CH_3CH_3 + C.H_2CH_2Cl \Rightarrow CH_3CH_2Cl + C.H_2CH_3)$ and the known $\Delta H^\circ_{f(298)}$ for ethane, chloroethane and ethyl radical. Entropies and $C_p(T)$ values of C_2H_3 , C_2H_5 are from use of Hydrogen Bond Increment(HBI)³ method. The HBI group technique is based on known thermodynamic properties of the parent molecule and calculated changes that occur upon formation of a radical via loss of an H atom. The HBI incorporates changes in radical formation, that result from loss or changes in vibrational frequencies, internal rotations, spin degeneracy and mass.

3.2 Thermodynamic Analysis for the Reactions

Arrhenius pre exponential factors on a per chlorine basis, energies of activation and enthalpies of reaction, A_{Rev} , $A_{Rev}/Cl\#$, E_{aRev} and $\Delta H^\circ_{rxn, fwd}$ are calculated using literature reference data on the forward reactions A_f and E_{a_f} , the evaluated thermodynamic properties of reactants and products, and microscopic reversibility. Forward reaction direction is defined as $R. + Cl_2 \Rightarrow R-Cl + Cl.$. C_3H_5 , allyl radical and C_3H_3 , propargyl

radical have resonant structures each having two radical sites with near equal population at temperature of the experimental data, 500-700K. (Ref. 4 in Table 1.1) We assess these radical reactions with Cl₂ as occurring via both radical sites, and estimate similar rates. The experimental rate constant for the forward direction is multiplied by 0.5 to obtain the forward rate constant on a per radical site basis.

3.3 *Ab initio* Calculations on CH₃ and C₂H₅ Plus Cl₂ Reaction Systems

Thermodynamic properties ($\Delta H_{f(298)}^{\circ}$, $S_{(298)}^{\circ}$ and $C_p(T)$ from 300 to 1500 K) for reactants, adduct intermediates, transition states, and products in reactions of CH₃ and C₂H₅ with Cl₂ are calculated using the established CBSQ//MP2/6-311G(d,p) composite method of Petersson's research group⁴⁻⁶. The CBSQ calculation sequence is performed on the MP2/6-311G(d,p) geometry and followed by single point calculations at the theory level of QCISD(T)/6-311+G(d,p), MP4(SDQ)/CbsB4 and MP2/CBSB3 CBSExtrap=(Nmin=10,Pop).

3.4 Determination of Enthalpies of Formation ($\Delta H_{f(298)}^{\circ}$)

$\Delta H_{f(298)}^{\circ}$ for reactants and products in reactions of CH₃ and C₂H₅ with Cl₂ are from literature data (see Table 1.2). $\Delta H_{f(298)}^{\circ}$ for transition states and adducts in reactions of CH₃ and C₂H₅ with Cl₂ are calculated using total energies obtained by CBSQ//MP2/6-311G(d,p) and MP2/6-311G(d,p) level. Total energies are corrected by zero point vibrational energies (ZPVE) which are scaled by 0.9748 as recommended by Scott et al.⁷. Thermal correction 0 K to 298.15 K is calculated to estimate $\Delta H_{f(298)}^{\circ}$ at 298.15 K.⁸

3.5 Determination of Entropy ($S^0_{(298)}$) and Heat Capacities ($C_p(T)$'s, $300 \leq T/K \leq 1500$)

$S^0_{(298)}$ and $C_p(T)$'s for reactants and products in reactions of CH_3 and C_2H_5 with Cl_2 are from literature data (see Table 1.2). $S^0_{(298)}$ and $C_p(T)$'s for transition states and adducts in reactions of CH_3 and C_2H_5 with Cl_2 are calculated based on vibration frequencies and moments of inertia of the optimized MP2/6-311G(d,p) structures. Contributions of internal rotation for $S^0_{(298)}$ and $C_p(T)$'s are calculated based on rotational barrier heights, moments of inertia of the rotors, and Pitzer and Gwinn's¹ general treatment.

CHAPTER 4

RESULT AND DISCUSSION FOR PART ONE

4.1 Cl + RCl \rightleftharpoons Cl₂ + R. Reaction

4.1.1 Overall

Data for the 20 reference reactions are listed in Table 1.1. The average A_{fwd} for reaction

$\text{R} + \text{Cl}_2 \Rightarrow \text{R-Cl} + \text{Cl}$ (defined forward direction) is

$$A_{\text{fwd}} = (2.35 \pm 3.07) \times 10^{12} \text{ cm}^3/\text{mole-sec and}$$

$$E_{a_{\text{fwd}}} = (0.38 \pm 0.04) * \Delta H_{\text{rxn,fwd}} + (10.10 \pm 0.77) \text{ kcal/mole.}$$

Figure 1.1 shows the data and the correlation with several exclusions noted. A correlation for the average Arrhenius pre-exponential factor for $\text{RCl} + \text{Cl} \Rightarrow \text{R} + \text{Cl}_2$ (reverse rxn) of

$A_{\text{rev}} = (4.44 \pm 1.58) \times 10^{13} \text{ cm}^3/\text{mol-sec}$ on a per chlorine basis is obtained with

$$E_{a_{\text{Rev}}} = (0.64 \pm 0.04) * \Delta H_{\text{rxn,Rev}} + (9.70 \pm 0.79),$$

where $E_{a_{\text{Rev}}}$ is 0.0 if ΔH_{rxnRev} is more than 15.2 kcal/mole exothermic.

4.1.2 Hydrocarbons

Reactions involving only hydrocarbons are selected and data are listed in Table 1.1 and shown in Figure 1.2. Data for CH_3 , C_2H_5 , C_3H_5 and C_3H_7 (Isopropyl, tertiary butyl and C_2H_3 radicals are excluded.) show a slope leading to

$$E_{a_{\text{fwd}}} = (0.39 \pm 0.11) * \Delta H_{\text{rxn,fwd}} + (10.49 \pm 2.21) \text{ kcal/mole and}$$

$$\text{Average } A_{\text{fwd}} = (5.89 \pm 2.48) \times 10^{12} \text{ cm}^3/\text{mole-sec.}$$

Table 1.1 Cl₂ + Radicals -----> Products + Cl

REACTIONS		A _{fwd} *	Ea _{fwd} *	A _{Rev} **	A _{Rev} /Cl#	Ea _{Rev} **	ΔH ^o _{rxn,fwd} **	P(torr)	T (K)	Reference*
<HYDROCARBONS>										
1.	Cl ₂ + CH ₃ -----> CH ₃ Cl + Cl	3.02E+12	0.53	2.99E+13	2.99E+13	26.10	-25.50	1.9-2.8	296-712	9
2.	Cl ₂ + C ₂ H ₅ -----> C ₂ H ₅ Cl + Cl	7.59E+12	-0.30	8.51E+13	8.51E+13	26.66	-27.18	1.7-2.2	295-498	9
3.	Cl ₂ + i-C ₃ H ₇ *** -----> i-C ₃ H ₇ Cl + Cl	1.51E+13	-0.48	1.03E+15	1.03E+15	25.82	-26.80	1.4-1.9	295-498	9
4.	Cl ₂ + t-C ₄ H ₉ *** -----> t-C ₄ H ₉ Cl + Cl	2.40E+13	-0.01	4.04E+15	4.04E+15	26.37	-27.11	1.4-1.8	295-498	9
5.	Cl ₂ + C ₂ H ₃ -----> CH ₂ CHCl + Cl	5.25E+12	-0.48	4.49E+13	4.49E+13	37.10	-37.72	1.4-1.7	298-435	10
6.	Cl ₂ + C ₃ H ₅ -----> C ₃ H ₅ Cl + Cl	4.67E+12	4.30	1.58E+13	1.58E+13	16.52	-12.29	2.0-3.6	487-693	10
7.	Cl ₂ + C ₃ H ₃ -----> C ₃ H ₃ Cl + Cl	8.30E+12	6.70	7.00E+13	7.00E+13	20.01	-13.49	2.6-4.1	525-693	10
	(Avg.)	9.70E+12			7.59E+14		(not recommended)			
	If i-C ₃ H ₇ , t-C ₄ H ₉ , C ₂ H ₃ are excluded, (Avg.)	(5.89 +/- 2.48)E+12			(5.02 +/- 3.27)E+13					
<C₁ CHLOROCARBONS>										
8.	Cl ₂ + CH ₂ Cl -----> CH ₂ Cl ₂ + Cl	9.10E+11	0.98	4.83E+13	2.42E+13	22.87	-21.90	1.7-4.3	295-719	11
9.	Cl ₂ + CHCl ₂ -----> CHCl ₃ + Cl	5.18E+11	2.46	1.30E+14	4.34E+13	21.09	-18.78	1.8-4.6	357-719	11
10.	Cl ₂ + CCl ₃ -----> CCl ₄ + Cl	4.08E+11	5.26	6.00E+13	1.50E+13	17.91	-13.02	3.1	690-700	12
11.	Cl ₂ + CF ₃ -----> CF ₃ Cl + Cl	2.69E+12	3.60	1.83E+14	1.83E+14	30.55	-27.27	2.3-2.6	487-693	12
12.	Cl ₂ + CF ₂ Cl -----> CF ₂ Cl ₂ + Cl	7.76E+11	1.91	6.89E+13	3.44E+13	24.13	-22.56	1.8-2.9	376-626	12
13.	Cl ₂ + CFCl ₂ -----> CFCl ₃ + Cl	8.32E+11	3.35	4.74E+13	1.58E+13	20.12	-17.18	1.5-2.6	435-693	12
	(Avg.)	1.02E+12			5.26E+13		(not recommended)			
	If CF ₃ is excluded, (Avg.)	(6.89 +/- 2.15)E+11			(2.66 +/- 1.22)E+13					
<C₂ CHLOROCARBONS>										
14.	Cl ₂ + C ₂ Cl ₅ -----> C ₂ Cl ₆ + Cl	2.00E+11	5.50	2.17E+14	3.61E+13	19.04	-13.94	50	298-423	13
15.	Cl ₂ + CHCl ₂ CHCl -----> (CHCl ₂) ₂ + Cl	6.31E+11	2.70	4.92E+14	1.23E+14	21.39	-18.83	50	298-423	13
16.	Cl ₂ + CH ₂ CICCl ₂ -----> CH ₂ CICCl ₃ + Cl	6.92E+11	4.10	4.29E+14	1.07E+14	18.49	-14.66	50-300	298-321	14
17.	Cl ₂ + CH ₂ CICHCl -----> CH ₂ CICHCl ₂ + Cl	2.00E+12	2.00	1.05E+15	3.49E+14	22.47	-20.61	80-280	298-328	15-(1)
18.	Cl ₂ + CHCl ₂ CH ₂ -----> CH ₂ CICHCl ₂ + Cl	6.31E+11	0.90	5.37E+13	1.79E+13	27.09	-26.19	50	298-423	13
19.	Cl ₂ + CCl ₃ CHCl -----> CHCl ₂ CCl ₃ + Cl	3.16E+11	5.10	7.96E+13	1.59E+13	21.61	-16.47	50	298-423	13
20.	Cl ₂ + CHCl ₂ CCl ₂ -----> CHCl ₂ CCl ₃ + Cl	3.16E+11	5.10	1.96E+14	3.91E+13	16.88	-12.01	50	298-423	13
	(Avg.)	6.84E+11			9.83E+13		(not recommended)			
	If CH ₂ CICHCl is excluded, (Avg.)	(4.64 +/- 2.10)E+11			(5.65 +/- 4.65)E+13					
TOTALS		(TOTAL Avg.)	3.80E+12			3.03E+14	(not recommended)			
	If i-C ₃ H ₇ , t-C ₄ H ₉ , C ₂ H ₃ , CF ₃ , CH ₂ CICHCl are excluded, (Avg.)	(2.35 +/- 3.07)E+12			(4.44 +/- 1.58)E+13					

 UNITS :: A_{fwd} and A_{Rev} : cm³/(mole-sec)

 Ea and ΔH^o_{rxn,fwd} : kcal/mole

 A_{fwd} = (2.35 +/- 3.07)*10¹² cm³/(mole-sec)

 A_{Rev}(avg)/cl = (4.44 +/- 1.58)*10¹³ cm³/(mole-sec)

 (i-C₃H₇, t-C₄H₉, C₂H₃, CF₃, CH₂CICHCl are excluded in calc. of A_{fwd} and A_{Rev}(avg)/cl.)

 * : references for A_{fwd} and Ea_{fwd}

** : calculated from Thermodynamic Properties of reactants and products

- microscopic reversibility -

 *** : i-C₃H₇, t-C₄H₉ Symmetries = 162 & 18 respectively

Table 1.2 Evaluated Thermodynamic Property Data

SPECIES	Hf(298)	S(298)	Cp300	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500	REF(a)
CH3	34.82	46.38	9.26	10.05	10.82	11.54	12.89	14.09	16.29	JANAF(16)
TSC ₃ H ₃ XCl ₂	32.10	74.11	15.86	17.27	18.43	19.42	21.06	22.41	24.82	CBSQ(in this study)
CH ₃ Cl	-19.60	56.00	9.77	11.51	13.19	14.66	17.05	18.87	21.76	TRC(17)
C ₂ H ₅	29.30	57.42	11.89	14.57	16.95	19.09	22.76	25.66		LAY/BOZ95(3)
TSC ₂ H ₅ XCl ₂	24.20	84.10	19.94	22.96	25.60	27.84	31.46	34.25	38.82	CBSQ(in this study)
C ₂ H ₅ Cl	-26.80	66.01	15.03	18.57	21.61	24.22	28.37	31.44	36.16	JANAF(16)
i-C ₃ H ₇	21.02	70.39	16.58	20.27	24.03	27.49	33.13	37.52	44.37	LAY/BOZ95(3)
i-C ₃ H ₇ Cl	-34.70	73.41	20.85	25.88	30.48	34.34	40.33	44.92		WONG/BOZ(26)
t-C ₄ H ₉	11.90	75.67	22.33	27.04	31.82	36.27	43.62	49.34	58.53	LAY/BOZ95(3)
t-C ₄ H ₉ Cl	-44.13	76.42	26.66	33.67	39.89	45.02	52.53	57.84		WONG/BOZ(26)
C ₂ H ₃	71.64	53.79	10.10	11.93	13.57	14.97	17.22	18.95		LAY/BOZ95(3)
CH ₂ CHCl	5.00	63.08	12.89	15.56	17.80	19.61	22.35	24.35		LI/BOZ98(22)
C ₃ H ₅	40.75	62.05	14.87	18.66	21.88	24.63	28.95	32.10	36.78	LAY/BOZ95(3)
C ₃ H ₅ Cl	-0.46	73.31	18.14	22.12	25.51	28.40	32.94	36.28	41.45	SWS(20)
C ₃ H ₃	81.58	59.57	13.76	16.10	18.10	19.80	22.48	24.43	27.31	LAY/BOZ95(3)
C ₃ H ₃ Cl	39.17	68.78	17.26	20.10	22.45	24.39	27.33	29.42	32.62	TRC(17)
CH ₂ Cl	27.99	58.61	10.08	11.45	12.53	13.38	14.66	15.64	17.30	TAY/DEL91(18)
CH ₂ Cl ₂	-22.83	64.57	12.20	14.24	15.93	17.30	19.32	20.76	22.91	JANAF(16)
CHCl ₂	23.50	68.10	12.90	14.16	15.09	15.79	16.76	17.44	18.46	KAFAFI89(freq.)X(19)
CHCl ₃	-24.20	70.66	15.76	17.83	19.34	20.44	21.91	22.86		SWS(20)
CCl ₃	19.00	70.92	15.25	16.66	17.56	18.16	18.83	19.18	19.56	JANAF(16)
CCl ₄	-22.94	74.02	19.98	21.92	23.09	23.82	24.64	25.05	25.47	JANAF(16)
CF ₃	-113.01	63.42	11.93	13.68	15.05	16.09	17.46	18.22	19.07	JANAF(16)
CF ₃ Cl	-169.20	68.17	16.04	18.53	20.32	21.59	23.16	24.02	24.98	JANAF(16)
CF ₂ Cl	-66.02	67.72	13.17	14.73	15.93	16.83	17.98	18.59	19.25	RAYEZ94(21)
CF ₂ Cl ₂	-117.50	71.91	17.36	19.68	21.28	22.37	23.68	24.39	25.16	JANAF(16)
CFCl ₂	-21.60	69.17	14.02	15.42	16.49	17.28	18.26	18.77	19.34	RAYEZ94(21)
CFCl ₃	-67.70	74.07	18.71	20.84	22.22	23.13	24.19	24.74	25.33	TRC(17)
C ₂ Cl ₅	9.06	95.68	28.56	31.13	32.72	33.75	34.93	35.54	36.20	TRC(17)
C ₂ Cl ₆	-33.80	94.77	32.67	36.11	38.29	39.69	41.29	42.11		SWS(20)
CHCl ₂ CHCl	11.75	84.51	21.49	24.59	26.84	28.49	30.64	32.05	34.08	TRC(17)
C ₂ H ₂ Cl ₄	-36.00	84.86	23.74	27.67	30.65	32.89	35.99	38.01	40.66	TRC(17)
CH ₂ ClCCl ₂	7.87	84.56	21.39	24.09	26.15	27.70	29.95	31.50	33.77	TRC(17)
CH ₂ ClCCl ₃	-35.71	85.07	24.67	28.36	31.16	33.28	36.24	38.17	40.70	TRC(17)
CH ₂ ClCHCl	14.73	78.56	18.33	21.15	23.40	25.19	27.82	29.73	32.70	TRC(17)
CH ₂ ClCHCl ₂	-34.80	79.71	20.40	24.47	27.74	30.29	33.85	36.15	39.29	TRC(17)
CHCl ₂ CH ₂	20.31	74.64	18.95	21.99	24.28	26.05	28.54	30.31	33.01	TRC(17)
CCl ₃ CHCl	10.59	88.26	25.57	28.51	30.38	31.62	33.13	34.03	35.25	TRC(17)
CHCl ₂ CCl ₃	-34.80	91.18	28.30	31.96	34.52	36.34	38.64	40.17	41.99	TRC(17)
CHCl ₂ CCl ₂	6.13	90.65	23.88	26.74	28.78	30.23	32.15	33.32	34.89	TRC(17)

UNITS : Hf(kcal/mol), S(cal/K*mol), Cp(cal/K*mol) (a) : reference for Cp(T) and S only



	R.	$\Delta H^\circ_{\text{rxn,fwd}}$	$E_{a,\text{fwd}}$	Reference
1	CH ₃	-25.50	0.53	JANAF(16)
2	C ₂ H ₅	-27.18	-0.30	CIO/LIU97(23)
3	i-C ₃ H ₇	-26.80	-0.48	LAY/BOZ95(3)
4	t-C ₄ H ₉	-27.11	-0.01	LAY/BOZ95(3)
5	C ₂ H ₃	-37.32	-0.48	LAY/BOZ95(3)
6	C ₃ H ₅	-12.29	4.30	LAY/BOZ95(3)
7	C ₃ H ₃	-13.49	6.70	LAY/BOZ95(3)
8	CH ₂ Cl	-21.90	0.98	Seet98(24)
9	CHCl ₂	-18.78	2.46	ROUX/PAD87(25)
10	CCl ₃	-13.02	5.26	JANAF(16)
11	CF ₃	-27.27	3.60	JANAF(16)
12	CF ₂ Cl	-22.56	1.91	RAYEZ94(21)
13	CFCl ₂	-17.18	3.35	RAYEZ94(21)
14	C ₂ Cl ₅	-13.94	5.50	CIO/LIU97(23)
15	CHCl ₂ CHCl	-18.83	2.70	CIO/LIU97(23)
16	CH ₂ ClCCl ₂	-14.66	4.10	CIO/LIU97(23)
17	CH ₂ ClCHCl	-20.61	2.00	CIO/LIU97(23)
18	CHCl ₂ CH ₂	-26.19	0.90	CIO/LIU97(23)
19	CCl ₃ CHCl	-16.47	5.10	CIO/LIU97(23)
20	CHCl ₂ CCl ₂	-12.01	5.10	CIO/LIU97(23)

$$E_{a,\text{fwd}}(\text{R} + \text{Cl}_2 \rightarrow \text{RCl} + \text{Cl}) = (0.38 \pm 0.04) \Delta H^\circ_{\text{rxn,fwd}} + (10.10 \pm 0.77)$$

$$E_{a,\text{Rev}}(\text{RCl} + \text{Cl} \rightarrow \text{R} + \text{Cl}_2) = (0.64 \pm 0.04) \Delta H^\circ_{\text{rxn,Rev}} + (9.70 \pm 0.79)$$

if $\Delta H^\circ_{\text{rxn,Rev}} \leq -15.16$ $E_{a,\text{Rev}} = 0.0$

(* : i-C₃H₇, t-C₄H₉, C₂H₃, CF₃, CH₂ClCHCl are excluded.)

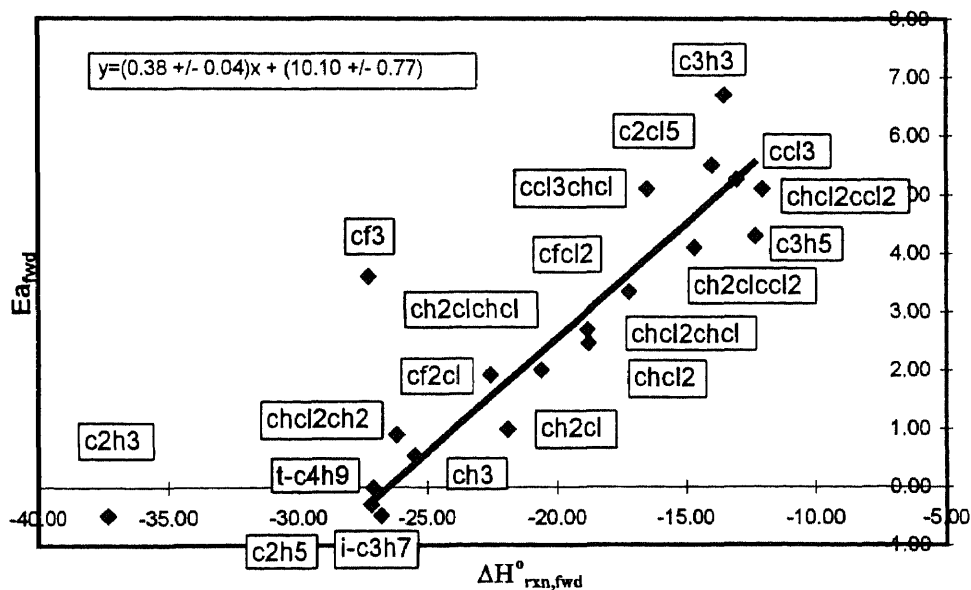


Figure 1.1 $E_{a,\text{fwd}}$ vs $\Delta H^\circ_{\text{rxn,fwd}}$

R.	$\Delta H^{\circ}_{\text{rxn,fwd}}$	$E_{a,\text{fwd}}$			
1	CH ₃	-25.50	0.53		
2	C ₂ H ₅	-27.18	-0.30		
				3	i-C ₃ H ₇
					-26.80
				4	t-C ₄ H ₉
					-27.11
				5	C ₂ H ₃
					-37.32
6	C ₃ H ₅	-12.29	4.30		
7	C ₃ H ₃	-13.49	6.70		

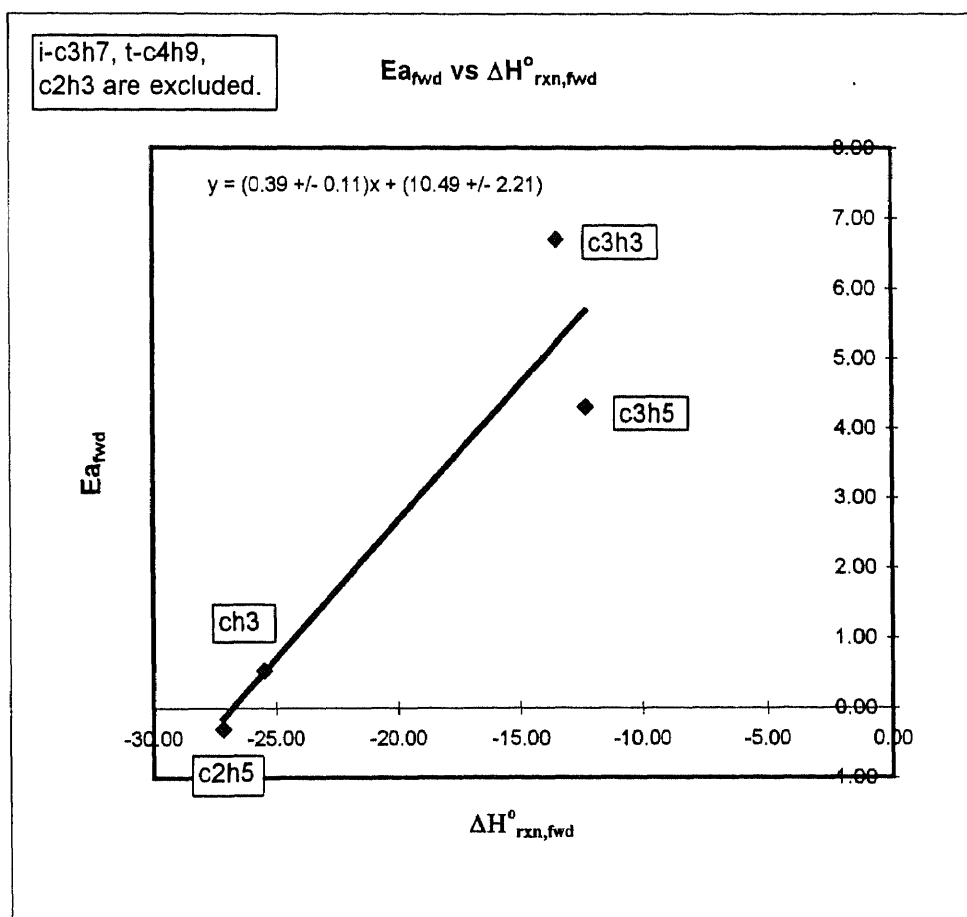


Figure 1.2 Hydrocarbons

Tertiary butyl, isopropyl and ethyl radicals show slightly negative E_a 's for the forward reactions. This may suggest adduct formation occurs before further reaction to $RCl + Cl$ products. The tertiary butyl and isopropyl radical reactions with Cl_2 are unusual. The literature values of Arrhenius pre-exponential factor show values of 1.5 and 2.4×10^{13} $cm^3/mol\text{-sec}$ respectively. Thermodynamic analysis of the reaction systems lead to calculated pre-exponential factors for reverse reaction of 1×10^{15} and 4×10^{15} $cm^3/mol\text{-sec}$ respectively; Approximately 2.5 to 10 times higher than the estimated collision rate at 300K. We have re-evaluated the thermodynamic properties of species in these reactions and do not find errors in entropy terms that can account for the unreasonably large reverse rate constants that are calculated. We choose to omit these reactions from our analysis.

4.1.3 C₁ Chlorocarbons

Data for C₁ chlorocarbons are shown in Table 1.1 and Figure 1.3. Data for CH_2Cl , $CHCl_2$, CCl_3 , CF_2Cl and $CFCl_2$ yield a slope leading to

$$E_{a_{fwd}} = (0.40 \pm 0.07) * \Delta H_{rxn,fwd} + (10.32 \pm 1.31) \text{ kcal/mole and}$$

$$\text{Average } A_{fwd} = (6.89 \pm 2.15) \times 10^{11} \text{ cm}^3/\text{mole}\text{-sec.}$$

The CF_3 value is considered an outlier and is excluded.

4.1.4 C₂ Chlorocarbons

Data for C₂ chlorocarbons are shown in Table 1.1 and Figure 1.4. Data for C_2Cl_5 , $CHCl_2CHCl$, CH_2ClCCl_2 , $CHCl_2CH_2$, CCl_3CHCl and $CHCl_2CCl_2$ show a slope resulting in $E_{a_{fwd}} = (0.33 \pm 0.07) * \Delta H_{rxn,fwd} + (9.46 \pm 1.17) \text{ kcal/mole and}$

R.	$\Delta H^\circ_{\text{rxn,fwd}}$	$E_{a,\text{fwd}}$
8 CH ₂ Cl	-21.90	0.98
9 CHCl ₂	-18.78	2.46
10 CCl ₃	-13.02	5.26
11 CF ₃	-27.27	3.58
12 CF ₂ Cl	-22.56	1.91
13 CFCl ₂	-17.18	3.35

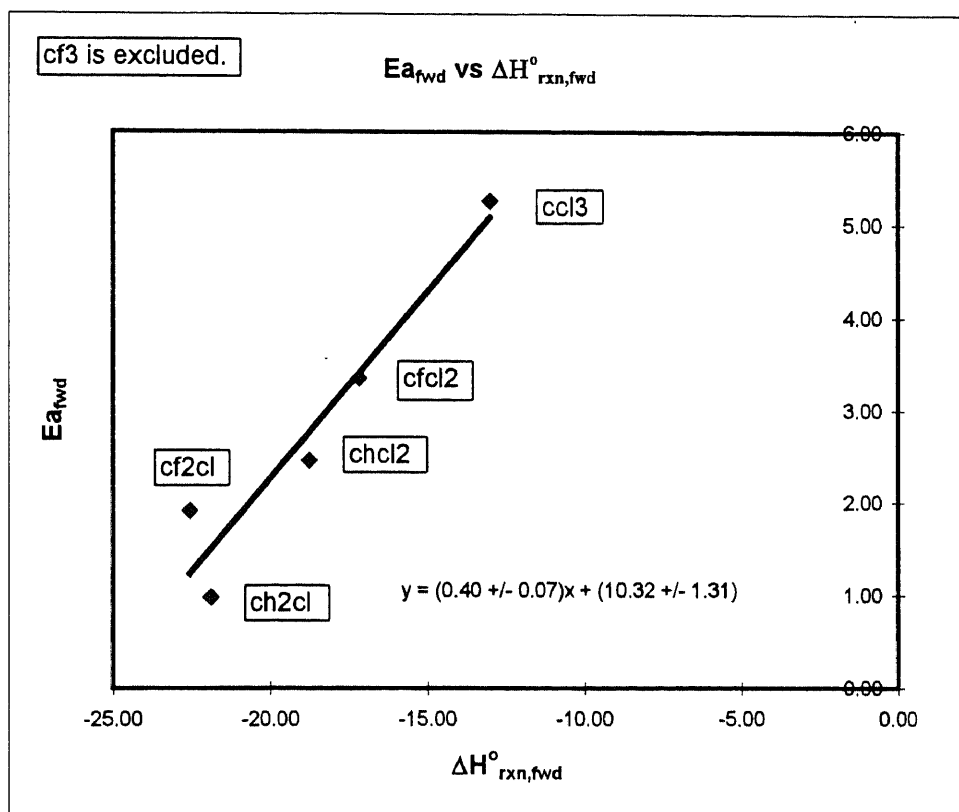


Figure 1.3 C₁ Chlorocarbons

R.	$\Delta H_{\text{rxn,fwd}}^{\circ}$	$E_{\text{a,fwd}}$
14 C2Cl5	-13.94	5.50
15 CHCl2CHCl	-18.83	2.70
16 CH2ClCCl2	-14.66	4.10
17 CH2ClCHCl	-20.61	2.00
18 CHCl2CH2	-26.19	0.90
19 CCl3CHCl	-16.47	5.10
20 CHCl2CCl2	-12.01	5.10

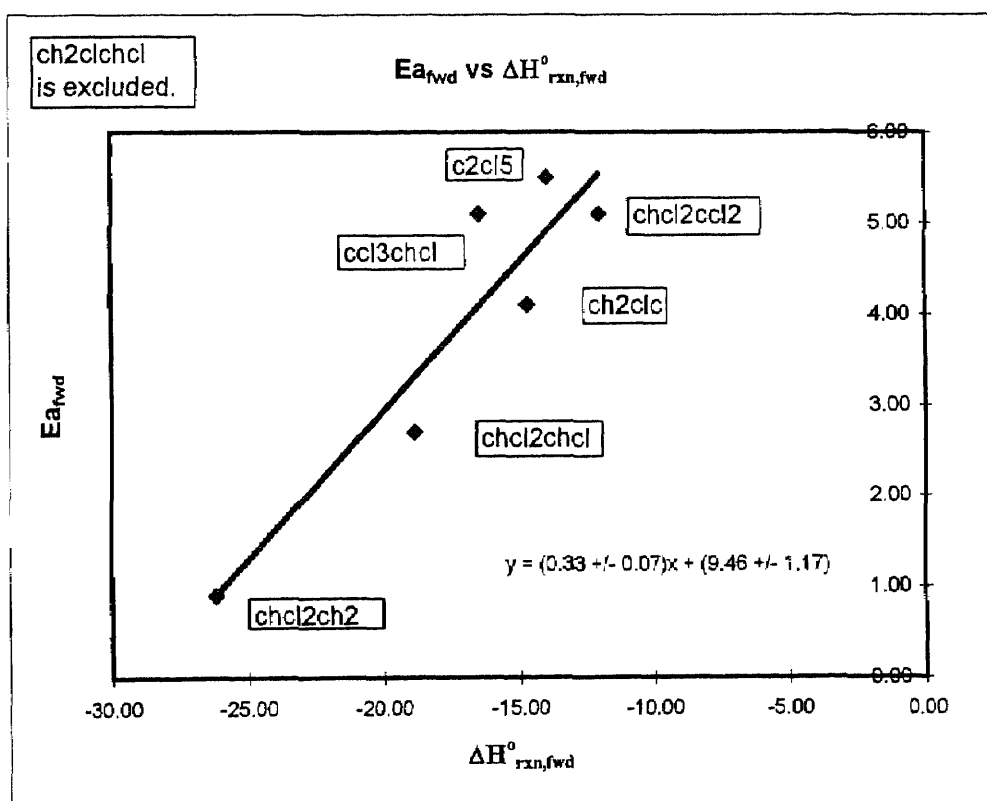


Figure 1.4 C₂ Chlorocarbons

Average $A_{\text{fwd}} = (4.64 \pm 2.10) \times 10^{11} \text{ cm}^3/\text{mole}\cdot\text{sec}$.

The CH_2ClCHCl value is considered an outlier and is excluded.

E_a 's for these reactions are determined by thermochemical analysis of experimental and theoretical data in the literature references (see Table 1.2).

4.1.5 Kinetic Trends

The more exothermic $\text{R} + \text{Cl}_2$ reactions ($\Delta H_{\text{fwd}}^{298} < -20 \text{ kcal/mole}$) are those which involve hydrocarbon free radicals; these are shown to have small activation energies (less than 1 kcal/mole) in Table 1.1. The calculated transition states in CH_3 and C_2H_5 reaction with Cl_2 in Table 1.1, have enthalpy values which are -2.7 and -5.1 kcal/mole relative to the reactants (at the CBSQ composite level), respectively, in these exothermic $\text{R} + \text{Cl}_2$ reactions. (Figure 1.5)

Timonen et al.¹⁰ studied the kinetics of the reactions of unsaturated hydrocarbon free radicals (vinyl, allyl, and propargyl) with molecular chlorine. They report the reactivities of C_3H_3 and C_3H_5 are significantly reduced below that of the vinyl radical in these Cl atom transfer reactions, and suggest the reduction is due entirely to the presence of energy barriers in reactions C_3H_3 and C_3H_5 . The Arrhenius preexponential factors of reactions C_2H_3 , C_3H_3 and C_3H_5 are all similar. They indicate that the relatively low exothermicities of reactions C_3H_3 and C_3H_5 ($\Delta H_{\text{fwd}}^{298} = -13.5$ and -12.3 kcal/mole , respectively) could account for the existence of the observed 4.3 - 6.7 kcal/mole activation energies.

Seetula²⁷ shows a linear correlation in a plot of the rate constants for $\text{R} + \text{Cl}_2$ reactions at 500K vs. Δ electronegativity of the radical species R. He suggests this results from a

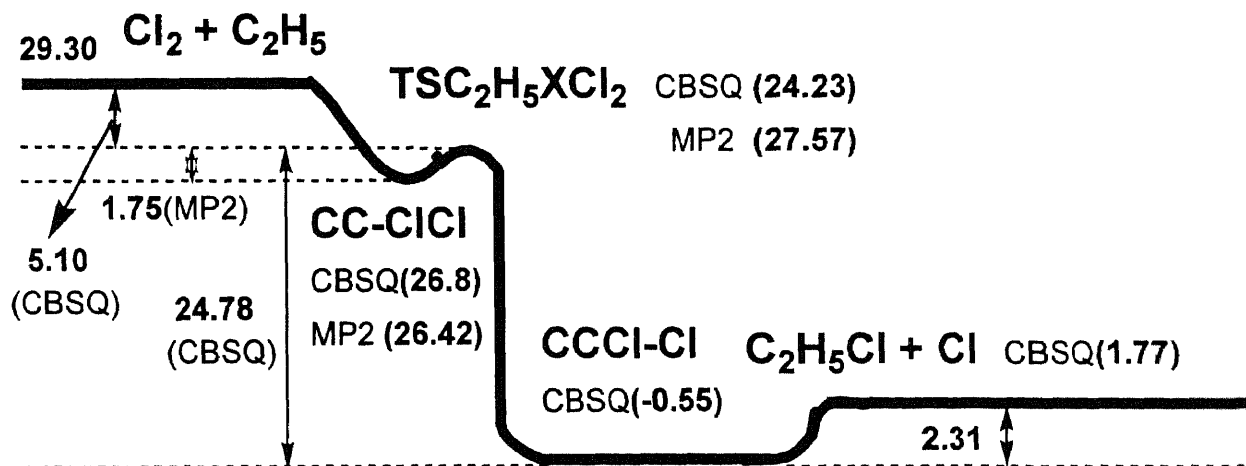
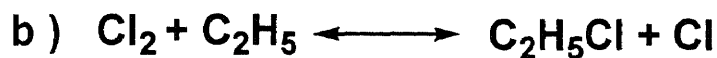
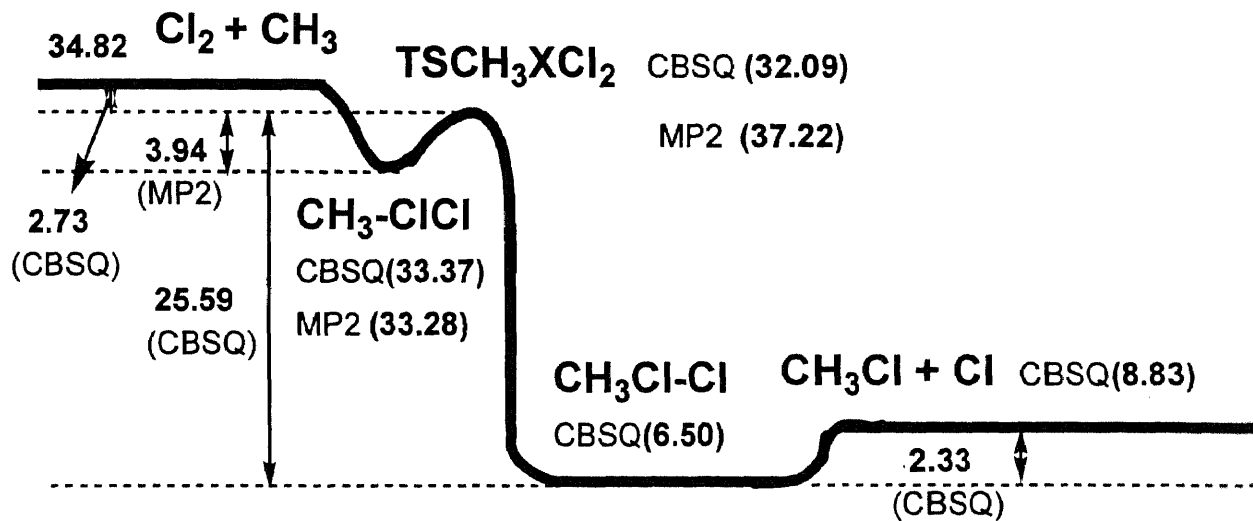
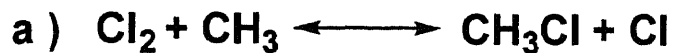


Figure 1.5 Reaction path diagrams in CH_3 with Cl_2 and C_2H_5 with Cl_2

polar transition state, which involves intramolecular electronic repulsion or attraction forces in R. and that these forces determine properties such as stability. They are driving forces behind reactivity of the radical. He suggests that an electronegative substituent at the radical site improves thermal stability of the radical and makes it less reactive by inductive effects.^{28,29} He also suggests that similar intramolecular electron delocalization forces act at the transition state of this radical reaction. Seetula concludes the trend in reactivity among R + Cl₂ reactions is due primarily to changes in the activation energies (which are related to the free energies of activation) for these reactions. This E_{a,fwd} vs $\Delta H_{\text{rxn,fwd}}$ trend is illustrated by our data in Figures 1.1 to 1.4. Table 1.3 shows the presence of Cl on the carbon of the radical site reduces bond energy of new R-Cl bonds being formed.

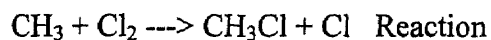
Table 1.3 Cl₂ + Radicals -----> Products + Cl (C-Cl bond energy)

REACTIONS	ΔH_f^{298}	C--Cl bond energy
1. Cl ₂ + CH ₃ -----> CH ₃ Cl + Cl	-25.50	83.34
8. Cl ₂ + CH ₂ Cl -----> CH ₂ Cl ₂ + Cl	-21.90	79.74
9. Cl ₂ + CHCl ₂ -----> CHCl ₃ + Cl	-18.78	76.62
10. Cl ₂ + CCl ₃ -----> CCl ₄ + Cl	-13.02	70.86
11. Cl ₂ + CF ₃ -----> CF ₃ Cl + Cl	-27.27	85.11
12. Cl ₂ + CF ₂ Cl -----> CF ₂ Cl ₂ + Cl	-22.56	80.40
13. Cl ₂ + CFCl ₂ -----> CFCl ₃ + Cl	-17.18	75.02

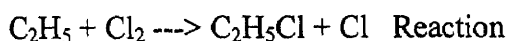
UNITS :: ΔH_f^{298} and bond energy : kcal/mole

4.2 *Ab initio* Calculations in Reactions of CH₃ and C₂H₅ with Cl₂

4.2.1 Results from *Ab initio* Calculations of Thermodynamic Properties in Reactions of CH₃ and C₂H₅ with Cl₂



CH₃ + Cl₂ forms an initial CH₃-ClCl adduct which has a shallow well 1.45 kcal/mole below that of the reactants (CBSQ//MP2/6-311G(d,p) level) with C-Cl bond length of 3.10Å and Cl-Cl bond length of 2.04Å. The Cl-Cl bond in this adduct is 0.01Å longer than calculated for Cl₂. This CH₃-ClCl adduct reacts to the Transition State (TS) which is 4 kcal/mole above the adduct at the MP2/6-311G(d,p) level, but not higher in energy at the CBSQ level of calculation. The C-Cl bond length is 0.77Å shorter and the Cl-Cl bond is 0.06Å longer in the TS than in the CH₃-ClCl adduct. The carbon-Cl bond is forming and the Cl-Cl bond is breaking. The TS has a 9.12 cal/mol-K lower S⁰₍₂₉₈₎ than the CH₃-ClCl adduct. The TS then goes to a CH₃Cl-Cl adduct which has a 25.59 kcal/mole well (CBSQ) with the C-Cl bond length 0.55Å shorter and the Cl-Cl bond length 1.20Å longer than in the TS. The CH₃Cl-Cl has a 6.34 cal/mol-K higher S⁰₍₂₉₈₎ than the TS structure. The CH₃Cl-Cl adduct dissociates to CH₃Cl + Cl with a low barrier of 2.33 kcal/mole.



C₂H₅ + Cl₂ forms an initial adduct CC-ClCl which also has a shallow well, about 2.5 kcal/mole below that of the reactants at the CBSQ//MP2/6-311G(d,p) level, with C-Cl bond length of 2.85Å and Cl-Cl bond length of 2.04Å. The Cl-Cl bond in this adduct is 0.01Å longer than calculated for Cl₂. This CC-ClCl adduct reacts to the TS which is 1.15 kcal/mole higher in energy at the MP2/6-311G(d,p) level, but not higher in energy at the CBSQ level of calculation. (see Figure 1.6) The C-Cl bond length is 0.45Å shorter and the Cl-Cl bond is 0.04Å longer in the TS than in the CC-ClCl adduct. The TS has a 3.37

cal/mol-K lower $S^{\circ}_{(298)}$ than the $\text{CH}_3\text{-ClCl}$ adduct. The TS goes to the CCCl-Cl which has a well of 24.78 kcal/mole at the CBSQ level where the C-Cl bond length is 0.61 Å shorter and the Cl-Cl bond is 1.17 Å longer than in the TS. The CCCl-Cl adduct has a 2.06 cal/mol-K higher $S^{\circ}_{(298)}$ than the TS structure. The CCCl-Cl adduct dissociates to products of $\text{C}_2\text{H}_5\text{Cl} + \text{Cl}$ with low barrier of 2.31 kcal/mole.

4.2.2 Geometries of Transition States

Structures of the adducts and transition states in CH_3 and C_2H_5 with Cl_2 are shown in Figure 1.6. The bond lengths of $\text{CH}_3\text{---Cl}_2$ and $\text{C}_2\text{H}_5\text{---Cl}_2$ in the transition state structures are 2.330 and 2.402, respectively. The bond length of $\text{C}_2\text{H}_5\text{---Cl}_2$ is 0.17 Å longer than that of $\text{CH}_3\text{---Cl}_2$. The C-Cl bond lengths of 2.33 and 2.40 are calculated to be longer than the Cl-Cl bond lengths of 2.10 and 2.08 in $\text{TSCH}_3\text{XCl}_2$ and $\text{TSC}_2\text{H}_5\text{XCl}_2$, respectively. The C-Cl-Cl angles in $\text{TSCH}_3\text{XCl}_2$ and $\text{TSC}_2\text{H}_5\text{XCl}_2$ are 180.0 and 177.3, respectively. Figure 1.8a shows changes in bond lengths from $\text{CH}_3 + \text{Cl}_2$ to $\text{CH}_3\text{Cl} + \text{Cl}$ via $\text{CH}_3\text{-ClCl}$, $\text{TSCH}_3\text{XCl}_2$ and $\text{CH}_3\text{Cl-Cl}$. Table 1.4 lists vibrational frequencies of adducts and transition states in MP2/6-311G(d,p).

The two transition states each have one imaginary frequency. Table 1.5 lists moments of inertia of adducts and transition states from MP2/6-311G(d,p) level calculations.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C1-H2	1.0797040				
C1-H3	1.0797040	H3-C1-H2	119.859270		
C1-H4	1.0797040	H4-C1-H2	119.859270	H4-C1-H2-H3	-172.533729
C1-Cl5	3.0975079	Cl5-C1-H2	93.733141	Cl5-C1-H2-H3	92.158888
Cl5-Cl6	2.0349651	Cl6-Cl5-C1	179.999899	Cl6-Cl5-C1-H2	-179.459202

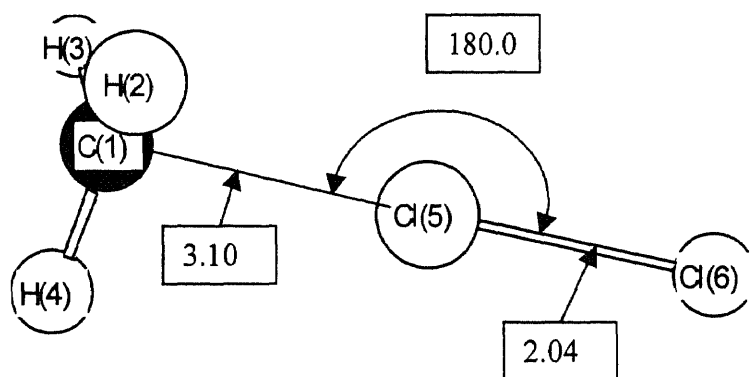
(a) CH₃-ClCl

Figure 1.6a Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory. (CH₃-ClCl)

Bond Length (A)		Bond Angle (deg)		Dihedral Angle (deg)	
C1-H2	1.0817521				
C1-H3	1.0817521	H3-C1-H2	118.024009		
C1-H4	1.0817521	H4-C1-H2	118.024003	H4-C1-H2-H3	-152.403027
C1-Cl5	2.3301785	Cl5-C1-H2	98.151660	Cl5-C1-H2-H3	103.798497
Cl5-Cl6	2.0978717	Cl6-Cl5-C1	179.999742	Cl6-Cl5-C1-H2	-179.009882

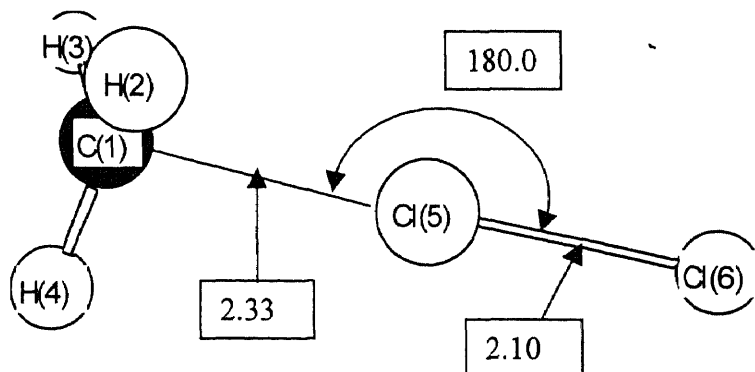
(b) $\text{TSCH}_3\text{XCl}_2$

Figure 1.6b Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory. ($\text{TSCH}_3\text{XCl}_2$)

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C1-H2	1.0878704				
C1-H3	1.0878704	H3-C1-H2	110.205132		
C1-H4	1.0878704	H4-C1-H2	110.205141	H4-C1-H2-H3	-121.641201
C1-Cl5	1.7786100	Cl5-C1-H2	108.678680	Cl5-C1-H2-H3	119.179376
Cl5-Cl6	3.3008227	Cl6-Cl5-C1	89.068799	Cl6-Cl5-C1-H2	179.951884

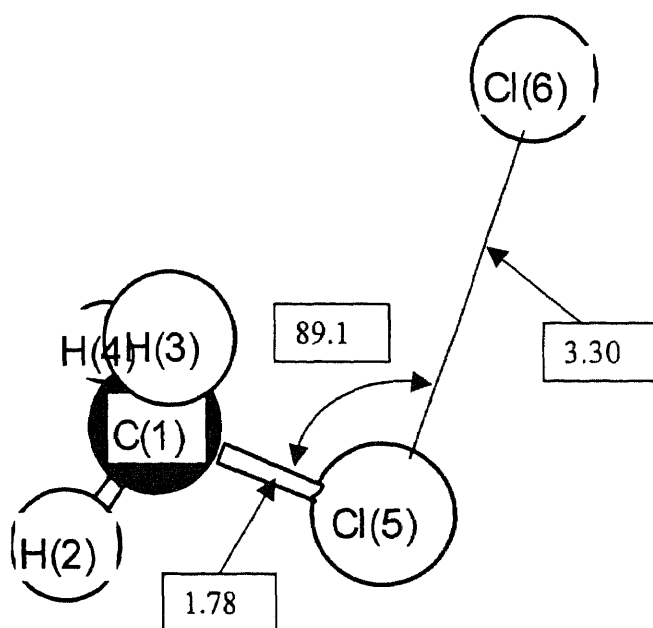
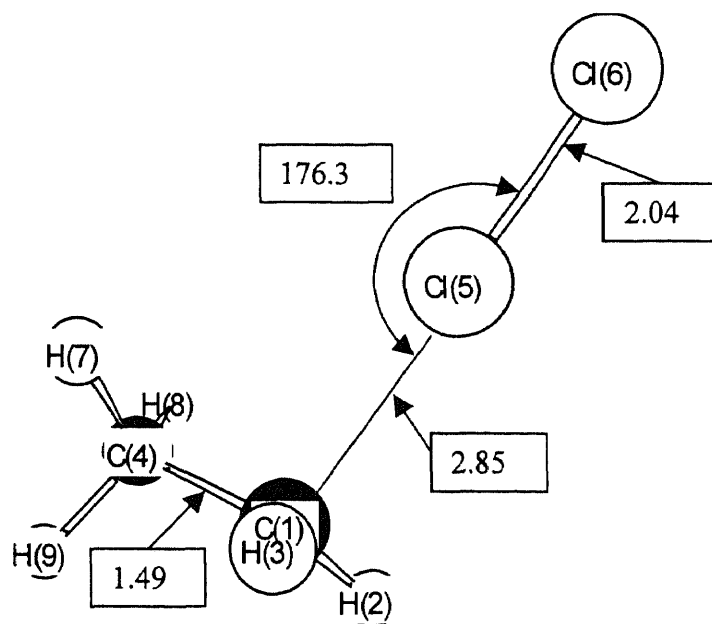
(c) $\text{CH}_3\text{Cl}-\text{Cl}$

Figure 1.6c Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory. ($\text{CH}_3\text{Cl}-\text{Cl}$)

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C1-H2	1.0832597				
C1-H3	1.0832618	H3-C1-H2	117.295260		
C1-C4	1.4918126	C4-C1-H2	120.192555	C4-C1-H2-H3	-162.731790
C1-Cl5	2.8512380	Cl5-C1-H2	94.185453	Cl5-C1-H2-H3	96.911657
Cl5-Cl6	2.0416507	Cl6-Cl5-C1	176.273561	Cl6-Cl5-C1-H2	121.199932
C4-H7	1.0928203	H7-C4-C1	111.366252	H7-C4-C1-H2	-159.402229
C4-H8	1.0928105	H8-C4-C1	111.367406	H8-C4-C1-H2	-38.279669
C4-H9	1.0999090	H9-C4-C1	111.055344	H9-C4-C1-H2	81.161692



(d) CC-ClCl

Figure 1.6d Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory. (CC-ClCl)

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C1-H2	1.0845277				
C1-H3	1.0845213	H3-C1-H2	116.330713		
C1-C4	1.4894599	C4-C1-H2	-119.133298	C4-C1-H2-H3	-153.918681
C1-Cl5	2.4021188	Cl5-C1-H2	95.431259	Cl5-C1-H2-H3	98.798312
Cl5-Cl6	2.0835974	Cl6-Cl5-C1	177.346547	Cl6-Cl5-C1-H2	119.768136
C4-H7	1.0916716	H7-C4-C1	111.368261	H7-C4-C1-H2	-164.638694
C4-H8	1.0917337	H8-C4-C1	111.356443	H8-C4-C1-H2	-42.914304
C4-H9	1.0999643	H9-C4-C1	109.714949	H9-C4-C1-H2	76.199249

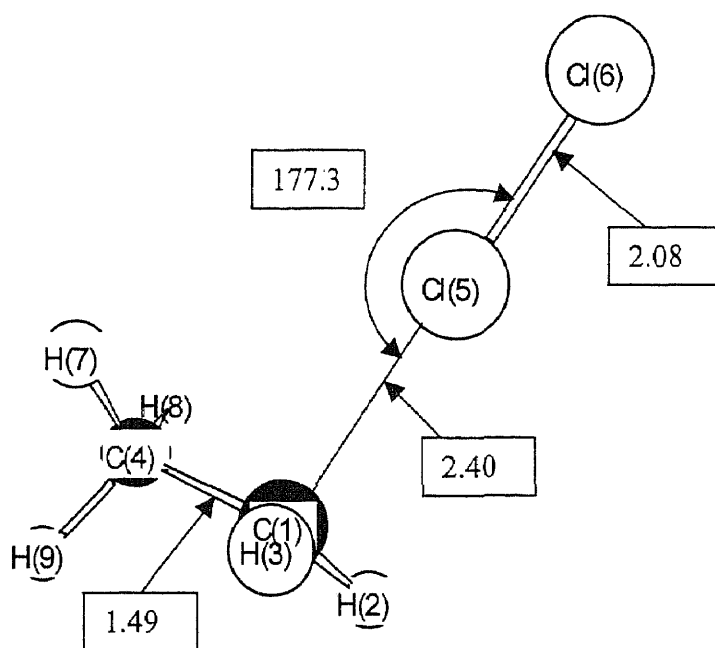
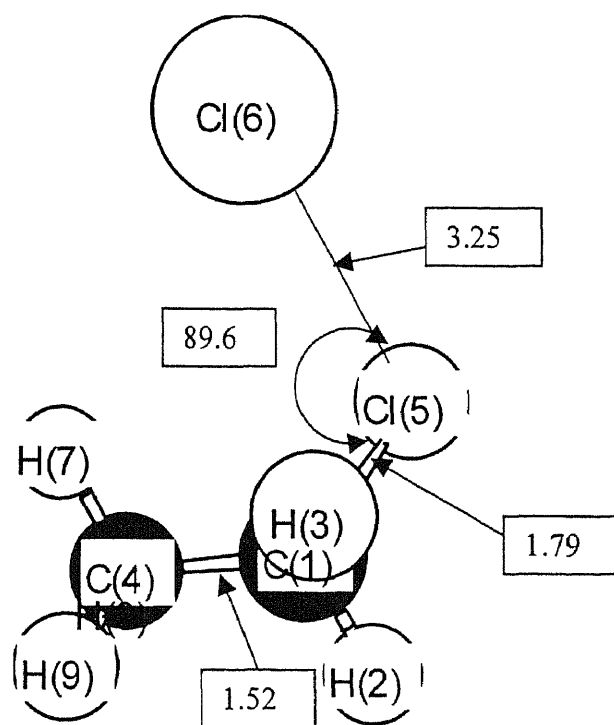
(e) $\text{TSC}_2\text{H}_5\text{XCl}_2$

Figure 1.6e Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory. ($\text{TSC}_2\text{H}_5\text{XCl}_2$)

Bond Length (Å)	Bond Angle (deg)	Dihedral Angle (deg)
C1-H2	1.0899852	
C1-H3	1.0900362	H3-C1-H2 109.175033
C1-C4	1.5163650	C4-C1-H2 111.610294
C1-Cl5	1.7906557	C4-C1-H2-H3 -123.711020
C15-Cl6	3.2529477	C15-C1-H2-H3 115.017378
C4-H7	1.0915756	C16-Cl5-C1 89.594795
C4-H8	1.0918485	C16-Cl5-C1-H2 -158.991415
C4-H9	1.0944691	H7-C4-C1 110.744746
		H7-C4-C1-H2 -179.287169
		H8-C4-C1 110.773085
		H8-C4-C1-H2 -58.815927
		H9-C4-C1 109.448585
		H9-C4-C1-H2 60.992411



(f) CCCI-Cl

Figure 1.6f Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory. (CCCI-Cl)

Table 1.4 Vibrational Frequencies^a (ν cm^{-1}) MP2/6-311G(d,p) level of calculation

Species	Vibrational Frequencies										
ch3-clcl	47	47	82	146	146	525	545	1447	1447	3170	
	3364	3364									
tsch3xcl2^b	-495 ^d	65	65	394	530	530	976	1446	1446	3158	
	3345	3345									
ch3cl-cl	42	43	61	779	1066	1067	1441	1494	1494	3121	
	3231	3232									
cc-clcl	48	63	87	120	131	271	579	607	822	1008	
	1092	1224	1420	1494	1504	1511	3040	3130	3176	3202	3314
tsc2h5xcl2^c	-348 ^d	72	87	170	196	433	517	814	825	1044	
	1102	1234	1414	1492	1493	1510	3045	3144	3192	3193	3305
cccl-cl	44	54	63	293	343	718	805	1014	1116	1120	
	1305	1369	1437	1504	1505	1518	3086	3134	3176	3185	3207

^a non-scaled. ^{b,c} Transition State Structure described in Figure 5.

^d Transition State, one imaginary frequency.

Table 1.5 Moments of Inertia ($\text{amu}\cdot\text{Bohr}^2$) MP2/6-311G(d,p) level of calculation

Species	I_A	I_B	I_C
ch3-clcl	12.57	1015.66	1015.66
tsch3xcl2	12.38	794.63	794.63
ch3cl-cl	131.82	833.62	953.99
cc-clcl	93.92	1461.85	1532.15
tsc2h5xcl2	89.57	1282.56	1348.56
cccl-cl	339.96	979.25	1230.03

4.2.3 Estimation of Entropy ($S^0_{(298)}$) and Heat Capacity ($C_p(T)$'s, 300 - 1500K) for Transition States and Adducts

$S^0_{(298)}$ and $C_p(T)$'s are calculated based on vibration frequencies and moments of inertia of the optimized MP2/6-311G(d,p) structures. The calculation results using MP2/6-311G(d,p) determined geometries and frequencies are summarized in Table 1.6. TVR represents the sum of the contributions from translations, vibrations and external rotations for $S^0_{(298)}$ and $C_p(T)$'s. Symmetry is incorporated in estimation of $S^0_{(298)}$ as described in Table 1.6. Contributions of internal rotation for $S^0_{(298)}$ and $C_p(T)$'s are calculated based on rotational barrier heights, moments of inertia of the rotors using the method of Pitzer and Gwinn's¹.

4.2.4 Calculated Enthalpies of Formation ($\Delta H^0_{f(298)}$)

$\Delta H^0_{f(298)}$ for reactants, adducts, transition states, and products in reactions of CH_3 and C_2H_5 with Cl_2 are calculated using CBSQ//MP2/6-311G(d,p) and MP2/6-311G(d,p). The calculation results are summarized in Table 1.7. The activation energies of $\text{TSCH}_3\text{XCl}_2$ are estimated by taking the difference of total energy between reactants and $\text{TSCH}_3\text{XCl}_2$ resulting in -2.73 and 2.4 kcal/mole for CBSQ//MP2/6-311G(d,p) and MP2/6-311G(d,p), and $\Delta H^0_{f(298)}$ of the $\text{CH}_3\text{-ClCl}$ intermediate adduct is calculated as 33.37 and 33.28 kcal/mole, respectively. Activation energies of $\text{TSC}_2\text{H}_5\text{XCl}_2$ are estimated by taking the difference of total energy between reactants and $\text{TSC}_2\text{H}_5\text{XCl}_2$ resulting in -5.07 and -1.73 kcal/mole for CBSQ//MP2/6-311G(d,p) and MP2/6-311G(d,p). $\Delta H^0_{f(298)}$ of CC-ClCl is calculated as 26.80 and 26.42 kcal/mole, respectively.

The overall energy diagram is illustrated in Figure 1.5.

Table 1.6 Ideal Gas Phase Thermodynamic Properties^a : $\Delta H_f^\circ_{298}$: CBSQ//MP2/6-311G(d,p), S°_{298} and $C_p(T)$: MP2/6-311G(d,p)

Species and Symmetry #		$\Delta H_f^\circ_{298}$	S°_{298} ^b	C_{p300} ^b	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
ch3-clcl (3)	TVR ^c		83.23	20.23	21.32	22.23	23.03	24.43	25.64	27.91
	Total ^f	33.37	83.23 ^e	20.23	21.32	22.23	23.03	24.43	25.64	27.91
tsch3xcl2 (3)	TVR		68.68	14.39	15.96	17.22	18.27	19.97	21.36	23.80
	Internal Rotor 1 ^d		5.42	1.48	1.31	1.21	1.15	1.08	1.05	1.02
	Total ^f	32.10	74.11 ^e	15.86	17.27	18.43	19.42	21.06	22.41	24.82
ch3cl-cl (3)	TVR		74.70	13.48	15.15	16.79	18.25	20.62	22.44	25.40
	Internal Rotor 1		5.75	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	Total ^f	6.23	80.45 ^e	14.47	16.14	17.79	19.24	21.61	23.43	26.39
cc-clcl (3)	TVR		83.09	21.39	24.37	27.05	29.35	33.06	35.92	40.63
	Internal Rotor 1		4.38	1.63	1.76	1.76	1.70	1.58	1.47	1.27
	Total ^f	26.8	87.47 ^e	23.02	26.13	28.81	31.05	34.64	37.39	41.90
tsc2h5xcl2 (3)	TVR		72.22	16.70	19.84	22.65	25.05	28.87	31.80	36.58
	Internal Rotor 1,2		11.89	3.24	3.11	2.95	2.79	2.59	2.44	2.24
	Total ^f	24.2	84.10 ^e	19.94	22.96	25.60	27.84	31.46	34.25	38.82
cccl-cl (3)	TVR		74.31	16.16	19.48	22.62	25.35	29.72	33.00	38.20
	Internal Rotor 1,2		11.85	3.46	3.33	3.16	2.99	2.76	2.58	2.32
	Total ^f	-1.19	86.16 ^e	19.62	22.81	25.78	28.35	32.47	35.58	40.52

^a Thermodynamic properties are referred to a standard state of an ideal gas of pure enantiomer at 1 atm. ^b In cal/mol-K. ^c The sum of contributions from translations, external rotations, and vibrations. ^d Contribution from internal rotation.

^e Symmetry number is taken into account ($-R * \ln(\text{number of symmetry})$)

^f Spin degeneracy contribution for entropy = $1.987 * \ln(2)$ (cal/mol-K) is taken into account.

Table 1.7 Total Energy, ZPVE, Thermal Correction, and $\Delta H_f^\circ_{298}$ in CBSQ and MP2/6-311G(d,p) Calculation^a

Species	Total Energy at 298K ^b		ZPVE ^c	Thermal Correction ^d	$\Delta H_f^\circ_{298}$	
	MP2/6-311G(d,p)	CBSQ			(MP2)	(CBSQ)
cl2	-919.2357806	-919.45662	0.0011961	0.0035010	0.00	0.00
ch3	-39.7072381	-39.7406173	0.0293571	0.0040820	34.82 ^e	34.82 ^e
ch3-clcl	-958.9454736	-959.1995455	0.0318214	0.0079400	33.28	33.37
tsch3xcl2	-958.9391929	-959.2015846	0.0339796	0.0061560	37.22	32.09
ch3cl-cl	-959.0137142	-959.2423618	0.0379109	0.0064490	-9.54	6.50
ch3cl	-499.4262791	-449.5581297	0.0372296	0.0039680	-	-
cl	-459.5851374	-459.6805237	0.0000000	0.0023600	-	-
c2h5	-78.9029613	-78.9664974	0.0589530	0.0048250	29.30 ^e	29.30 ^e
cc-clcl	-998.1433280	-998.4270989	0.0618296	0.0085130	26.42	26.80
tsc2h5xcl2	-998.1414941	-998.4311891	0.0628073	0.0072330	27.57	24.23
cccl-cl	-998.2137368	-998.4706799	0.0666130	0.0073610	-17.76	-0.55
c2h5cl	-538.6258002	-538.7864702	0.0660780	0.0048980	-	-

^a Unit in Hartree 1 HF=627.51 kcal/mol. ^b Scaled ZPVE are included. Scaling factor is recommended as 0.9748 by Scott et al.²⁴ for MP2/6-311G(d,p). ^c Scaled by 0.9748 ^d Non-scaled.

^e $\Delta H_f^\circ_{298}$ CH₃ and C₂H₅ are set to literature values in Table 2 for isodesmic reaction.

4.2.5 Thermodynamic Analysis for reactions of CH₃ and C₂H₅ with Cl₂

ΔH_{rxn} , ΔU_{rxn} and the Arrhenius pre-exponential factor are calculated using thermodynamic properties of the transition state structures for temperature from 300K to 2000K and results are shown in Table 1.8. The experimental A_{fwd} of $3.02 * 10^{12}$ for Cl₂ + CH₃ => CH₃Cl + Cl reaction in Table 1.1, corresponds to the calculated A_{fwd} value near 700K in Table 1.8 (a). The experimental A_{Rev} of $2.99 * 10^{13}$ in CH₃Cl + Cl => Cl₂ + CH₃ reaction in Table 1.1, corresponds to the calculated A_{Rev} near 500K in Table 1.8 (b). The experimental A_{fwd} of $7.59 * 10^{12}$ for Cl₂ + C₂H₅ => C₂H₅Cl + Cl reaction in Table 1.1, corresponds to the calculated A_{fwd} near 1100K in Table 1.8 (c). The experimental A_{Rev} of $8.51 * 10^{13}$ for C₂H₅Cl + Cl => Cl₂ + C₂H₅ reaction in Table 1.1, corresponds to the calculated A_{Rev} near 1200K in Table 1.8 (d).

4.2.6 Atomic Charges in Reactants, Adducts, Transition States, and Products

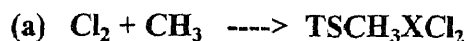
CH₃ + Cl₂ ---> CH₃Cl + Cl and C₂H₅ + Cl₂ ---> C₂H₅Cl + Cl Reactions

Table 1.9 illustrates Mulliken Atomic Charges on the H, C, and Cl atoms in the CH₃ + Cl₂ and C₂H₅ + Cl₂ reaction systems. Calculated charges on the H atoms remain positive throughout the reaction process at ca. 0.1. Charges on the carbon bonding to Cl are negative 0.34 in CH₃ with a progressive increase to -0.26 in CH₃Cl. The corresponding carbon in the C₂H₅ reaction experiences a decrease from -0.25 to -0.31 when C₂H₅ + Cl₂ react to the TSC₂H₅XCl₂ and then increases to -0.21 in C₂H₅Cl. The Cl atom bonding to the carbon has no charge in Cl₂, positive 0.01 and 0.02 charges in the TSC₃XCl₂ and the TSC₂H₅XCl₂, respectively, then decreases to -0.16 in the Cl atom of the products (both CH₃Cl and C₂H₅Cl). The leaving Cl has no charge in Cl₂, negative

0.13 charge in both the $\text{TSCH}_3\text{XCl}_2$ and the $\text{TSC}_2\text{H}_5\text{XCl}_2$, then increases near zero (-0.01) in both the $\text{CH}_3\text{Cl-Cl}$ adduct and the CCCl-Cl adduct.

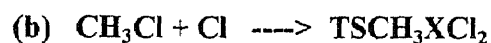
Figure 1.7 and the description of charges show that H atoms donate e^- to the carbon radical center and to chlorine in R-Cl. Replacement of the H's with electronegative halogens or other electronegative species must reduce the available e^- density to/at the carbon site. This likely reduces bond energy of additional R-Cl bonds being formed. Repulsive effects may also be important in the reduced bond energies.

Table 1.8 Thermodynamic and Kinetic analysis for reactions of CH₃ and C₂H₅ with Cl₂ comparing with experiment data* (Timonen/Gutman1986)



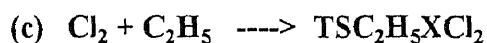
T(K)	ΔH ^a rxn	ΔU ^a rxn	Af ^a
300	-2.723	-2.127	1.08E+12
400	-2.862	-2.068	1.57E+12
500	-2.975	-1.982	2.15E+12
600	-3.068	-1.876	2.85E+12
800	-3.218	-1.628	4.54E+12
1000	-3.344	-1.357	6.61E+12
1200	-3.464	-1.080	9.00E+12
1500	-3.639	-0.659	1.32E+13
2000	-3.868	0.106	2.19E+13

P(torr)	T(K)		
1.9 - 2.8	296-712	Expt.*	3.02E+12



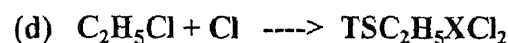
T(K)	ΔHrxn	ΔUrxn	Af
300	22.78	23.38	9.04E+12
400	22.84	23.63	1.74E+13
500	22.84	23.84	2.75E+13
600	22.80	24.00	3.82E+13
800	22.61	24.20	5.93E+13
1000	22.30	24.29	7.78E+13
1200	21.91	24.29	9.37E+13
1500	21.25	24.23	1.14E+14
2000	20.11	24.08	1.46E+14

P(torr)	T(K)		
1.9 - 2.8	296-712	Expt.*	2.99E+13



T(K)	ΔHrxn	ΔUrxn	Af
300	-5.1	-4.504	6.39E+11
400	-5.11	-4.315	1.12E+12
500	-5.108	-4.114	1.75E+12
600	-5.103	-3.911	2.54E+12
800	-5.112	-3.523	4.48E+12
1000	-5.165	-3.178	6.80E+12
1200	-5.259	-2.875	9.38E+12
1500	-5.439	-2.458	1.37E+13
2000	-5.7	-1.726	2.26E+13

P(torr)	T(K)		
1.7 - 2.2	295-498	Expt.*	7.59E+12

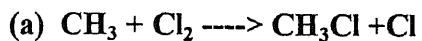


T(K)	ΔHrxn	ΔUrxn	Af
300	22.08	22.68	9.98E+12
400	22.07	22.87	1.75E+13
500	22.03	23.02	2.60E+13
600	21.95	23.14	3.49E+13
800	21.71	23.30	5.25E+13
1000	21.40	23.38	6.87E+13
1200	21.03	23.41	8.36E+13
1500	20.43	23.41	1.05E+14
2000	19.43	23.40	1.39E+14

P(torr)	T(K)		
1.7 - 2.2	295-498	Expt.*	8.51E+13

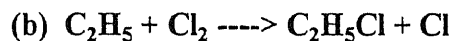
^a Units ; ΔH and ΔU : kcal/mole, Af : cm³/mole-sec

Table 1.9 Calculated atomic charges, bond lengths(A) and bond angles(deg)
MP2/6-311G(d,p)



Expt. $E_a = 0.53$ kcal/mole

	CH_3	$\text{Cl}_1\text{-Cl}_2$	$\text{CH}_3\text{-Cl}_1\text{Cl}_2$	$\text{TSC}_3\text{H}_3\text{XCl}_2$	$\text{CH}_3\text{Cl-Cl}$	CH_3Cl
Charges						
H	0.11		0.12	0.16	0.145	0.14
C	-0.34		-0.36	-0.35	-0.264	-0.26
Cl_1		0	0.02	0.01	-0.161	-0.159
Cl_2		0	-0.04	-0.13	-0.011	
Bond Length						
C-Cl			3.10	2.33	1.78	1.78
Cl-Cl		2.03	2.04	2.10	3.30	
Bond Angle						
C-Cl-Cl			180.0	180.0	89.1	



Expt. $E_a = -0.30$ kcal/mole

	C_2H_5	$\text{Cl}_5\text{-Cl}_6$	$\text{C}_3\text{C}_4\text{-Cl}_5\text{Cl}_6$	$\text{TSC}_2\text{H}_5\text{XCl}_2$	CCl-Cl	$\text{C}_2\text{H}_5\text{Cl}$
Charges						
H_1	0.095		0.105	0.12	0.11	0.1
H_2	0.11		0.13	0.153	0.147	0.11
C_3	-0.25		-0.24	-0.23	-0.234	-0.24
C_4	-0.25		-0.29	-0.31	-0.22	-0.21
Cl_5		0	0.03	0.02	-0.161	-0.16
Cl_6		0	-0.06	-0.13	-0.01	
Bond Length						
C-Cl			2.85	2.40	1.79	1.79
Cl-Cl		2.03	2.04	2.08	3.25	
Bond Angle						
C-Cl-Cl			176.3	177.3	89.6	

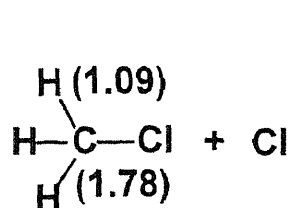
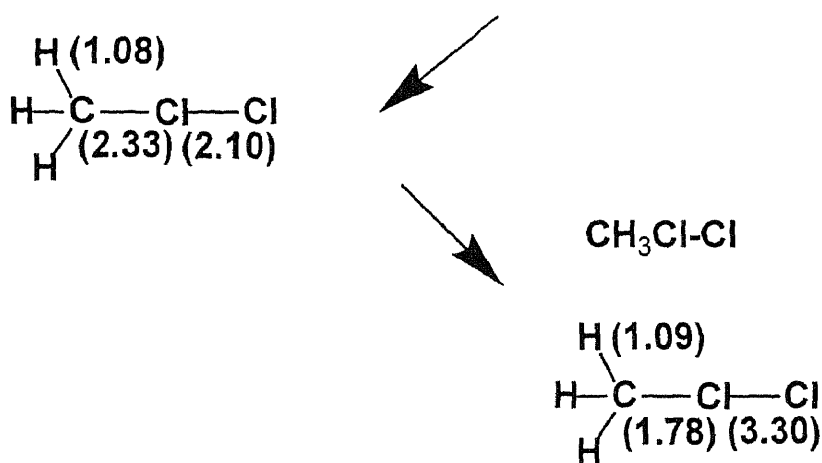
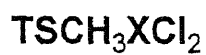
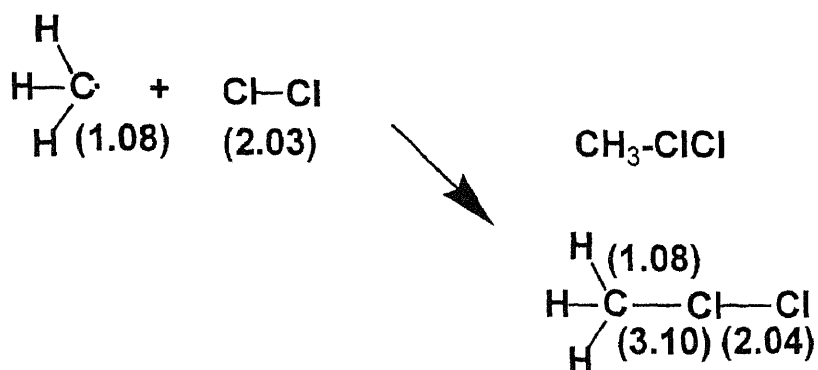
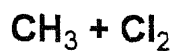
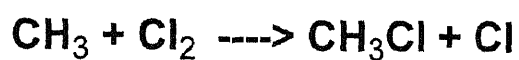
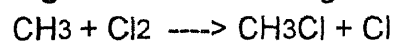


Figure 1.7a Bond lengths MP2/6-311G(d,p)



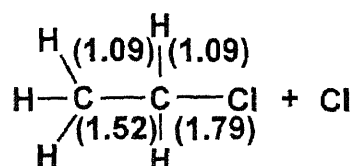
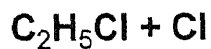
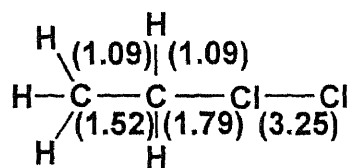
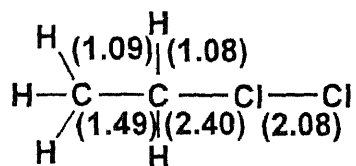
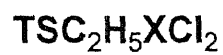
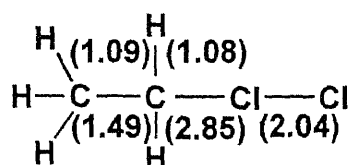
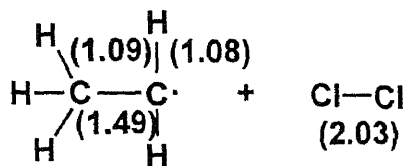
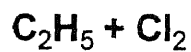


Figure 1.7b Bond lengths MP2/6-311G(d,p)
 $\text{C}_2\text{H}_5 + \text{Cl}_2 \longrightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Cl}$

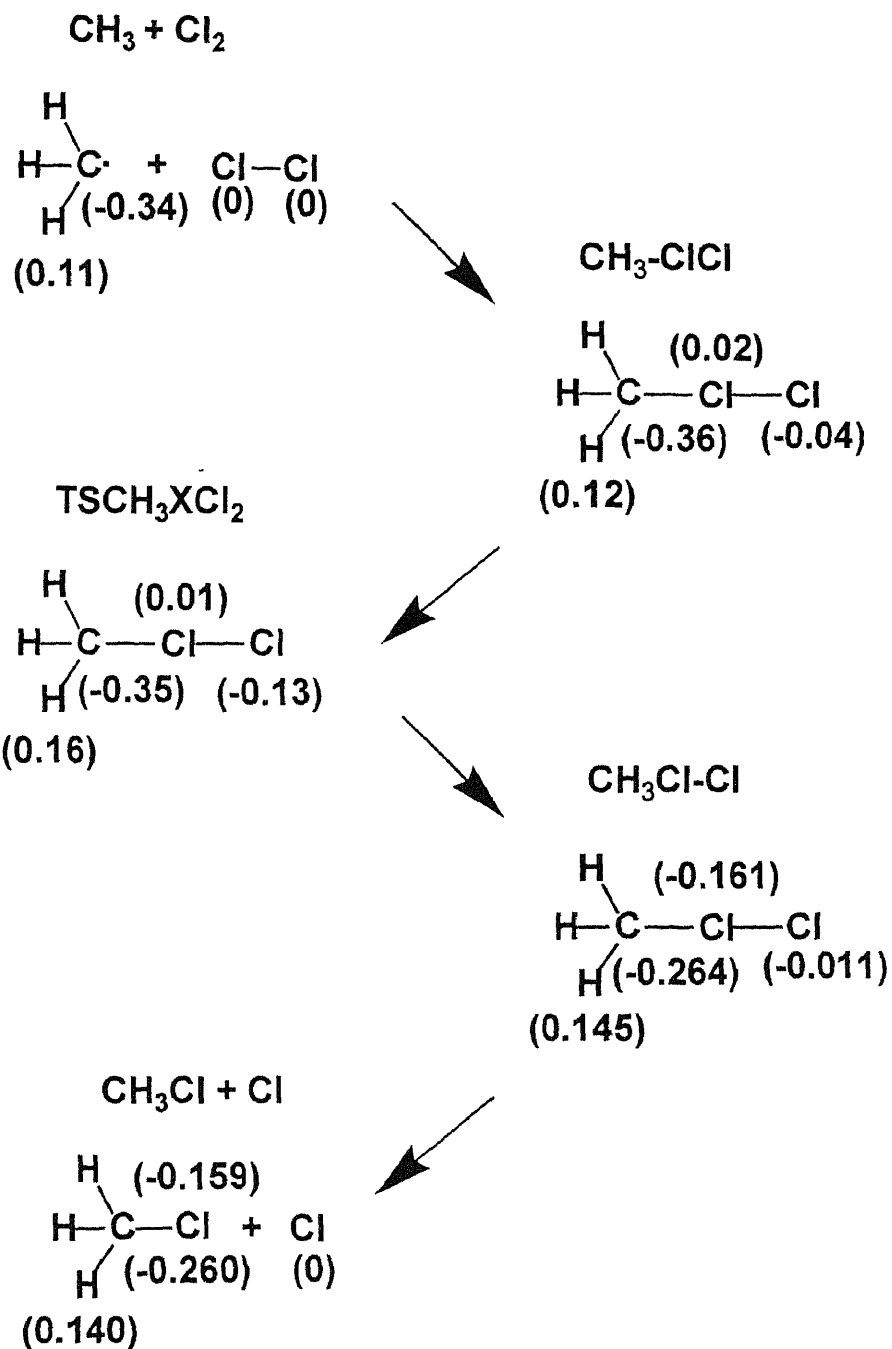
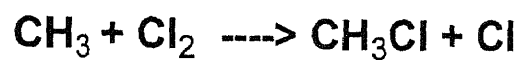


Figure 1.8a Calculated atomic charges MP2/6-311G(d,p)
 $\text{CH}_3 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{Cl}$

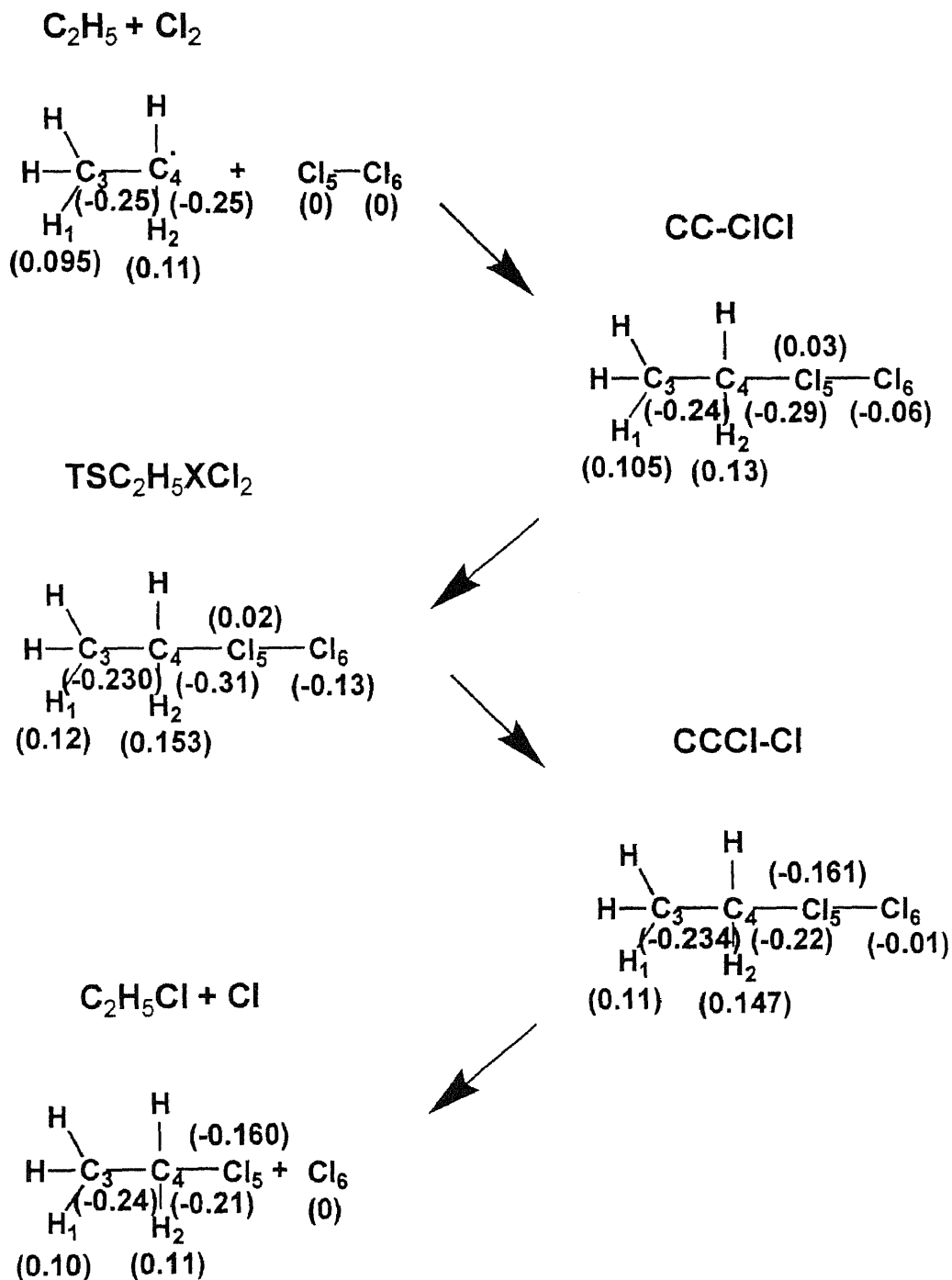


Figure 1.8b Calculated atomic charges MP2/6-311G(d,p)
 $\text{C}_2\text{H}_5 + \text{Cl}_2 \longrightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Cl}$

CHAPTER 5

SUMMARY FOR PART ONE

Thermodynamic Parameters, $\Delta H_{f(298)}^\circ$, $S_{(298)}^\circ$ and $C_p(T)$ are evaluated for reactants and products in $R + Cl_2 \rightleftharpoons R-Cl + Cl$ reactions. The forward rate constants are evaluated from the literature. The reverse rate constants are calculated from thermodynamic properties of reactants and products and microscopic reversibility. The trends of $E_{a_{fwd}}$ vs $\Delta H_{rxn,fwd}$ and Arrhenius pre-exponential factor for overall, hydrocarbons, C_1 chlorocarbons, and C_2 chlorocarbons are evaluated.

We recommend rate expression of average $A_{fwd} = (2.35 \pm 3.07) \times 10^{12}$ cm³/mole-sec and $E_{a_{fwd}} = (0.38 \pm 0.04) * \Delta H_{rxn,fwd} + (10.10 \pm 0.77)$ kcal/mole for overall, average $A_{fwd} = (5.89 \pm 2.48) \times 10^{12}$ cm³/mole-sec and $E_{a_{fwd}} = (0.39 \pm 0.11) * \Delta H_{rxn,fwd} + (10.49 \pm 2.21)$ kcal/mole for hydrocarbons, average A_{fwd} of $(6.89 \pm 2.15) \times 10^{11}$ cm³/mole-sec and $E_{a_{fwd}} = (0.40 \pm 0.07) * \Delta H_{rxn,fwd} + (10.32 \pm 1.31)$ kcal/mole for C_1 chlorocarbons, and average A_{fwd} of $(4.64 \pm 2.10) \times 10^{11}$ cm³/mole-sec and $E_{a_{fwd}} = (0.33 \pm 0.07) * \Delta H_{rxn,fwd} + (9.46 \pm 1.17)$ kcal/mole for C_2 chlorocarbons.

We have performed *ab initio* calculation on $CH_3 + Cl_2 \rightleftharpoons CH_3Cl + Cl$ and $C_2H_5 + Cl_2 \rightleftharpoons C_2H_5Cl + Cl$ reaction. We show canonical transition state calculations agree well with experimental data for these two, low $E_{a_{fwd}}$, reaction systems. The carbon atom which undergoes bonding to the Cl has a slightly increasing negative charge in the transition state then the charge increases, becomes less negative.

APPENDIX 1.1

THERMODYNAMIC ANALYSIS FOR $\text{Cl}_2 + \text{R} \leftrightarrow \text{RCl} + \text{Cl}$

THERMODYNAMIC ANALYSIS for REACTION

Rx Cl_2 + CH_3 = CH_3Cl + Cl
Hf {Kcal/mol} .000 34.820 -19.600 28.920
S {cal/mol K} 53.290 46.380 56.000 39.460

dHr {kcal/mol} (298K) = -25.50 dHr avg (298., 1000. K) = -25.57

dU (dE) {kcal/mol} (") = -25.50 dUr avg (298., 1000. K) = -25.57

dSr {cal/mol K} (") = -4.21 dSr avg (298., 1000. K) = -4.56

dGr {kcal/mol} (") = -24.24 dGr avg (298., 1000. K) = -22.62

Af/Ar (") = 1.202E-01 Af/Ar avg (298., 1000. K) = 1.010E-01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.550E+01	-2.550E+01	-4.225E+00	1.193E-01	-2.424E+01
400.00	-2.570E+01	-2.570E+01	-4.789E+00	8.982E-02	-2.378E+01
500.00	-2.582E+01	-2.582E+01	-5.057E+00	7.848E-02	-2.329E+01
600.00	-2.587E+01	-2.587E+01	-5.158E+00	7.456E-02	-2.278E+01
800.00	-2.583E+01	-2.583E+01	-5.105E+00	7.662E-02	-2.175E+01
1000.00	-2.565E+01	-2.565E+01	-4.900E+00	8.490E-02	-2.075E+01
1200.00	-2.537E+01	-2.537E+01	-4.654E+00	9.610E-02	-1.979E+01
1500.00	-2.489E+01	-2.489E+01	-4.294E+00	1.152E-01	-1.845E+01
2000.00	-2.397E+01	-2.397E+01	-3.769E+00	1.500E-01	-1.644E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx Cl_2 + C_2H_5 = $\text{C}_2\text{H}_5\text{Cl}$ + Cl
Hf {Kcal/mol} .000 29.300 -26.800 28.920
S {cal/mol K} 53.290 57.420 66.010 39.460

dHr {kcal/mol} (298K) = -27.18 dHr avg (298., 1000. K) = -26.96

dU (dE) {kcal/mol} (") = -27.18 dUr avg (298., 1000. K) = -26.96

dSr {cal/mol K} (") = -5.24 dSr avg (298., 1000. K) = -4.80

dGr {kcal/mol} (") = -25.62 dGr avg (298., 1000. K) = -23.85

Af/Ar (") = 7.157E-02 Af/Ar avg (298., 1000. K) = 8.918E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.718E+01	-2.718E+01	-5.239E+00	7.162E-02	-2.561E+01
400.00	-2.712E+01	-2.712E+01	-5.069E+00	7.800E-02	-2.509E+01
500.00	-2.700E+01	-2.700E+01	-4.803E+00	8.917E-02	-2.460E+01
600.00	-2.684E+01	-2.684E+01	-4.510E+00	1.034E-01	-2.413E+01
800.00	-2.644E+01	-2.644E+01	-3.946E+00	1.372E-01	-2.329E+01
1000.00	-2.602E+01	-2.602E+01	-3.468E+00	1.745E-01	-2.255E+01
1200.00	-2.559E+01	-2.559E+01	-3.078E+00	2.125E-01	-2.189E+01
1500.00	-2.496E+01	-2.496E+01	-2.611E+00	2.688E-01	-2.104E+01
2000.00	-2.393E+01	-2.393E+01	-2.019E+00	3.619E-01	-1.989E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + CC.C = CCCLC + CL
Hf {Kcal/mol} .000 21.020 -34.700 28.920
S {cal/mol K} 53.290 69.010 73.410 39.460

dHr {kcal/mol} (298K) = -26.80 dHr avg (298., 1000. K) = -26.30
dU (dE) {kcal/mol} (") = -26.80 dUr avg (298., 1000. K) = -26.30
dSr {cal/mol K} (") = -9.43 dSr avg (298., 1000. K) = -8.38
dGr {kcal/mol} (") = -23.99 dGr avg (298., 1000. K) = -20.86
Af/Ar (") = 8.688E-03 Af/Ar avg (298., 1000. K) = 1.473E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.680E+01	-2.680E+01	-9.421E+00	8.728E-03	-2.397E+01
400.00	-2.660E+01	-2.660E+01	-8.847E+00	1.165E-02	-2.306E+01
500.00	-2.631E+01	-2.631E+01	-8.220E+00	1.597E-02	-2.220E+01
600.00	-2.598E+01	-2.598E+01	-7.614E+00	2.167E-02	-2.141E+01
800.00	-2.524E+01	-2.524E+01	-6.554E+00	3.693E-02	-2.000E+01
1000.00	-2.449E+01	-2.449E+01	-5.716E+00	5.632E-02	-1.878E+01
1200.00	-2.377E+01	-2.377E+01	-5.055E+00	7.853E-02	-1.770E+01
1500.00	-2.274E+01	-2.274E+01	-4.287E+00	1.156E-01	-1.630E+01
2000.00	-2.117E+01	-2.117E+01	-3.382E+00	1.823E-01	-1.440E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + C3C. = C3CCL + CL
Hf {Kcal/mol} .000 11.900 -44.130 28.920
S {cal/mol K} 53.290 74.290 76.420 39.460

dHr {kcal/mol} (298K) = -27.11 dHr avg (298., 1000. K) = -26.38
dU (dE) {kcal/mol} (") = -27.11 dUr avg (298., 1000. K) = -26.38
dSr {cal/mol K} (") = -11.70 dSr avg (298., 1000. K) = -10.18
dGr {kcal/mol} (") = -23.62 dGr avg (298., 1000. K) = -19.77
Af/Ar (") = 2.772E-03 Af/Ar avg (298., 1000. K) = 5.942E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.711E+01	-2.711E+01	-1.169E+01	2.785E-03	-2.360E+01
400.00	-2.685E+01	-2.685E+01	-1.095E+01	4.034E-03	-2.246E+01
500.00	-2.643E+01	-2.643E+01	-1.002E+01	6.444E-03	-2.142E+01
600.00	-2.592E+01	-2.592E+01	-9.096E+00	1.028E-02	-2.046E+01
800.00	-2.482E+01	-2.482E+01	-7.516E+00	2.277E-02	-1.881E+01
1000.00	-2.379E+01	-2.379E+01	-6.364E+00	4.065E-02	-1.742E+01
1200.00	-2.290E+01	-2.290E+01	-5.549E+00	6.125E-02	-1.624E+01
1500.00	-2.175E+01	-2.175E+01	-4.696E+00	9.409E-02	-1.471E+01
2000.00	-2.015E+01	-2.015E+01	-3.769E+00	1.500E-01	-1.261E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + C2H3 = CH2CHCL + CL
 Hf {Kcal/mol} .000 71.640 5.000 28.920
 S {cal/mol K} 53.290 53.790 63.080 39.460

dHr {kcal/mol} (298K) = -37.72 dHr avg (298., 1000. K) = -37.58
 dU (dE) {kcal/mol} (") = -37.72 dUr avg (298., 1000. K) = -37.58
 dSr {cal/mol K} (") = -4.54 dSr avg (298., 1000. K) = -4.27
 dGr {kcal/mol} (") = -36.37 dGr avg (298., 1000. K) = -34.81
 Af/Ar (") = 1.018E-01 Af/Ar avg (298., 1000. K) = 1.169E-01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-3.772E+01	-3.772E+01	-4.540E+00	1.018E-01	-3.636E+01
400.00	-3.770E+01	-3.770E+01	-4.474E+00	1.052E-01	-3.591E+01
500.00	-3.762E+01	-3.762E+01	-4.305E+00	1.146E-01	-3.547E+01
600.00	-3.750E+01	-3.750E+01	-4.097E+00	1.272E-01	-3.505E+01
800.00	-3.720E+01	-3.720E+01	-3.667E+00	1.579E-01	-3.427E+01
1000.00	-3.685E+01	-3.685E+01	-3.277E+00	1.922E-01	-3.358E+01
1200.00	-3.648E+01	-3.648E+01	-2.938E+00	2.280E-01	-3.296E+01
1500.00	-3.590E+01	-3.590E+01	-2.504E+00	2.836E-01	-3.214E+01
2000.00	-3.489E+01	-3.489E+01	-1.924E+00	3.797E-01	-3.104E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + C3H5 = C3H5CL + CL
 Hf {Kcal/mol} .000 40.750 -460 28.920
 S {cal/mol K} 53.290 62.050 73.310 39.460

dHr {kcal/mol} (298K) = -12.29 dHr avg (298., 1000. K) = -12.22
 dU (dE) {kcal/mol} (") = -12.29 dUr avg (298., 1000. K) = -12.22
 dSr {cal/mol K} (") = -2.57 dSr avg (298., 1000. K) = -2.42
 dGr {kcal/mol} (") = -11.52 dGr avg (298., 1000. K) = -10.65
 Af/Ar (") = 2.743E-01 Af/Ar avg (298., 1000. K) = 2.958E-01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.229E+01	-1.229E+01	-2.568E+00	2.746E-01	-1.152E+01
400.00	-1.226E+01	-1.226E+01	-2.471E+00	2.883E-01	-1.127E+01
500.00	-1.222E+01	-1.222E+01	-2.384E+00	3.012E-01	-1.102E+01
600.00	-1.217E+01	-1.217E+01	-2.306E+00	3.133E-01	-1.079E+01
800.00	-1.208E+01	-1.208E+01	-2.172E+00	3.352E-01	-1.034E+01
1000.00	-1.197E+01	-1.197E+01	-2.055E+00	3.555E-01	-9.920E+00
1200.00	-1.185E+01	-1.185E+01	-1.942E+00	3.763E-01	-9.520E+00
1500.00	-1.161E+01	-1.161E+01	-1.765E+00	4.114E-01	-8.964E+00
2000.00	-1.106E+01	-1.106E+01	-1.452E+00	4.817E-01	-8.160E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + C3H3 = C3H3CL + CL
Hf {Kcal/mol} .000 81.580 39.170 28.920
S {cal/mol K} 53.290 59.570 68.780 39.460

dHr {kcal/mol} (298K) = -13.49 dHr avg (298., 1000. K) = -13.31
dU (dE) {kcal/mol} (") = -13.49 dUr avg (298., 1000. K) = -13.31
dSr {cal/mol K} (") = -4.62 dSr avg (298., 1000. K) = -4.24
dGr {kcal/mol} (") = -12.11 dGr avg (298., 1000. K) = -10.56
Af/Ar (") = 9.777E-02 Af/Ar avg (298., 1000. K) = 1.185E-01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.349E+01	-1.349E+01	-4.616E+00	9.796E-02	-1.210E+01
400.00	-1.341E+01	-1.341E+01	-4.396E+00	1.094E-01	-1.165E+01
500.00	-1.331E+01	-1.331E+01	-4.170E+00	1.226E-01	-1.122E+01
600.00	-1.319E+01	-1.319E+01	-3.955E+00	1.366E-01	-1.082E+01
800.00	-1.293E+01	-1.293E+01	-3.577E+00	1.652E-01	-1.007E+01
1000.00	-1.265E+01	-1.265E+01	-3.266E+00	1.933E-01	-9.383E+00
1200.00	-1.236E+01	-1.236E+01	-3.003E+00	2.207E-01	-8.757E+00
1500.00	-1.190E+01	-1.190E+01	-2.661E+00	2.620E-01	-7.909E+00
2000.00	-1.106E+01	-1.106E+01	-2.181E+00	3.336E-01	-6.702E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + CH2CL = CH2CL2 + CL
Hf {Kcal/mol} .000 27.990 -22.830 28.920
S {cal/mol K} 53.290 58.610 64.570 39.460

dHr {kcal/mol} (298K) = -21.90 dHr avg (298., 1000. K) = -21.89
dU (dE) {kcal/mol} (") = -21.90 dUr avg (298., 1000. K) = -21.89
dSr {cal/mol K} (") = -7.87 dSr avg (298., 1000. K) = -7.89
dGr {kcal/mol} (") = -19.55 dGr avg (298., 1000. K) = -16.77
Af/Ar (") = 1.905E-02 Af/Ar avg (298., 1000. K) = 1.884E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.190E+01	-2.190E+01	-7.875E+00	1.900E-02	-1.954E+01
400.00	-2.195E+01	-2.195E+01	-8.025E+00	1.762E-02	-1.874E+01
500.00	-2.196E+01	-2.196E+01	-8.034E+00	1.754E-02	-1.794E+01
600.00	-2.192E+01	-2.192E+01	-7.965E+00	1.816E-02	-1.714E+01
800.00	-2.174E+01	-2.174E+01	-7.716E+00	2.059E-02	-1.557E+01
1000.00	-2.147E+01	-2.147E+01	-7.414E+00	2.396E-02	-1.406E+01
1200.00	-2.114E+01	-2.114E+01	-7.114E+00	2.787E-02	-1.260E+01
1500.00	-2.059E+01	-2.059E+01	-6.708E+00	3.418E-02	-1.053E+01
2000.00	-1.962E+01	-1.962E+01	-6.148E+00	4.531E-02	-7.322E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + CHCL2 = CHCL3 + CL
Hf {Kcal/mol} .000 23.500 -24.200 28.920
S {cal/mol K} 53.290 68.100 70.660 39.460

dHr {kcal/mol} (298K) = -18.78 dHr avg (298., 1000. K) = -18.63
dU (dE) {kcal/mol} (") = -18.78 dUr avg (298., 1000. K) = -18.63
dSr {cal/mol K} (") = -11.27 dSr avg (298., 1000. K) = -10.98
dGr {kcal/mol} (") = -15.42 dGr avg (298., 1000. K) = -11.51
Af/Ar (") = 3.441E-03 Af/Ar avg (298., 1000. K) = 3.975E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.878E+01	-1.878E+01	-1.127E+01	3.441E-03	-1.540E+01
400.00	-1.875E+01	-1.875E+01	-1.119E+01	3.586E-03	-1.427E+01
500.00	-1.867E+01	-1.867E+01	-1.101E+01	3.917E-03	-1.316E+01
600.00	-1.856E+01	-1.856E+01	-1.080E+01	4.352E-03	-1.207E+01
800.00	-1.826E+01	-1.826E+01	-1.038E+01	5.396E-03	-9.956E+00
1000.00	-1.791E+01	-1.791E+01	-9.990E+00	6.554E-03	-7.920E+00
1200.00	-1.754E+01	-1.754E+01	-9.654E+00	7.763E-03	-5.956E+00
1500.00	-1.696E+01	-1.696E+01	-9.222E+00	9.644E-03	-3.127E+00
2000.00	-1.596E+01	-1.596E+01	-8.645E+00	1.290E-02	1.334E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + CCL3 = CCL4 + CL
Hf {Kcal/mol} .000 19.000 -22.940 28.920
S {cal/mol K} 53.290 70.920 74.020 39.460

dHr {kcal/mol} (298K) = -13.02 dHr avg (298., 1000. K) = -12.65
dU (dE) {kcal/mol} (") = -13.02 dUr avg (298., 1000. K) = -12.65
dSr {cal/mol K} (") = -10.73 dSr avg (298., 1000. K) = -9.92
dGr {kcal/mol} (") = -9.82 dGr avg (298., 1000. K) = -6.21
Af/Ar (") = 4.516E-03 Af/Ar avg (298., 1000. K) = 6.803E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.302E+01	-1.302E+01	-1.072E+01	4.541E-03	-9.801E+00
400.00	-1.282E+01	-1.282E+01	-1.017E+01	5.993E-03	-8.757E+00
500.00	-1.261E+01	-1.261E+01	-9.692E+00	7.614E-03	-7.765E+00
600.00	-1.239E+01	-1.239E+01	-9.282E+00	9.359E-03	-6.817E+00
800.00	-1.193E+01	-1.193E+01	-8.621E+00	1.305E-02	-5.030E+00
1000.00	-1.147E+01	-1.147E+01	-8.116E+00	1.683E-02	-3.358E+00
1200.00	-1.103E+01	-1.103E+01	-7.714E+00	2.061E-02	-1.776E+00
1500.00	-1.038E+01	-1.038E+01	-7.227E+00	2.633E-02	4.619E-01
2000.00	-9.296E+00	-9.296E+00	-6.604E+00	3.602E-02	3.912E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + C2CL5 = C2CL6 + CL
Hf {Kcal/mol} .000 9.060 -33.800 28.920
S {cal/mol K} 53.290 95.680 94.770 39.460

dHr {kcal/mol} (298K) = -13.94 dHr avg (298., 1000. K) = -13.54
dU (dE) {kcal/mol} (") = -13.94 dUr avg (298., 1000. K) = -13.54
dSr {cal/mol K} (") = -14.74 dSr avg (298., 1000. K) = -13.88
dGr {kcal/mol} (") = -9.55 dGr avg (298., 1000. K) = -4.53
Af/Ar (") = 6.002E-04 Af/Ar avg (298., 1000. K) = 9.233E-04

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.394E+01	-1.394E+01	-1.473E+01	6.028E-04	-9.518E+00
400.00	-1.376E+01	-1.376E+01	-1.423E+01	7.766E-04	-8.070E+00
500.00	-1.353E+01	-1.353E+01	-1.371E+01	1.007E-03	-6.673E+00
600.00	-1.327E+01	-1.327E+01	-1.324E+01	1.277E-03	-5.326E+00
800.00	-1.273E+01	-1.273E+01	-1.247E+01	1.882E-03	-2.759E+00
1000.00	-1.223E+01	-1.223E+01	-1.191E+01	2.499E-03	-3.240E-01
1200.00	-1.176E+01	-1.176E+01	-1.148E+01	3.097E-03	2.013E+00
1500.00	-1.108E+01	-1.108E+01	-1.097E+01	4.004E-03	5.377E+00
2000.00	-9.957E+00	-9.957E+00	-1.032E+01	5.539E-03	1.069E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + CF3 = CF3CL + CL
Hf {Kcal/mol} .000 -113.010 -169.200 28.920
S {cal/mol K} 53.290 63.420 68.170 39.460

dHr {kcal/mol} (298K) = -27.27 dHr avg (298., 1000. K) = -26.95
dU (dE) {kcal/mol} (") = -27.27 dUr avg (298., 1000. K) = -26.95
dSr {cal/mol K} (") = -9.08 dSr avg (298., 1000. K) = -8.38
dGr {kcal/mol} (") = -24.56 dGr avg (298., 1000. K) = -21.50
Af/Ar (") = 1.036E-02 Af/Ar avg (298., 1000. K) = 1.471E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.727E+01	-2.727E+01	-9.072E+00	1.040E-02	-2.455E+01
400.00	-2.712E+01	-2.712E+01	-8.648E+00	1.288E-02	-2.366E+01
500.00	-2.693E+01	-2.693E+01	-8.236E+00	1.585E-02	-2.282E+01
600.00	-2.673E+01	-2.673E+01	-7.858E+00	1.916E-02	-2.201E+01
800.00	-2.629E+01	-2.629E+01	-7.227E+00	2.633E-02	-2.051E+01
1000.00	-2.585E+01	-2.585E+01	-6.738E+00	3.368E-02	-1.911E+01
1200.00	-2.542E+01	-2.542E+01	-6.348E+00	4.099E-02	-1.780E+01
1500.00	-2.478E+01	-2.478E+01	-5.872E+00	5.208E-02	-1.597E+01
2000.00	-2.372E+01	-2.372E+01	-5.259E+00	7.090E-02	-1.320E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + CF2CL = CF2CL2 + CL
 Hf {Kcal/mol} .000 -66.020 -117.500 28.920
 S {cal/mol K} 53.290 67.720 71.910 39.460

dHr {kcal/mol} (298K) = -22.56 dHr avg (298., 1000. K) = -22.22
 dU (dE) {kcal/mol} (") = -22.56 dUr avg (298., 1000. K) = -22.22
 dSr {cal/mol K} (") = -9.64 dSr avg (298., 1000. K) = -8.91
 dGr {kcal/mol} (") = -19.69 dGr avg (298., 1000. K) = -16.44
 Af/Ar (") = 7.816E-03 Af/Ar avg (298., 1000. K) = 1.127E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.256E+01	-2.256E+01	-9.632E+00	7.848E-03	-1.967E+01
400.00	-2.240E+01	-2.240E+01	-9.186E+00	9.825E-03	-1.873E+01
500.00	-2.221E+01	-2.221E+01	-8.754E+00	1.221E-02	-1.783E+01
600.00	-2.199E+01	-2.199E+01	-8.362E+00	1.487E-02	-1.697E+01
800.00	-2.154E+01	-2.154E+01	-7.713E+00	2.062E-02	-1.537E+01
1000.00	-2.110E+01	-2.110E+01	-7.217E+00	2.646E-02	-1.388E+01
1200.00	-2.067E+01	-2.067E+01	-6.825E+00	3.222E-02	-1.248E+01
1500.00	-2.003E+01	-2.003E+01	-6.348E+00	4.097E-02	-1.050E+01
2000.00	-1.896E+01	-1.896E+01	-5.733E+00	5.583E-02	-7.490E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + CFCL2 = CFCL3 + CL
 Hf {Kcal/mol} .000 -21.600 -67.700 28.920
 S {cal/mol K} 53.290 69.170 74.070 39.460

dHr {kcal/mol} (298K) = -17.18 dHr avg (298., 1000. K) = -16.77
 dU (dE) {kcal/mol} (") = -17.18 dUr avg (298., 1000. K) = -16.77
 dSr {cal/mol K} (") = -8.93 dSr avg (298., 1000. K) = -8.03
 dGr {kcal/mol} (") = -14.52 dGr avg (298., 1000. K) = -11.55
 Af/Ar (") = 1.117E-02 Af/Ar avg (298., 1000. K) = 1.757E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.718E+01	-1.718E+01	-8.919E+00	1.124E-02	-1.450E+01
400.00	-1.697E+01	-1.697E+01	-8.327E+00	1.513E-02	-1.364E+01
500.00	-1.673E+01	-1.673E+01	-7.796E+00	1.977E-02	-1.283E+01
600.00	-1.648E+01	-1.648E+01	-7.334E+00	2.495E-02	-1.208E+01
800.00	-1.597E+01	-1.597E+01	-6.598E+00	3.613E-02	-1.069E+01
1000.00	-1.548E+01	-1.548E+01	-6.058E+00	4.742E-02	-9.425E+00
1200.00	-1.503E+01	-1.503E+01	-5.642E+00	5.846E-02	-8.257E+00
1500.00	-1.436E+01	-1.436E+01	-5.143E+00	7.515E-02	-6.642E+00
2000.00	-1.326E+01	-1.326E+01	-4.510E+00	1.033E-01	-4.237E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + CHCL2CHCL = C2H2CL4 + CL
Hf {Kcal/mol} .000 11.750 -36.000 28.920
S {cal/mol K} 53.290 84.510 84.860 39.460

dHr {kcal/mol} (298K) = -18.83 dHr avg (298., 1000. K) = -18.69
dU (dE) {kcal/mol} (") = -18.83 dUr avg (298., 1000. K) = -18.69
dSr {cal/mol K} (") = -13.48 dSr avg (298., 1000. K) = -13.23
dGr {kcal/mol} (") = -14.81 dGr avg (298., 1000. K) = -10.11
Af/Ar (") = 1.132E-03 Af/Ar avg (298., 1000. K) = 1.283E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.883E+01	-1.883E+01	-1.348E+01	1.130E-03	-1.479E+01
400.00	-1.883E+01	-1.883E+01	-1.348E+01	1.133E-03	-1.344E+01
500.00	-1.876E+01	-1.876E+01	-1.333E+01	1.222E-03	-1.210E+01
600.00	-1.864E+01	-1.864E+01	-1.310E+01	1.367E-03	-1.077E+01
800.00	-1.827E+01	-1.827E+01	-1.258E+01	1.782E-03	-8.204E+00
1000.00	-1.779E+01	-1.779E+01	-1.205E+01	2.328E-03	-5.742E+00
1200.00	-1.726E+01	-1.726E+01	-1.157E+01	2.966E-03	-3.382E+00
1500.00	-1.645E+01	-1.645E+01	-1.096E+01	4.014E-03	-6.244E-03
2000.00	-1.515E+01	-1.515E+01	-1.021E+01	5.856E-03	5.278E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + CH2CLCCL2 = CH2CLCCL3 + CL
Hf {Kcal/mol} .000 7.870 -35.710 28.920
S {cal/mol K} 53.290 84.560 85.070 39.460

dHr {kcal/mol} (298K) = -14.66 dHr avg (298., 1000. K) = -14.39
dU (dE) {kcal/mol} (") = -14.66 dUr avg (298., 1000. K) = -14.39
dSr {cal/mol K} (") = -13.32 dSr avg (298., 1000. K) = -12.77
dGr {kcal/mol} (") = -10.69 dGr avg (298., 1000. K) = -6.10
Af/Ar (") = 1.227E-03 Af/Ar avg (298., 1000. K) = 1.614E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.466E+01	-1.466E+01	-1.332E+01	1.228E-03	-1.066E+01
400.00	-1.458E+01	-1.458E+01	-1.310E+01	1.367E-03	-9.341E+00
500.00	-1.444E+01	-1.444E+01	-1.278E+01	1.610E-03	-8.047E+00
600.00	-1.423E+01	-1.423E+01	-1.241E+01	1.936E-03	-6.787E+00
800.00	-1.372E+01	-1.372E+01	-1.167E+01	2.807E-03	-4.379E+00
1000.00	-1.312E+01	-1.312E+01	-1.101E+01	3.925E-03	-2.112E+00
1200.00	-1.250E+01	-1.250E+01	-1.044E+01	5.222E-03	3.149E-02
1500.00	-1.158E+01	-1.158E+01	-9.760E+00	7.358E-03	3.057E+00
2000.00	-1.016E+01	-1.016E+01	-8.938E+00	1.113E-02	7.719E+00

THERMODYNAMIC ANALYSIS for REACTION



Hf {Kcal/mol} .000 14.730 -34.800 28.920

S {cal/mol K} 53.290 78.560 79.710 39.460

dHr {kcal/mol} (298K) = -20.61 dHr avg (298., 1000. K) = -20.47

dU (dE) {kcal/mol} (") = -20.61 dUr avg (298., 1000. K) = -20.47

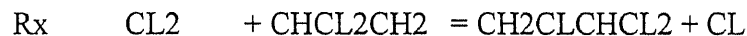
dSr {cal/mol K} (") = -12.68 dSr avg (298., 1000. K) = -12.44

dGr {kcal/mol} (") = -16.83 dGr avg (298., 1000. K) = -12.39

Af/Ar (") = 1.693E-03 Af/Ar avg (298., 1000. K) = 1.909E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.061E+01	-2.061E+01	-1.269E+01	1.688E-03	-1.681E+01
400.00	-2.064E+01	-2.064E+01	-1.277E+01	1.621E-03	-1.553E+01
500.00	-2.057E+01	-2.057E+01	-1.261E+01	1.753E-03	-1.426E+01
600.00	-2.042E+01	-2.042E+01	-1.235E+01	1.999E-03	-1.301E+01
800.00	-1.999E+01	-1.999E+01	-1.173E+01	2.732E-03	-1.060E+01
1000.00	-1.945E+01	-1.945E+01	-1.113E+01	3.697E-03	-8.319E+00
1200.00	-1.887E+01	-1.887E+01	-1.060E+01	4.815E-03	-6.147E+00
1500.00	-1.801E+01	-1.801E+01	-9.962E+00	6.648E-03	-3.067E+00
2000.00	-1.664E+01	-1.664E+01	-9.173E+00	9.886E-03	1.706E+00

THERMODYNAMIC ANALYSIS for REACTION



Hf {Kcal/mol} .000 20.310 -34.800 28.920

S {cal/mol K} 53.290 74.640 79.710 39.460

dHr {kcal/mol} (298K) = -26.19 dHr avg (298., 1000. K) = -26.19

dU (dE) {kcal/mol} (") = -26.19 dUr avg (298., 1000. K) = -26.19

dSr {cal/mol K} (") = -8.76 dSr avg (298., 1000. K) = -8.83

dGr {kcal/mol} (") = -23.58 dGr avg (298., 1000. K) = -20.46

Af/Ar (") = 1.217E-02 Af/Ar avg (298., 1000. K) = 1.176E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.619E+01	-2.619E+01	-8.769E+00	1.212E-02	-2.356E+01
400.00	-2.629E+01	-2.629E+01	-9.050E+00	1.052E-02	-2.267E+01
500.00	-2.630E+01	-2.630E+01	-9.079E+00	1.036E-02	-2.176E+01
600.00	-2.624E+01	-2.624E+01	-8.976E+00	1.092E-02	-2.086E+01
800.00	-2.597E+01	-2.597E+01	-8.590E+00	1.326E-02	-1.910E+01
1000.00	-2.556E+01	-2.556E+01	-8.135E+00	1.667E-02	-1.743E+01
1200.00	-2.508E+01	-2.508E+01	-7.699E+00	2.076E-02	-1.584E+01
1500.00	-2.433E+01	-2.433E+01	-7.140E+00	2.751E-02	-1.362E+01
2000.00	-2.308E+01	-2.308E+01	-6.421E+00	3.950E-02	-1.024E+01

THERMODYNAMIC ANALYSIS for REACTION



Hf {Kcal/mol} .000 10.590 -34.800 28.920

S {cal/mol K} 53.290 88.260 91.180 39.460

dHr {kcal/mol} (298K) = -16.47 dHr avg (298., 1000. K) = -16.51

dU (dE) {kcal/mol} (") = -16.47 dUr avg (298., 1000. K) = -16.51

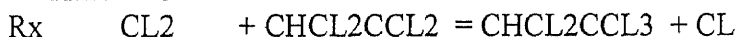
dSr {cal/mol K} (") = -10.91 dSr avg (298., 1000. K) = -10.99

dGr {kcal/mol} (") = -13.22 dGr avg (298., 1000. K) = -9.38

Af/Ar (") = 4.125E-03 Af/Ar avg (298., 1000. K) = 3.972E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.647E+01	-1.647E+01	-1.091E+01	4.130E-03	-1.320E+01
400.00	-1.647E+01	-1.647E+01	-1.089E+01	4.161E-03	-1.211E+01
500.00	-1.650E+01	-1.650E+01	-1.097E+01	4.001E-03	-1.102E+01
600.00	-1.654E+01	-1.654E+01	-1.104E+01	3.862E-03	-9.915E+00
800.00	-1.654E+01	-1.654E+01	-1.105E+01	3.850E-03	-7.703E+00
1000.00	-1.639E+01	-1.639E+01	-1.089E+01	4.176E-03	-5.507E+00
1200.00	-1.612E+01	-1.612E+01	-1.064E+01	4.722E-03	-3.354E+00
1500.00	-1.563E+01	-1.563E+01	-1.028E+01	5.673E-03	-2.175E-01
2000.00	-1.472E+01	-1.472E+01	-9.751E+00	7.392E-03	4.786E+00

THERMODYNAMIC ANALYSIS for REACTION



Hf {Kcal/mol} .000 6.130 -34.800 28.920

S {cal/mol K} 53.290 90.650 91.180 39.460

dHr {kcal/mol} (298K) = -12.01 dHr avg (298., 1000. K) = -11.78

dU (dE) {kcal/mol} (") = -12.01 dUr avg (298., 1000. K) = -11.78

dSr {cal/mol K} (") = -13.30 dSr avg (298., 1000. K) = -12.77

dGr {kcal/mol} (") = -8.04 dGr avg (298., 1000. K) = -3.49

Af/Ar (") = 1.239E-03 Af/Ar avg (298., 1000. K) = 1.615E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.201E+01	-1.201E+01	-1.329E+01	1.247E-03	-8.020E+00
400.00	-1.184E+01	-1.184E+01	-1.281E+01	1.584E-03	-6.718E+00
500.00	-1.172E+01	-1.172E+01	-1.253E+01	1.821E-03	-5.451E+00
600.00	-1.161E+01	-1.161E+01	-1.233E+01	2.014E-03	-4.208E+00
800.00	-1.136E+01	-1.136E+01	-1.198E+01	2.405E-03	-1.777E+00
1000.00	-1.104E+01	-1.104E+01	-1.162E+01	2.883E-03	5.839E-01
1200.00	-1.064E+01	-1.064E+01	-1.126E+01	3.452E-03	2.872E+00
1500.00	-1.002E+01	-1.002E+01	-1.080E+01	4.365E-03	6.179E+00
2000.00	-8.949E+00	-8.949E+00	-1.018E+01	5.947E-03	1.142E+01

APPENDIX 1.2

KINETIC ANALYSIS

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + CH3 = TSCXCL2

Hf {Kcal/mol} .000 34.820 32.100

S {cal/mol K} 53.290 46.380 74.110

dHr {kcal/mol} (298K) = -2.72 dHr avg (298., 1500. K) = -3.18

dU (dE) {kcal/mol} (") = -2.13 dUr avg (298., 1500. K) = -1.39

dSr {cal/mol K} (") = -25.56 dSr avg (298., 1500. K) = -26.28

dGr {kcal/mol} (") = 4.90 dGr avg (298., 1500. K) = 20.45

 Af/Ar (") = 1.723E-01 Af/Ar avg (298., 1500. K) = 3.622E-01

Fit Af/Ar : A = 2.154E-02 n = .34 alpha = -2.993E-04 avg error 1.71 %

Fit Af/Ar w/ddU: A = 2.740E-03 n = .71 alpha = -2.359E-04 avg error 2.47 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.723E+00	-2.127E+00	-2.557E+01	1.725E-01	4.948E+00
400.00	-2.862E+00	-2.068E+00	-2.597E+01	1.877E-01	7.527E+00
500.00	-2.975E+00	-1.982E+00	-2.623E+01	2.067E-01	1.014E+01
600.00	-3.068E+00	-1.876E+00	-2.640E+01	2.277E-01	1.277E+01
800.00	-3.218E+00	-1.628E+00	-2.661E+01	2.722E-01	1.807E+01
1000.00	-3.344E+00	-1.357E+00	-2.675E+01	3.169E-01	2.341E+01
1200.00	-3.464E+00	-1.080E+00	-2.686E+01	3.599E-01	2.877E+01
1500.00	-3.639E+00	-6.588E-01	-2.699E+01	4.213E-01	3.685E+01
2000.00	-3.868E+00	1.057E-01	-2.713E+01	5.253E-01	5.038E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{prime} * T^n * \exp(-E_a/RT)$

$A_{prime} = 5.2703E+07$ $n = 1.61232$ $E_a = -2.5676E+03$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.079E+12	9.861E+03	3.824E+13	3.859E+13
400.00	1.565E+12	1.568E+04	2.111E+13	2.090E+13
500.00	2.154E+12	2.247E+04	1.583E+13	1.570E+13
600.00	2.848E+12	3.015E+04	1.374E+13	1.369E+13
800.00	4.541E+12	4.794E+04	1.264E+13	1.271E+13
1000.00	6.607E+12	6.870E+04	1.308E+13	1.318E+13
1200.00	9.004E+12	9.218E+04	1.416E+13	1.426E+13
1500.00	1.318E+13	1.321E+05	1.643E+13	1.648E+13
2000.00	2.190E+13	2.101E+05	2.133E+13	2.112E+13

THERMODYNAMIC ANALYSIS for REACTION

Rx CH3CL-CL = TSCXCL2
 Hf {Kcal/mol} 6.230 32.100
 S {cal/mol K} 80.450 74.110

dHr {kcal/mol} (298K) = 25.87 dHr avg (298., 1500. K) = 25.54
 dU (dE) {kcal/mol} (") = 25.87 dUr avg (298., 1500. K) = 25.54
 dSr {cal/mol K} (") = -6.34 dSr avg (298., 1500. K) = -6.44
 dGr {kcal/mol} (") = 27.76 dGr avg (298., 1500. K) = 31.33
 Af/Ar (") = 4.114E-02 Af/Ar avg (298., 1500. K) = 3.919E-02
 Fit Af/Ar : A = 8.306E-04 n = .75 alpha = 1.098E-03 avg error 3.91 %
 Fit Af/Ar w/ddU: A = 1.142E-04 n = 1.15 alpha = 1.847E-03 avg error 9.19 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.587E+01	2.587E+01	-6.331E+00	4.133E-02	2.777E+01
400.00	2.599E+01	2.599E+01	-5.979E+00	4.935E-02	2.839E+01
500.00	2.607E+01	2.607E+01	-5.808E+00	5.376E-02	2.897E+01
600.00	2.610E+01	2.610E+01	-5.747E+00	5.544E-02	2.955E+01
800.00	2.606E+01	2.606E+01	-5.807E+00	5.379E-02	3.070E+01
1000.00	2.590E+01	2.590E+01	-5.986E+00	4.916E-02	3.188E+01
1200.00	2.565E+01	2.565E+01	-6.205E+00	4.403E-02	3.310E+01
1500.00	2.521E+01	2.521E+01	-6.533E+00	3.734E-02	3.501E+01
2000.00	2.440E+01	2.440E+01	-6.997E+00	2.956E-02	3.840E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$
 $A_{\text{prime}} = 4.9360E+09$ $n = .79197$ $E_a = 2.6226E+04$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.583E+11	9.158E+01	3.651E-08	3.533E-08
400.00	4.113E+11	1.150E+02	2.573E-03	2.654E-03
500.00	5.601E+11	1.372E+02	2.251E+00	2.326E+00
600.00	6.932E+11	1.586E+02	2.149E+02	2.188E+02
800.00	8.967E+11	1.991E+02	6.815E+04	6.720E+04
1000.00	1.024E+12	2.376E+02	2.242E+06	2.174E+06
1200.00	1.101E+12	2.745E+02	2.340E+07	2.266E+07
1500.00	1.167E+12	3.276E+02	2.473E+08	2.440E+08
2000.00	1.232E+12	4.114E+02	2.651E+09	2.765E+09

THERMODYNAMIC ANALYSIS for REACTION

Rx CH₃CL + CL = TSCXCL₂
 Hf {Kcal/mol} -19.600 28.920 32.100
 S {cal/mol K} 56.000 39.460 74.110

dHr {kcal/mol} (298K) = 22.78 dHr avg (298., 1500. K) = 22.01
 dU (dE) {kcal/mol} (") = 23.37 dUr avg (298., 1500. K) = 23.80
 dSr {cal/mol K} (") = -21.35 dSr avg (298., 1500. K) = -22.02
 dGr {kcal/mol} (") = 29.15 dGr avg (298., 1500. K) = 41.82

Af/Ar (") = 1.433E+00 Af/Ar avg (298., 1500. K) = 3.078E+00

Fit Af/Ar : A = 7.364E-04 n = 1.40 alpha = 1.106E-03 avg error 4.25 %

Fit Af/Ar w/ddU: A = 5.664E-06 n = 2.33 alpha = 2.153E-03 avg error 11.46 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.278E+01	2.338E+01	-2.135E+01	1.446E+00	2.918E+01
400.00	2.284E+01	2.363E+01	-2.118E+01	2.090E+00	3.131E+01
500.00	2.284E+01	2.384E+01	-2.117E+01	2.633E+00	3.343E+01
600.00	2.280E+01	2.400E+01	-2.124E+01	3.053E+00	3.555E+01
800.00	2.261E+01	2.420E+01	-2.151E+01	3.553E+00	3.982E+01
1000.00	2.230E+01	2.429E+01	-2.185E+01	3.733E+00	4.415E+01
1200.00	2.191E+01	2.429E+01	-2.221E+01	3.745E+00	4.856E+01
1500.00	2.125E+01	2.423E+01	-2.270E+01	3.657E+00	5.530E+01
2000.00	2.011E+01	2.408E+01	-2.336E+01	3.501E+00	6.682E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$

$A_{\text{prime}} = 2.4686E+09$ $n = 1.42724$ $E_a = 2.3358E+04$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	9.044E+12	3.431E+03	8.402E-05	8.125E-05
400.00	1.743E+13	5.173E+03	2.133E+00	2.201E+00
500.00	2.745E+13	7.113E+03	1.045E+03	1.081E+03
600.00	3.820E+13	9.227E+03	6.928E+04	7.055E+04
800.00	5.927E+13	1.391E+04	1.447E+07	1.426E+07
1000.00	7.782E+13	1.913E+04	3.823E+08	3.705E+08
1200.00	9.369E+13	2.482E+04	3.521E+09	3.409E+09
1500.00	1.144E+14	3.412E+04	3.370E+10	3.326E+10
2000.00	1.460E+14	5.145E+04	3.410E+11	3.557E+11

THERMODYNAMIC ANALYSIS for REACTION

Rx CH3CL + CL = CH3CL-CL
 Hf {Kcal/mol} -19.600 28.920 6.230
 S {cal/mol K} 56.000 39.460 80.450

dHr {kcal/mol} (298K) = -3.09 dHr avg (298., 1500. K) = -3.53
 dU (dE) {kcal/mol} (") = -2.50 dUr avg (298., 1500. K) = -1.74
 dSr {cal/mol K} (") = -15.01 dSr avg (298., 1500. K) = -15.59
 dGr {kcal/mol} (") = 1.39 dGr avg (298., 1500. K) = 10.49
 Af/Ar (") = 3.484E+01 Af/Ar avg (298., 1500. K) = 7.854E+01
 Fit Af/Ar : A = 8.866E-01 n = .65 alpha = 8.294E-06 avg error .33 %
 Fit Af/Ar w/ddU: A = 4.958E-02 n = 1.17 alpha = 3.057E-04 avg error 2.05 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-3.091E+00	-2.495E+00	-1.501E+01	3.499E+01	1.413E+00
400.00	-3.158E+00	-2.363E+00	-1.521E+01	4.235E+01	2.924E+00
500.00	-3.227E+00	-2.234E+00	-1.536E+01	4.898E+01	4.453E+00
600.00	-3.298E+00	-2.106E+00	-1.549E+01	5.507E+01	5.996E+00
800.00	-3.445E+00	-1.855E+00	-1.570E+01	6.605E+01	9.116E+00
1000.00	-3.594E+00	-1.607E+00	-1.587E+01	7.592E+01	1.227E+01
1200.00	-3.744E+00	-1.359E+00	-1.600E+01	8.506E+01	1.546E+01
1500.00	-3.963E+00	-9.824E-01	-1.617E+01	9.794E+01	2.029E+01
2000.00	-4.298E+00	-3.244E-01	-1.636E+01	1.185E+02	2.842E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{prime} * T^n * \exp(-E_a/RT)$
 $A_{prime} = 1.0421E+10$ $n = 1.63527$ $E_a = -2.8673E+03$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.188E+14	1.124E+04	1.439E+16	1.438E+16
400.00	3.532E+14	1.799E+04	6.908E+15	6.914E+15
500.00	5.106E+14	2.591E+04	4.837E+15	4.840E+15
600.00	6.889E+14	3.492E+04	4.031E+15	4.031E+15
800.00	1.102E+15	5.589E+04	3.539E+15	3.537E+15
1000.00	1.583E+15	8.050E+04	3.554E+15	3.551E+15
1200.00	2.128E+15	1.085E+05	3.763E+15	3.762E+15
1500.00	3.063E+15	1.562E+05	4.259E+15	4.260E+15
2000.00	4.940E+15	2.501E+05	5.360E+15	5.362E+15

THERMODYNAMIC ANALYSIS for REACTION

Rx CL2 + C2H5 = TSCCXCL2
Hf {Kcal/mol} .000 29.300 24.200
S {cal/mol K} 53.290 57.420 84.100

dHr {kcal/mol} (298K) = -5.10 dHr avg (298., 1500. K) = -5.27
dU (dE) {kcal/mol} (") = -4.51 dUr avg (298., 1500. K) = -3.48
dSr {cal/mol K} (") = -26.61 dSr avg (298., 1500. K) = -26.76
dGr {kcal/mol} (") = 2.83 dGr avg (298., 1500. K) = 18.79

Af/Ar (") = 1.016E-01 Af/Ar avg (298., 1500. K) = 2.836E-01

Fit Af/Ar : A = 1.867E-04 n = 1.12 alpha = 2.635E-04 avg error .86 %

Fit Af/Ar w/ddU: A = 1.389E-06 n = 2.02 alpha = 8.979E-04 avg error 2.54 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-5.100E+00	-4.504E+00	-2.661E+01	1.021E-01	2.883E+00
400.00	-5.110E+00	-4.315E+00	-2.664E+01	1.342E-01	5.546E+00
500.00	-5.108E+00	-4.114E+00	-2.663E+01	1.682E-01	8.210E+00
600.00	-5.103E+00	-3.911E+00	-2.663E+01	2.027E-01	1.087E+01
800.00	-5.112E+00	-3.523E+00	-2.664E+01	2.686E-01	1.620E+01
1000.00	-5.165E+00	-3.178E+00	-2.670E+01	3.262E-01	2.153E+01
1200.00	-5.259E+00	-2.875E+00	-2.678E+01	3.749E-01	2.688E+01
1500.00	-5.439E+00	-2.458E+00	-2.692E+01	4.382E-01	3.493E+01
2000.00	-5.700E+00	-1.726E+00	-2.707E+01	5.414E-01	4.843E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$

A_{prime} = 5.4494E+06 n = 1.89769 E_a = -5.0051E+03

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	6.388E+11	5.021E+04	1.222E+15	1.212E+15
400.00	1.119E+12	8.668E+04	2.552E+14	2.565E+14
500.00	1.753E+12	1.324E+05	1.102E+14	1.112E+14
600.00	2.535E+12	1.871E+05	6.740E+13	6.787E+13
800.00	4.480E+12	3.230E+05	4.109E+13	4.102E+13
1000.00	6.800E+12	4.933E+05	3.366E+13	3.337E+13
1200.00	9.380E+12	6.972E+05	3.132E+13	3.100E+13
1500.00	1.370E+13	1.065E+06	3.126E+13	3.111E+13
2000.00	2.257E+13	1.838E+06	3.485E+13	3.529E+13

THERMODYNAMIC ANALYSIS for REACTION

Rx CCCL-CL = TSCCXCL2
 Hf {Kcal/mol} -1.190 24.200
 S {cal/mol K} 86.160 84.100

dHr {kcal/mol} (298K) = 25.39 dHr avg (298., 1500. K) = 24.79
 dU (dE) {kcal/mol} (") = 25.39 dUr avg (298., 1500. K) = 24.79
 dSr {cal/mol K} (") = -2.06 dSr avg (298., 1500. K) = -2.62
 dGr {kcal/mol} (") = 26.00 dGr avg (298., 1500. K) = 27.15
 Af/Ar (") = 3.546E-01 Af/Ar avg (298., 1500. K) = 2.672E-01
 Fit Af/Ar : A = 1.312E-01 n = .22 alpha = 7.671E-04 avg error 2.66 %
 Fit Af/Ar w/ddU: A = 1.292E-01 n = .25 alpha = 1.150E-03 avg error 5.57 %

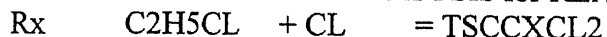
T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.539E+01	2.539E+01	-2.058E+00	3.550E-01	2.601E+01
400.00	2.541E+01	2.541E+01	-1.999E+00	3.658E-01	2.621E+01
500.00	2.540E+01	2.540E+01	-2.013E+00	3.630E-01	2.641E+01
600.00	2.537E+01	2.537E+01	-2.076E+00	3.518E-01	2.661E+01
800.00	2.522E+01	2.522E+01	-2.285E+00	3.166E-01	2.705E+01
1000.00	2.499E+01	2.499E+01	-2.547E+00	2.776E-01	2.753E+01
1200.00	2.469E+01	2.469E+01	-2.816E+00	2.424E-01	2.807E+01
1500.00	2.419E+01	2.419E+01	-3.185E+00	2.013E-01	2.897E+01
2000.00	2.334E+01	2.334E+01	-3.675E+00	1.573E-01	3.069E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{prime} * T^n * \exp(-E_a/RT)$
 $A_{prime} = 1.9116E+11$ $n = .55094$ $E_a = 2.5816E+04$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.219E+12	2.316E+01	7.040E-07	6.878E-07
400.00	3.048E+12	2.714E+01	3.974E-02	4.060E-02
500.00	3.782E+12	3.069E+01	2.971E+01	3.042E+01
600.00	4.398E+12	3.393E+01	2.523E+03	2.557E+03
800.00	5.277E+12	3.976E+01	6.790E+05	6.723E+05
1000.00	5.784E+12	4.496E+01	2.001E+07	1.957E+07
1200.00	6.062E+12	4.971E+01	1.931E+08	1.887E+08
1500.00	6.293E+12	5.621E+01	1.878E+09	1.860E+09
2000.00	6.554E+12	6.587E+01	1.844E+10	1.900E+10

THERMODYNAMIC ANALYSIS for REACTION



Hf {Kcal/mol} -26.800 28.920 24.200

S {cal/mol K} 65.790 39.460 84.100

dHr {kcal/mol} (298K) = 22.08 dHr avg (298., 1500. K) = 21.26

dU (dE) {kcal/mol} (") = 22.67 dUr avg (298., 1500. K) = 23.04

dSr {cal/mol K} (") = -21.15 dSr avg (298., 1500. K) = -22.01

dGr {kcal/mol} (") = 28.39 dGr avg (298., 1500. K) = 41.05

Af/Ar (") = 1.585E+00 Af/Ar avg (298., 1500. K) = 3.094E+00

Fit Af/Ar : A = 6.529E-03 n = 1.01 alpha = 7.453E-04 avg error 3.13 %

Fit Af/Ar w/ddU: A = 1.869E-04 n = 1.69 alpha = 1.477E-03 avg error 8.31 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.208E+01	2.268E+01	-2.115E+01	1.596E+00	2.842E+01
400.00	2.207E+01	2.287E+01	-2.118E+01	2.100E+00	3.054E+01
500.00	2.203E+01	2.302E+01	-2.127E+01	2.497E+00	3.266E+01
600.00	2.195E+01	2.314E+01	-2.141E+01	2.793E+00	3.480E+01
800.00	2.171E+01	2.330E+01	-2.175E+01	3.146E+00	3.911E+01
1000.00	2.140E+01	2.338E+01	-2.210E+01	3.294E+00	4.350E+01
1200.00	2.103E+01	2.341E+01	-2.244E+01	3.340E+00	4.795E+01
1500.00	2.043E+01	2.341E+01	-2.288E+01	3.342E+00	5.475E+01
2000.00	1.943E+01	2.340E+01	-2.346E+01	3.328E+00	6.634E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$

$A_{\text{prime}} = 3.9790\text{E}+09$ $n = 1.35426$ $E_a = 2.2629\text{E}+04$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	9.980E+12	2.263E+03	3.007E-04	2.939E-04
400.00	1.751E+13	3.341E+03	5.616E+00	5.740E+00
500.00	2.603E+13	4.520E+03	2.255E+03	2.307E+03
600.00	3.493E+13	5.786E+03	1.299E+05	1.315E+05
800.00	5.247E+13	8.542E+03	2.257E+07	2.233E+07
1000.00	6.867E+13	1.156E+04	5.321E+08	5.208E+08
1200.00	8.355E+13	1.479E+04	4.546E+09	4.449E+09
1500.00	1.045E+14	2.001E+04	4.050E+10	4.016E+10
2000.00	1.388E+14	2.954E+04	3.846E+11	3.956E+11

THERMODYNAMIC ANALYSIS for REACTION

Rx C2H5CL + CL = CCCL-CL
 Hf {Kcal/mol} -26.800 28.920 -1.190
 S {cal/mol K} 65.790 39.460 86.160

dHr {kcal/mol} (298K) = -3.31 dHr avg (298., 1500. K) = -3.53
 dU (dE) {kcal/mol} (") = -2.72 dUr avg (298., 1500. K) = -1.75
 dSr {cal/mol K} (") = -19.09 dSr avg (298., 1500. K) = -19.39
 dGr {kcal/mol} (") = 2.38 dGr avg (298., 1500. K) = 13.90
 Af/Ar (") = 4.470E+00 Af/Ar avg (298., 1500. K) = 1.158E+01
 Fit Af/Ar : A = 4.975E-02 n = .79 alpha = -2.173E-05 avg error .50 %
 Fit Af/Ar w/ddU: A = 1.447E-03 n = 1.44 alpha = 3.272E-04 avg error 2.65 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-3.310E+00	-2.714E+00	-1.909E+01	4.495E+00	2.417E+00
400.00	-3.340E+00	-2.545E+00	-1.918E+01	5.742E+00	4.330E+00
500.00	-3.378E+00	-2.385E+00	-1.926E+01	6.878E+00	6.252E+00
600.00	-3.421E+00	-2.229E+00	-1.934E+01	7.939E+00	8.182E+00
800.00	-3.508E+00	-1.918E+00	-1.946E+01	9.937E+00	1.206E+01
1000.00	-3.589E+00	-1.602E+00	-1.955E+01	1.187E+01	1.597E+01
1200.00	-3.661E+00	-1.277E+00	-1.962E+01	1.377E+01	1.988E+01
1500.00	-3.759E+00	-7.789E-01	-1.969E+01	1.660E+01	2.578E+01
2000.00	-3.914E+00	5.984E-02	-1.978E+01	2.116E+01	3.565E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$
 $A_{\text{prime}} = 4.3372E+08$ $n = 1.80332$ $E_a = -3.1876E+03$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.811E+13	2.931E+04	2.670E+15	2.671E+15
400.00	4.788E+13	4.924E+04	1.178E+15	1.178E+15
500.00	7.170E+13	7.364E+04	7.907E+14	7.902E+14
600.00	9.931E+13	1.023E+05	6.439E+14	6.431E+14
800.00	1.657E+14	1.719E+05	5.540E+14	5.537E+14
1000.00	2.474E+14	2.570E+05	5.541E+14	5.545E+14
1200.00	3.446E+14	3.571E+05	5.888E+14	5.896E+14
1500.00	5.191E+14	5.340E+05	6.741E+14	6.748E+14
2000.00	8.823E+14	8.971E+05	8.691E+14	8.677E+14

**REFERENCES
(PART ONE)**

1. Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* 1942, 10, 428.
2. Earl, B. L.; Titus, R. L. *Collect. Czech. Chem. Commun.* 1995, 60, 104.
3. Lay, T. H.; Bozzelli, J. W.; Dean, A. M.; Ritter, E. R. *J. Phys. Chem.* 1995, 99(39), 14514-14527.
4. Petersson, G. A.; Nyden, M. R. *J. Chem. Phys.* 1981, 75, 3423.
5. Petersson, G. A.; Al-Laham, M.A. *J. Chem. Phys.* 1994, 94, 6081.
6. Montgomery, Jr. J. A.; Ochterski, J. W.; Petersson, G. A. *J. Phys. Chem.* 1994, 101, 5900.
7. Scott, A. P.; Random, L. *J. Phys. Chem.* 1996, 100, 16502.
8. Hehre, W. J.; Random, L.; Schleyer, P. R.; Pople, J. A. *Ab-Initio Molecular Orbital Theory*; John Wiley & Sons: New York, NY, 1986.
9. Timonen, R. S.; Gutman, D. *J. Phys. Chem.* 1986, 90, 2987.
10. Timonen, R. S.; Russell, J. J.; Sarzynski, D.; Gutman, D. *J. Phys. Chem.* 1987, 91, 1873.
11. Seetula, J. A.; Gutman, D.; Lightfoot, P. D.; Rayes, M. T.; Senkan, S. M. *J. Phys. Chem.* 1991, 95, 10688-10693.
12. Timonen, R. S.; Russell, J. J.; Gutman, D. *Int. J. Chem. Kinet.* 1986, 18, 1193.
13. Ayscough, P. B.; Cocker, A. J.; Dainton, F. S.; Hirst, S.; Weston, M. *Proc. Chem. Soc.* 1961, 244.
14. Ayscough, P. B.; Dainton, F. S.; Fleischfresser, B. E. *Trans. Faraday Soc.* 1966, 62, 1838.
15. Bertrand, L.; Bizongwako, J.; Huybrechts, G.; Olbregts, J. *Bull. Soc. Chim. Belg.* 1972, 81, 73-80. (1) Using $R. + O_2 = 6.31E+10$ for k_{ref} .
16. Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables*; 2nd Ed.(NSRDS-NBS37). U.S.Government Printing Office: Washington D.C., 1970.

17. Rodgers, A. S. *Selected Values for Properties of Chemical Compounds*; Thermodynamic Research Center, Texas A&M University : College Station, TX, 1982.
18. Taylor, P. H.; Dellinger, B.; Tirey, D. A. *Int. J. Chem. Kinet.* 1991, 23, 1051-1074.
19. Kafafi, S. A.; Hudgens, J. W. *J. Phys. Chem.* 1989, 93, 3474-3479. : I took the frequencies in this article for calculating S, Cp.
20. Stull, D. R.; Westrum, E. F. Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Robert E. Krieger Publishing : Malabar, FL, 1987.
21. Rayez, M. T.; Rayez, J. C.; Sawerysyn, J. P. *J. Phys. Chem.* 1994, 98(44), 11342-11352.
22. Zhu, L.; Bozzelli, J. W.; Lay, T. H. *Ind. Eng. Chem. Res.* 1998, 37, 3497-3507.
23. Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Am. Chem. Soc.* 1997, 119(47), 11452-11457.
24. Seetula, J. A. *J. Chem. Soc., Faraday Trans.* 1998, 94(7), 891-898.
25. Tschuikow-Roux, E.; Paddison, S. *Int. J. Chem. Kinet.* 1987, 19, 15-24.
26. Wong, D. K.; Kretkowski, D. A.; Bozzelli, J. W. *Ind. Eng. Chem. Res.* 1993, 32, 3184-3188.
27. Seetula, J. A. *J. Chem. Soc., Faraday Trans.* 1998, 94, 3561-3567.
28. Seetula, J. A. *J. Chem. Soc., Faraday Trans.* 1996, 92, 3069-3078.
29. Seetula, J. A.; Gutman, D. *J. Phys. Chem.* 1991, 95, 3626-3630.

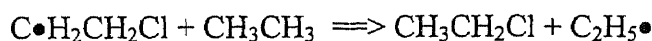
PART II

EVALUATED THERMODYNAMIC PROPERTY DATA OF C₁ AND C₂ CHLOROCARBON MOLECULES AND RADICALS

CHAPTER 1

ABSTRACT FOR PART TWO

Ideal gas thermodynamic parameters, $\Delta H_{f(298)}^{\circ}$, $S_{(298)}^{\circ}$ and $C_p(T)$ are evaluated for C_1 and C_2 chlorocarbon molecules and radicals from literature data. Enthalpies of some chlorocarbon radicals are from a combination of literature data and *ab initio* or density functional calculations along with isodesmic reactions: for example $C\bullet H_2CH_2Cl$ is from a calculated ΔH_{rxn} for



and the known $\Delta H_{f(298)}^{\circ}$ for ethane, chloroethane and ethyl radical. Entropies and $C_p(T)$ values of C_2H_5 are from evaluated literature.

Evaluated thermodynamic property data are presented for all isomers of the stable molecules CH_3Cl , CH_2Cl_2 , $CHCl_3$, CCl_4 , C_2H_5Cl , $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5 , C_2Cl_6 , C_2H_3Cl , $C_2H_2Cl_2$, C_2HCl_3 , and C_2Cl_4 .

Evaluated thermodynamic property data are also presented for the alkyl radicals, (including isomers when they exist) $C\bullet H_2Cl$, $C\bullet HCl_2$, $C\bullet Cl_3$, $C_2H_4Cl\bullet$, $C_2H_3Cl_2\bullet$, $C_2H_2Cl_3\bullet$, $C_2HCl_4\bullet$, and $C_2Cl_5\bullet$, for the olefin radicals (including isomers) $C_2H_2Cl\bullet$, $C_2HCl_2\bullet$, and $C_2Cl_3\bullet$.

CHAPTER 2

INTRODUCTION FOR PART TWO

Chlorocarbons are widely used chemicals or solvents in synthesis and in chemical industry, as cleaning agents and starting materials in synthesis of polymers, pesticides, and other products. Many chlorocarbons are present in the atmosphere and chlorinated organic species are present in both municipal and hazardous wastes as polyvinyl chloride and other halogenated polymers and products. Thermodynamic properties of chlorocarbons are important to industries utilizing them, in analysis of environmental effects and in evaluation of kinetics or thermodynamic equilibrium for both destruction and synthesis processes. These properties are also needed as input in kinetic modeling and in equilibrium codes. The presence of chlorocarbon is known to slow the overall oxidation rate of hydrocarbons through studies of flame velocity, temperature, and flame stability.⁷³ Reports of studies under varied condition sets indicate that both acceleration and inhibition effects can be observed in hydrocarbon reaction systems with a chlorinated hydrocarbon present.⁷⁴⁻⁷⁶ It would be of significant value to have knowledge of their fundamental thermodynamic properties for equilibrium calculations and for an accurate and fundamental understanding of the reaction pathways relating to chlorocarbon formation, destruction, and interactions in synthesis, combustion, and other environmental degradation/transformation processes.

CHAPTER 3

CALCULATION OF C₂ CHLOROCARBON RADICAL ΔH_f^{298} FROM *AB INITIO* DATA FOR PART TWO

ΔH_{rxn} is calculated for reactions involving a number of C₂ chlorocarbon radicals when *ab initio* data are available by the G2 composite calculation method from the study of Cioslowski et al.[12]. The calculations use equations which are illustrated in the example below. $\Delta H_f^{\circ}(298)$ of evaluated experimental or accepted *ab initio* data are taken for the stable molecule species : ethane (-20.20 kcal/mole[3]), chloroethane (-26.80[3]) and for the ethyl radical (29.30[this study]). The known $\Delta H_f^{\circ}(298)$ of the three species and the calculated ΔH_{rxn} allows calculation of $\Delta H_f^{\circ}(298)$ for the target radical, C•H₂CH₂Cl, in the example equation.

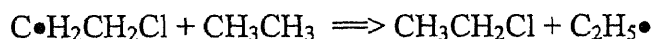


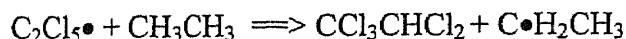
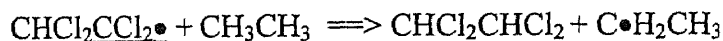
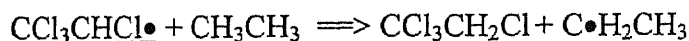
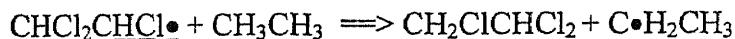
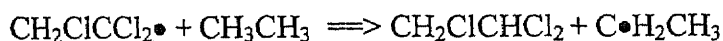
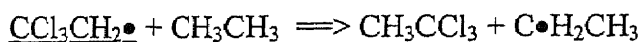
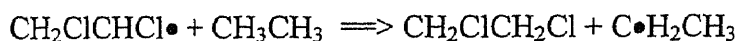
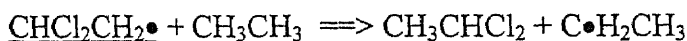
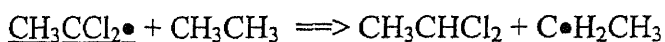
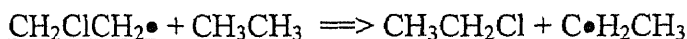
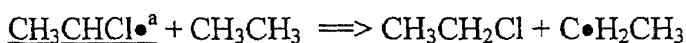
Table II.1 below is a listing of the isodesmic reactions used for the C₂ chlorocarbon radicals with G2 *ab initio* energies determined from atomization analysis reported by Cioslowski et al.[12].

This same method, isodesmic reactions for $\Delta H_f^{\circ}(298)$, is also utilized to determine $\Delta H_f^{\circ}(298)$ for C₂ chlorocarbon radicals using the density functional calculations B3LYP/6-311G** values of Cioslowski et al.[12]. We find the B3LYP/6-311G** values from isodesmic reactions yield slightly lower values than those obtained from the G2 isodesmic reactions.

We also compare these B3LYP-isodesmic reaction values and G2-isodesmic reaction values to the direct(atomization) B3LYP values of Cioslowski et al.[12] and to our evaluated literature data. We find a near constant bias of 2.7 kcal/mole from comparison with the values from G2 isodesmic reaction in this work, values for Seetula's[9] or other experimental values[29,48].

A third estimation method is the use of this constant applied to B3LYP/6-311G** calculations of chlorocarbons. Data are listed in Table II.2.

Table 2.1 Isodesmic Reactions



^a underlined species are the target radicals in the equations.

Table 2.2 Thermodynamic Property Data ^a																															
												^a UNITS : H _f ^o ₂₉₈ (kcal/mol), S ^o ₂₉₈ (cal/K * mol)																			
SPECIES	REFERENCE []	H _f ^o ₂₉₈	S ^o ₂₉₈	C _p ³⁰⁰	C _p ⁴⁰⁰	C _p ⁵⁰⁰	C _p ⁶⁰⁰	C _p ⁸⁰⁰	C _p ¹⁰⁰⁰	C _p ¹⁵⁰⁰	ELEMENTS																				
*CL	Benson[1]	28.90	39.50	5.32	5.32	5.32	5.32	5.32	5.32	5.32	5.32	0	0	CL	1	0	G	0													
	JANAF[3]	28.92	39.46	5.22	5.37	5.44	5.45	5.39	5.31	5.18		0	0	CL	1	0	G	0													
	TRC[2]	28.99	39.48	5.22	5.37	5.43	5.44	5.39	5.31	5.17		0	0	CL	1	0	G	0													
	MELIUS93[7]	29.00										0	0	CL	1	0	G	0													
	Seet98[9]	28.99										0	0	CL	1	0	G	0													
	89COX/WAG[44]	28.992+-0.002										0	0	CL	1	0	G	0													
	NJIT99	28.92	39.46	5.22	5.37	5.44	5.45	5.39	5.31	5.18		0	0	CL	1	0	G	0													
CL2	Benson[1]	0.00	53.30	8.16	8.39	8.57	8.71	8.89	8.99	9.11		0	0	CL	2	0	G	0													
	JANAF[3]	0.00	53.29	8.12	8.44	8.62	8.74	8.88	8.96	9.07		0	0	CL	2	0	G	0													
	TRC[2]	0.00	53.32	8.12	8.44	8.62	8.74	8.87	8.95	9.07		0	0	CL	2	0	G	0													
	NJIT99	0.00	53.29	8.12	8.44	8.62	8.74	8.88	8.96	9.07		0	0	CL	2	0	G	0													
CCL	ROD/HOP96[14]	104.30										C	1	CL	1		0	0	G	0											
	85LIAS[52]	104.00										C	1	CL	1		0	0	G	0											
	85CHASE[51]	120.00										C	1	CL	1		0	0	G	0											
¹ CCL2	ROD/HOP96[14]	54.50										C	1	CL	2		0	0	G	0											
	91PAULINO[41]	52.40										C	1	CL	2		0	0	G	0											
	93KOHN[37]	51.00										C	1	CL	2		0	0	G	0											
CCL3	BSN,RADI[1,72]	19.00	72.01	15.89	17.00	17.81	18.37	19.00	19.26	19.59		C	1	CL	3		0	0	G	0											
	JANAF[3]	19.00	70.92	15.25	16.66	17.56	18.16	18.83	19.18	19.56		C	1	CL	3		0	0	G	0											
	MELIUS93[7]	16.60										C	1	CL	3		0	0	G	0											
	73MEN/GOL[63]	19.00										C	1	CL	3		0	0	G	0											
	88HOL/LOS[48]	18.0 +- 2.0										C	1	CL	3		0	0	G	0											
	91HUD/SEET[39]	17.0 +- 0.6										C	1	CL	3		0	0	G	0											

Table 2.2 (Continued)																				
SPECIES	REFERENCE []	Hf° ₂₉₈	S° ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰	ELEMENTS									
	ROD/HOP96[14]	18.00									C	1	CL	3		0	0	G	0	
	NJIT99	19.00	70.92	15.25	16.66	17.56	18.16	18.83	19.18	19.56	C	1	CL	3		0	0	G	0	
CCL4	SWS[4]	-22.90	74.21	19.92	21.55	22.72	23.55	24.48	24.88	25.38	C	1	CL	4		0	0	G	0	
	JANAF[3]	-22.94	74.02	19.98	21.92	23.09	23.82	24.64	25.05	25.47	C	1	CL	4		0	0	G	0	
	TRC[2]	-22.90	74.09	19.98	21.92	23.09	23.82	24.64	25.05	25.50	C	1	CL	4		0	0	G	0	
	MELIUS93[7]	-20.20									C	1	CL	4		0	0	G	0	
	74ROD/CHAO[62]	-22.90									C	1	CL	4		0	0	G	0	
	NJIT99	-22.94	74.02	19.98	21.92	23.09	23.82	24.64	25.05	25.47	C	1	CL	4		0	0	G	0	
CF3	JANAF[3]	-113.01	63.42	11.93	13.68	15.05	16.09	17.46	18.22	19.07	C	1	F	3		0	0	G	0	
	MELIUS93[7]	-112.79	65.43	12.00		15.12		17.48	18.23	19.09	C	1	F	3		0	0	G	0	
	TRC[2]	-111.71	63.22	11.90	13.70	15.11	16.16	17.49	18.25	19.10	C	1	F	3		0	0	G	0	
	86TSA[50]	-110.00									C	1	F	3		0	0	G	0	
	ROUX/PAD87[26]	-112.00									C	1	F	3		0	0	G	0	
	NJIT99	-113.01	63.42	11.93	13.68	15.05	16.09	17.46	18.22	19.07	C	1	F	3		0	0	G	0	
CF2CL	RAYEZ94[17]	-66.02	67.72	13.17	14.73	15.93	16.83	17.98	18.59	19.25	C	1	CL	1	F	2	0	G	0	
	MELIUS93[7]	-66.20									C	1	CL	1	F	2	0	G	0	
	NJIT99	-66.02	67.72	13.17	14.73	15.93	16.83	17.98	18.59	19.25	C	1	CL	1	F	2	0	G	0	
CF3CL	PED&JANAF[3,27]	-168.82	68.32	16.10	18.42	20.19	21.50	23.17	24.03	24.97	C	1	CL	1	F	3	0	G	0	
	JANAF[3]	-169.20	68.17	16.04	18.53	20.32	21.59	23.16	24.02	24.98	C	1	CL	1	F	3	0	G	0	
	TRC[2]	-168.30	68.21	16.04	18.52	20.32	21.59	23.16	24.02	24.98	C	1	CL	1	F	3	0	G	0	
	MELIUS93[7]	-169.80									C	1	CL	1	F	3	0	G	0	
	NJIT99	-169.20	68.17	16.04	18.53	20.32	21.59	23.16	24.02	24.98	C	1	CL	1	F	3	0	G	0	
CFCL2	RAYEZ94[17]	-21.60	69.17	14.02	15.42	16.49	17.28	18.26	18.77	19.34	C	1	CL	2	F	1	0	G	0	
	MELIUS93[7]	-22.80									C	1	CL	2	F	1	0	G	0	
	NJIT99	-21.60	69.17	14.02	15.42	16.49	17.28	18.26	18.77	19.34	C	1	CL	2	F	1	0	G	0	

Table 2.2 (Continued)																				
SPECIES	REFERENCE []	Hf ^o ₂₉₈	S ^o ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰	ELEMENTS									
CF2CL2	PED&JANAF[3,27]	-114.12	72.02	17.39	19.52	21.11	22.27	23.68	24.37	25.14	C	1	CL	2	F	2	0	G	0	
	JANAF[3]	-117.50	71.91	17.36	19.68	21.28	22.37	23.68	24.39	25.16	C	1	CL	2	F	2	0	G	0	
	TRC[2]	-117.30	71.84	17.33	19.67	21.27	22.37	23.68	24.38	25.17	C	1	CL	2	F	2	0	G	0	
	MELIUS93[7]	-117.70									C	1	CL	2	F	2	0	G	0	
	NJIT99	-117.50	71.91	17.36	19.68	21.28	22.37	23.68	24.39	25.16	C	1	CL	2	F	2	0	G	0	
CFCL3	PED&JANAF[3,27]	-64.12	74.12	18.78	20.66	22.04	23.03	24.20	24.73	25.32	C	1	CL	3	F	1	0	G	0	
	JANAF[3]	-69.00	74.00	18.70	20.83	22.21	23.12	24.18	24.73	25.32	C	1	CL	3	F	1	0	G	0	
	TRC[2]	-67.80	74.07	18.71	20.84	22.22	23.13	24.19	24.74	25.33	C	1	CL	3	F	1	0	G	0	
	MELIUS93[7]	-67.70									C	1	CL	3	F	1	0	G	0	
	NJIT99	-67.70	74.07	18.71	20.84	22.22	23.13	24.19	24.74	25.33	C	1	CL	3	F	1	0	G	0	
CH	ROD/HOP96[14]	142.40									C	1	H	1			0	G	0	
	91GREV/JAN[40]	142.50									C	1	H	1			0	G	0	
	69HERZ/JONES[70]	142.30									C	1	H	1			0	G	0	
¹ CH2	ROD/HOP96[14]	102.70									C	1	H	2			0	G	0	
	78LENGEL[59]	101.70									C	1	H	2			0	G	0	
	78LENGEL[59]	102.60									C	1	H	2			0	G	0	
³ CH2	ROD/HOP96[14]	93.80									C	1	H	2			0	G	0	
	78LENGEL[59]	93.60									C	1	H	2			0	G	0	
	65DIBELER[71]	93.90									C	1	H	2			0	G	0	
	78LENGEL[59]	94.10									C	1	H	2			0	G	0	
	85LEOPOLD[53]	92.80									C	1	H	2			0	G	0	
¹ CHCL	ROD/HOP96[14]	76.80									C	1	H	1	CL	1	0	G	0	
	94BORN[35]	76.00									C	1	H	1	CL	1	0	G	0	
	85LIAS[52]	71.00									C	1	H	1	CL	1	0	G	0	
	85CHASE[51]	80.00									C	1	H	1	CL	1	0	G	0	

Table 2.2 (Continued)																			
SPECIES	REFERENCE []	Hf ^o ₂₉₈	S ^o ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰	ELEMENTS								
³ CHCL	ROD/HOP96[14]	83.30									C	1	H	1	CL	1	0	G	0
	94BORN[35]	82.40									C	1	H	1	CL	1	0	G	0
	85LIAS[52]	73.00									C	1	H	1	CL	1	0	G	0
CHCL2	ROUX,RADI[26,72]	23.50	66.71	12.35	13.73	14.79	15.59	16.67	17.34	18.46	C	1	H	1	CL	2	0	G	0
	89TSC/CHE[46]	23.50	67.40	13.11		14.68		16.83	17.98	19.80	C	1	H	1	CL	2	0	G	0
	TAY/DEL91[21]	23.50	67.30	11.75		14.36		16.44	17.23	18.39	C	1	H	1	CL	2	0	G	0
	MOPAC[5]	11.04	66.78	12.41	13.91	14.97	15.72	16.74	17.42	18.45	C	1	H	1	CL	2	0	G	0
	KAFAFI89[24]		68.10	12.90	14.16	15.09	15.79	16.76	17.44	18.46	C	1	H	1	CL	2	0	G	0
	MELIUS93[7]	19.50									C	1	H	1	CL	2	0	G	0
	Seet98[9]	21.27									C	1	H	1	CL	2	0	G	0
	SEET96[10]	21.27	66.92								C	1	H	1	CL	2	0	G	0
	ROUX/PAD87[26]	23.50									C	1	H	1	CL	2	0	G	0
	83WEI/BEN[54]	25.70									C	1	H	1	CL	2	0	G	0
	88HOL/LOS[48]	22.3+-2.0									C	1	H	1	CL	2	0	G	0
	ROD/HOP96[14]	22.40									C	1	H	1	CL	2	0	G	0
	NJIT99	23.50	68.10	12.90	14.16	15.09	15.79	16.76	17.44	18.46	C	1	H	1	CL	2	0	G	0
CHCL3	SWS[4]	-24.20	70.66	15.76	17.83	19.34	20.44	21.91	22.86		C	1	H	1	CL	3	0	G	0
	RAYEZ94[17]	-23.30	69.83	15.37	17.29	18.80	19.99	21.63	22.64	24.06	C	1	H	1	CL	3	0	G	0
	TRC[2]	-24.59	70.65	15.67	17.75	19.26	20.38	21.87	22.83	24.16	C	1	H	1	CL	3	0	G	0
	JANAF[3]	-24.66	70.63	15.67	17.75	19.27	20.38	21.87	22.83	24.16	C	1	H	1	CL	3	0	G	0
	MELIUS93[7]	-23.30									C	1	H	1	CL	3	0	G	0
	74ROD/CHAO[62]	-24.60									C	1	H	1	CL	3	0	G	0
	ROD/HOP96[14]	-25.40									C	1	H	1	CL	3	0	G	0
	88LIAS[47]	-25.00									C	1	H	1	CL	3	0	G	0
	NJIT99	-24.20	70.66	15.76	17.83	19.34	20.44	21.91	22.86		C	1	H	1	CL	3	0	G	0
	CH2CL	ROUX,RADI[26,72]	29.10	58.51	9.97	11.42	12.60	13.55	14.94	15.88	17.31	C	1	H	2	CL	1	0	G
MOPAC[5]			58.61	10.08	11.45	12.53	13.38	14.66	15.64	17.30	C	1	H	2	CL	1	0	G	0
89TSC/CHE[46]		29.10	59.60	9.32		11.14		14.10	15.83	18.31	C	1	H	2	CL	1	0	G	0
TAY/DEL91[21]		29.10	58.17	9.56		12.03		14.49	15.59	17.36	C	1	H	2	CL	1	0	G	0

Table 2.2 (Continued)																			
SPECIES	REFERENCE []	Hf ^o ₂₉₈	S ^o ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰	ELEMENTS								
	MELIUS93[7]	27.10									C	1	H	2	CL	1	0	G	0
	Seet98[9]	28.04									C	1	H	2	CL	1	0	G	0
	SEET96[10]	28.04	64.77								C	1	H	2	CL	1	0	G	0
	ROUX/PAD87[26]	29.10									C	1	H	2	CL	1	0	G	0
	83WEI/BEN[54]	31.10									C	1	H	2	CL	1	0	G	0
	88HOL/LOS[48]	27.7 ± 2.0									C	1	H	2	CL	1	0	G	0
	ROD/HOP96[14]	28.20									C	1	H	2	CL	1	0	G	0
	NJIT99	27.99	58.51	9.97	11.42	12.60	13.55	14.94	15.88	17.31	C	1	H	2	CL	1	0	G	0
CH2CL2	SWS[4]	-22.80	64.61	12.24	14.19	15.83	17.20	19.32	20.82	23.01	C	1	H	2	CL	2	0	G	0
	JANAF[3]	-22.83	64.57	12.20	14.24	15.93	17.30	19.32	20.76	22.91	C	1	H	2	CL	2	0	G	0
	TRC[2]	-22.80	64.64	12.20	14.24	15.93	17.30	19.32	20.76	22.90	C	1	H	2	CL	2	0	G	0
	85CHASE[51]	-22.83	64.60								C	1	H	2	CL	2	0	G	0
	MELIUS93[7]	-22.60									C	1	H	2	CL	2	0	G	0
	74ROD/CHAO[62]	-22.80									C	1	H	2	CL	2	0	G	0
	ROD/HOP96[14]	-23.20									C	1	H	2	CL	2	0	G	0
	88LIAS[47]	-22.90									C	1	H	2	CL	2	0	G	0
	NJIT99	-22.83	64.57	12.20	14.24	15.93	17.30	19.32	20.76	22.91	C	1	H	2	CL	2	0	G	0
CH3	JANAF[3]	34.82	46.38	9.26	10.05	10.82	11.54	12.89	14.09	16.29	C	1	H	3		0	0	G	0
	TRC[2]	35.11	46.46	9.20	9.99	10.76	11.49	12.86	14.07	16.29	C	1	H	3		0	0	G	0
	MELIUS93[7]	34.90									C	1	H	3		0	0	G	0
	Seet98[9]	34.89									C	1	H	3		0	0	G	0
	NICOVICH91[22]	35.30									C	1	H	3		0	0	G	0
	RUSS/SEET88[25]	35.37	50.91								C	1	H	3		0	0	G	0
	81HEN/KNO[56]	35.10									C	1	H	3		0	0	G	0
	NJIT99	34.82	46.38	9.26	10.05	10.82	11.54	12.89	14.09	16.29	C	1	H	3		0	0	G	0
CH3CL	74ROD/CHAO[62]	-19.59	56.01	9.76	11.57	13.18	14.61	16.99	18.84	21.76	C	1	H	3	CL	1	0	G	0
	TRC[2]	-19.60	56.00	9.77	11.51	13.19	14.66	17.05	18.87	21.76	C	1	H	3	CL	1	0	G	0
	JANAF[3]	-20.66	55.99	9.76	11.50	13.17	14.64	17.03	18.86	21.75	C	1	H	3	CL	1	0	G	0
	85CHASE[51]	-20.00	56.01								C	1	H	3	CL	1	0	G	0

Table 2.2 (Continued)																			
SPECIES	REFERENCE []	Hf ^o ₂₉₈	S ^o ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰	ELEMENTS								
	MELIUS93[7]	-20.10									C	1	H	3	CL	1	0	G	0
	74ROD/CHAO[62]	-19.60									C	1	H	3	CL	1	0	G	0
	ROD/HOP96[14]	-20.10									C	1	H	3	CL	1	0	G	0
	88LIAS[47]	-19.60									C	1	H	3	CL	1	0	G	0
	NJIT99	-19.60	56.00	9.77	11.51	13.19	14.66	17.05	18.87	21.76	C	1	H	3	CL	1	0	G	0
C2CL3	RADICALC[72]	53.00	79.11	19.25	20.20	21.23	22.25	24.03	25.24	25.80	C	2	CL	3		0	0	G	0
	TAY/DEL91[21]	48.00	78.12	18.66		21.82		23.81	24.54	25.86	C	2	CL	3		0	0	G	0
	MELIUS93[7]	54.40									C	2	CL	3		0	0	G	0
	NJIT99	54.40	79.11	19.25	20.20	21.23	22.25	24.03	25.24	25.80	C	2	CL	3		0	0	G	0
C2CL4	SWS[4]	-3.40	81.41	22.43	24.86	26.66	27.95	29.40	29.95	30.78	C	2	CL	4		0	0	G	0
	JANAF[3]	-2.97	82.05	22.89	25.19	26.78	27.91	29.30	30.09	30.98	C	2	CL	4		0	0	G	0
	TRC[2]	-2.89	81.49	22.74	25.10	26.72	27.86	29.28	30.07	30.97	C	2	CL	4		0	0	G	0
	MOPAC[5]	(-8.081)	82.70	23.06	25.38	26.91	27.98	29.31	30.08	30.96	C	2	CL	4		0	0	G	0
	MELIUS93[7]	-5.70									C	2	CL	4		0	0	G	0
	93BEN/COH[36]	-3.40	81.45								C	2	CL	4		0	0	G	0
	CHEN/BOZ98[8]	-3.15	81.47	22.73	25.10	26.72	27.86	29.28	30.07	30.97	C	2	CL	4		0	0	G	0
	NJIT99	-3.40	81.41	22.43	24.86	26.66	27.95	29.40	29.95	30.78	C	2	CL	4		0	0	G	0
C2CL5	OLK84[28]	7.50	92.21	27.61	30.17	32.10	33.53	35.28	36.14	37.01	C	2	CL	5		0	0	G	1
	TRC[2]	8.60	95.82	27.15	30.07	31.93	33.17	34.58	35.32	36.09	C	2	CL	5		0	0	G	1
	TAY/DEL91[21]	7.70	96.37	32.04		36.34		38.04	38.43	38.63	C	2	CL	5		0	0	G	1
	MOPAC[5]	-10.50	95.68	28.56	31.13	32.72	33.75	34.93	35.54	36.20	C	2	CL	5		0	0	G	1
	80WEI/BSN[57]	7.7+- 1									C	2	CL	5		0	0	G	1
	MC/GOL82[29]	8.4+- 1.9									C	2	CL	5		0	0	G	1
	CIO/LIU97[12]	9.06	G2(isodesmic)								C	2	CL	5		0	0	G	1
	CIO/LIU97[12]	7.44	B3LYP(isodesmic)								C	2	CL	5		0	0	G	1
	CIO/LIU97[12]	7.63	B3LYP(adjusted)								C	2	CL	5		0	0	G	1
	MELIUS93[7]	7.40									C	2	CL	5		0	0	G	1
	NJIT99	9.06	95.68	28.56	31.13	32.72	33.75	34.93	35.54	36.20	C	2	CL	5		0	0	G	1

Table 2.2 (Continued)												ELEMENTS								
SPECIES	REFERENCE []	Hf ^o ₂₉₈	S ^o ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰										
C2CL6	SWS[4]	-33.80	94.77	32.67	36.11	38.29	39.69	41.29	42.11		C	2	CL	6	0	0	G	1		
	JANAF[3]	-32.08	95.07	33.29	36.68	38.78	40.14	41.71	42.55	43.37	C	2	CL	6	0	0	G	1		
	TRC[2]	-33.20	95.33	32.76	36.21	38.40	39.82	41.48	42.38	43.31	C	2	CL	6	0	0	G	1		
	CHAO74[31]	-33.20	95.30	32.76	36.21	38.40	39.82	41.48	42.38	43.34	C	2	CL	6	0	0	G	1		
	83KOL/PAP[55]	-32.9, -34.7, -33.0, -36.1										C	2	CL	6	0	0	G	1	
	80WEI/BSN[57]	-33.70										C	2	CL	6	0	0	G	1	
	MELIUS93[7]	-32.40										C	2	CL	6	0	0	G	1	
	NJIT99	-33.80	94.77	32.67	36.11	38.29	39.69	41.29	42.11			C	2	CL	6	0	0	G	1	
CHCLCCL	RADICALC[72]	55.30	70.51	15.78	17.56	18.99	20.13	21.73	22.72	24.02	C	2	H	1	CL	2	0	G	0	
	TAY/DEL91[21]	55.99	71.91	15.39		18.78		21.49	22.60	25.04	C	2	H	1	CL	2	0	G	0	
	MOPAC[5]	47.72	73.62	15.53	17.35	18.72	19.78	21.31	22.37	23.89	C	2	H	1	CL	2	0	G	0	
	MELIUS93[7]	56.00										C	2	H	1	CL	2	0	G	0
	NJIT99	56.00	73.62	15.53	17.35	18.72	19.78	21.31	22.37	23.89	C	2	H	1	CL	2	0	G	0	
CCL2CH	RADICALC[72]	58.21	69.51	15.70	17.63	19.12	20.26	21.77	22.61	23.72	C	2	H	1	CL	2	0	G	0	
	TAY/DEL91[21]	62.30	71.47	15.30		19.04		21.71	22.76	24.85	C	2	H	1	CL	2	0	G	0	
	HO/BAR92[19]	58.20	68.88	17.52		22.16		25.74	26.90	28.60	C	2	H	1	CL	2	0	G	0	
	MOPAC[5]	54.86	71.28	16.75	18.60	19.82	20.70	21.91	22.75	24.02	C	2	H	1	CL	2	0	G	0	
	MELIUS93[7]	62.30										C	2	H	1	CL	2	0	G	0
	NJIT99	62.30	71.28	16.75	18.60	19.82	20.70	21.91	22.75	24.02	C	2	H	1	CL	2	0	G	0	
C2HCL3	TRC[2]	-2.29	77.72	19.23	21.80	23.68	25.07	26.95	28.16	29.79	C	2	H	1	CL	3	0	G	0	
	69STU/WES[69]	-1.40	77.63	19.22		23.75		26.80	27.60	28.98	C	2	H	1	CL	3	0	G	0	
	MELIUS93[7]	-3.90										C	2	H	1	CL	3	0	G	0
	93BEN/COH[36]	-1.10	77.50									C	2	H	1	CL	3	0	G	0
	PEDLEY86[27]	-2.30										C	2	H	1	CL	3	0	G	0
	CHEN/BOZ98[8]	-1.88	77.67	19.26	21.80	23.67	25.06	26.94	28.15	29.79	C	2	H	1	CL	3	0	G	0	
	NJIT99	-2.29	77.72	19.23	21.80	23.68	25.07	26.95	28.16	29.79	C	2	H	1	CL	3	0	G	0	
CHCL2CCL2 (1,1,2,2)	RADICALC[72]	5.80	87.81	24.19	26.58	28.44	29.88	31.83	32.98	34.53	C	2	H	1	CL	4	0	G	1	
	TRC[2]	5.21	90.65	23.88	26.74	28.78	30.23	32.15	33.32	34.89	C	2	H	1	CL	4	0	G	1	

Table 2.2 (Continued)												ELEMENTS									
SPECIES	REFERENCE []	Hf ^o ₂₉₈	S ^o ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰											
CHCL2CHCL (1,2,2)	RADICALC[72]	9.80	82.11	20.91	23.54	25.63	27.28	29.66	31.25	33.72	C	2	H	2	CL	3	0	G	1		
	TRC[2]	11.09	84.51	21.49	24.59	26.84	28.49	30.64	32.05	34.08	C	2	H	2	CL	3	0	G	1		
	HO/BAR92[19]	8.50	83.10	20.21		25.68		30.14	31.77	34.50		C	2	H	2	CL	3	0	G	1	
	TAY/DEL91[21]	9.80	82.23	20.94		26.42		30.20	31.59	35.02		C	2	H	2	CL	3	0	G	1	
	MELIUS93[7]	10.30										C	2	H	2	CL	3	0	G	1	
	CIO/LIU97[12]	11.53	G2(isodesmic)										C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	9.93	B3LYP(isodesmic)										C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	10.12	B3LYP(adjusted)										C	2	H	2	CL	3	0	G	1
NJIT99	11.53	84.51	21.49	24.59	26.84	28.49	30.64	32.05	34.08		C	2	H	2	CL	3	0	G	1		
CH2CLCCL2 (1,1,2)	RADICALC[72]	7.00	81.31	20.82	23.31	25.33	26.98	29.41	31.08	33.61	C	2	H	2	CL	3	0	G	1		
	TRC[2]	6.31	84.56	21.39	24.09	26.15	27.70	29.95	31.50	33.77	C	2	H	2	CL	3	0	G	1		
	HO/BAR92[19]	7.05	83.20	20.21		25.68		30.14	31.77	34.50		C	2	H	2	CL	3	0	G	1	
	TAY/DEL91[21]	8.20	82.15	20.69		25.99		29.86	31.33	34.89		C	2	H	2	CL	3	0	G	1	
	CIO/LIU97[12]	7.65	G2(isodesmic)										C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	6.30	B3LYP(isodesmic)										C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	6.49	B3LYP(adjusted)										C	2	H	2	CL	3	0	G	1
	MELIUS93[7]	6.00										C	2	H	2	CL	3	0	G	1	
NJIT99	7.65	84.56	21.39	24.09	26.15	27.70	29.95	31.50	33.77		C	2	H	2	CL	3	0	G	1		
CCL3CH2 (2,2,2)	RADICALC[72]	14.80	81.41	22.04	24.60	26.63	28.22	30.46	31.91	34.07	C	2	H	2	CL	3	0	G	1		
	TRC[2]	17.21	80.50	22.01	24.86	26.86	28.35	30.40	31.83	33.94	C	2	H	2	CL	3	0	G	1		
	89ATK/BAU[45]	10.70										C	2	H	2	CL	3	0	G	1	
	CIO/LIU97[12]	18.39	G2(isodesmic)										C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	16.72	B3LYP(isodesmic)										C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	16.91	B3LYP(adjusted)										C	2	H	2	CL	3	0	G	1
	MELIUS93[7]	18.80										C	2	H	2	CL	3	0	G	1	
	NJIT99	18.39	80.50	22.01	24.86	26.86	28.35	30.40	31.83	33.94		C	2	H	2	CL	3	0	G	1	
CH2CLCCL3 (1,1,1,2)	THERM[6]	-35.16	84.46	24.62	28.29	31.07	33.17	36.11	37.68		C	2	H	2	CL	4	0	G	1		
	TRC[2]	-35.71	85.07	24.67	28.36	31.16	33.28	36.24	38.17	40.70	C	2	H	2	CL	4	0	G	1		
	SWS[4]	-37.20	86.01	27.17	30.13	32.52	34.42	37.08	38.71	40.67	C	2	H	2	CL	4	0	G	1		

Table 2.2 (Continued)																				
SPECIES	REFERENCE []	Hf ^o ₂₉₈	S ^o ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰	ELEMENTS									
	MELIUS93[7]	20.20									C	2	H	3	CL	2	0	G	1	
	NJIT99	20.31	74.64	18.95	21.99	24.28	26.05	28.54	30.31	33.01	C	2	H	3	CL	2	0	G	1	
CH ₂ CLCHCL ₂ (1,1,2)	TRC[2]	-34.80	79.71	20.40	24.47	27.74	30.29	33.85	36.15	39.29	C	2	H	3	CL	3	0	G	1	
	69STU/WES[69]	-33.10	80.57	21.34		27.92		33.28	35.42	38.91	C	2	H	3	CL	3	0	G	1	
	83KOL/PAP[55]	-34.58 +- 0.45									C	2	H	3	CL	3	0	G	1	
	94Lide[33]	-36.14									C	2	H	3	CL	3	0	G	1	
	MELIUS93[7]	-33.90									C	2	H	3	CL	3	0	G	1	
	93BEN/COH[36]	-34.60	81.50								C	2	H	3	CL	3	0	G	1	
	PEDLEY86[27]	-34.80									C	2	H	3	CL	3	0	G	1	
	CHEN/BOZ98[8]	-33.99	81.22	21.31	24.85	27.65	29.81	33.00	35.03	38.09	C	2	H	3	CL	3	0	G	1	
	NJIT99	-34.80	79.71	20.40	24.47	27.74	30.29	33.85	36.15	39.29	C	2	H	3	CL	3	0	G	1	
CH ₃ CCL ₃ (1,1,1)	TRC[2]	-34.01	76.51	22.14	25.72	28.52	30.68	33.75	35.81	38.80	C	2	H	3	CL	3	0	G	1	
	PEDLEY86[27]	-30.90	78.60	22.52		28.45		33.70	35.73	38.91	C	2	H	3	CL	3	0	G	1	
	CHAO74[31]	-34.01	76.49	22.07							C	2	H	3	CL	3	0	G	1	
	83KOL/PAP[55]	-34.56+- 0.19									C	2	H	3	CL	3	0	G	1	
	MELIUS93[7]	-33.60									C	2	H	3	CL	3	0	G	1	
	NJIT99	-34.01	76.51	22.14	25.72	28.52	30.68	33.75	35.81	38.80	C	2	H	3	CL	3	0	G	1	
C ₂ H ₄	JANAF[3]	12.54	52.40	10.29	12.68	14.93	16.89	20.04	22.44	26.29	C	2	H	4		0	0	G	0	
	SWS[4]	12.50	52.45	10.45	12.90	15.16	17.10	20.20	22.57		C	2	H	4		0	0	G	0	
	MELIUS93[7]	12.30									C	2	H	4		0	0	G	0	
	NJIT99	12.54	52.40	10.29	12.68	14.93	16.89	20.04	22.44	26.29	C	2	H	4		0	0	G	0	
CH ₃ CHCL a	TRC[2]	18.50	68.69	14.65	17.28	19.67	21.70	24.93	27.37	31.24	C	2	H	4	CL	1	0	G	1	
	89TSC/CHE[46]	17.51	67.31	14.10		19.79		25.42	27.99	32.50	C	2	H	4	CL	1	0	G	1	
	CHEN/ROUX92[18]	18.26	68.86	14.84	17.57	20.00	22.05	25.29	27.72	31.51	C	2	H	4	CL	1	0	G	1	
	Seet98[9]	18.28									C	2	H	4	CL	1	0	G	1	
	SEET96[10]	18.28	66.68								C	2	H	4	CL	1	0	G	1	
	88HOL/LOS[48]	19.3+-2.0									C	2	H	4	CL	1	0	G	1	
	CIO/LIU97[12]	19.18	G2(isodesmic)								C	2	H	4	CL	1	0	G	1	

Table 2.2 (Continued)																				
SPECIES	REFERENCE []	Hf ^o ₂₉₈	S ^o ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰	ELEMENTS									
	CIO/LIU97[12]	19.09	B3LYP(isodesmic)									C	2	H	4	CL	1	0	G	1
	CIO/LIU97[12]	19.25	B3LYP(adjusted)									C	2	H	4	CL	1	0	G	1
	MELIUS93[7]	18.20										C	2	H	4	CL	1	0	G	1
	MIYO/ROUX90[23]	17.60										C	2	H	4	CL	1	0	G	1
	NJIT99	19.18	68.86	14.84	17.57	20.00	22.05	25.29	27.72	31.51		C	2	H	4	CL	1	0	G	1
CH2CLCH2	TRC[2]	22.39	68.00	15.65	18.55	20.96	22.92	25.88	28.08	31.57		C	2	H	4	CL	1	0	G	1
b	HO/BAR92[19]	20.78	68.50	14.01		20.09		25.88	28.98	33.44		C	2	H	4	CL	1	0	G	1
	CHEN/ROUX92[18]	22.44	69.07	15.51	18.09	20.37	22.30	25.37	27.71	31.44		C	2	H	4	CL	1	0	G	1
	Seet98[9]	22.23										C	2	H	4	CL	1	0	G	1
	88HOL/LOS[48]	22.8 +/- 2.0										C	2	H	4	CL	1	0	G	1
	CIO/LIU97[12]	23.20	G2(isodesmic)									C	2	H	4	CL	1	0	G	1
	CIO/LIU97[12]	21.97	B3LYP(isodesmic)									C	2	H	4	CL	1	0	G	1
	CIO/LIU97[12]	22.16	B3LYP(adjusted)									C	2	H	4	CL	1	0	G	1
	MELIUS93[7]	23.00										C	2	H	4	CL	1	0	G	1
	MIYO/ROUX90[23]	21.80										C	2	H	4	CL	1	0	G	1
	NJIT99	23.20	69.07	15.51	18.09	20.37	22.30	25.37	27.71	31.44		C	2	H	4	CL	1	0	G	1
CH2CLCH2CL	TRC[2]	-30.31	73.12	18.54	21.95	24.96	27.45	31.16	33.78	37.64		C	2	H	4	CL	2	0	G	1
	69STU/WES[69]	-31.00	73.66	18.99		24.74		30.32	33.06	38.79		C	2	H	4	CL	2	0	G	1
	83KOL/PAP[55]	-32.1 +/- 0.3										C	2	H	4	CL	2	0	G	1
	94Lide[33]	-30.33										C	2	H	4	CL	2	0	G	1
	93BEN/COH[36]	-33.40	76.34									C	2	H	4	CL	2	0	G	1
	PEDLEY86[27]	-30.33										C	2	H	4	CL	2	0	G	1
	CHEN/BOZ98[8]	-31.05	75.05	18.23	21.54	24.39	26.70	30.25	32.89	36.94		C	2	H	4	CL	2	0	G	1
	MELIUS93[7]	-32.40	75.05									C	2	H	4	CL	2	0	G	1
	NJIT99	-31.22	73.12	18.54	21.95	24.96	27.45	31.16	33.78	37.64		C	2	H	4	CL	2	0	G	1
CH3CHCL2	TRC[2]	-31.09	72.94	18.32	21.84	24.79	27.18	30.79	33.40	37.40		C	2	H	4	CL	2	0	G	1
	69STU/WES[69]	-31.05	72.89	18.29		24.81		30.87	33.44	37.80		C	2	H	4	CL	2	0	G	1
	CHAO74[31]	-31.10	72.88	18.24								C	2	H	4	CL	2	0	G	1
	83KOL/PAP[55]	-31.2 +/- 0.7										C	2	H	4	CL	2	0	G	1

Table 2.2 (Continued)												ELEMENTS							
SPECIES	REFERENCE []	Hf ^o ₂₉₈	S ^o ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰	C	H	CL	O	G				
	94Lide[33]	-30.52									C	2	H	4	CL	2	0	G	1
	MELIUS93[7]	-32.10									C	2	H	4	CL	2	0	G	1
	93BEN/COH[36]	-27.90	71.82								C	2	H	4	CL	2	0	G	1
	PEDLEY86[27]	-30.52									C	2	H	4	CL	2	0	G	1
	CHEN/BOZ98[8]	-31.04	73.03	18.18	21.82	24.93	27.41	31.11	33.57	37.01	C	2	H	4	CL	2	0	G	1
	NJIT99	-31.09	72.94	18.32	21.84	24.79	27.18	30.79	33.40	37.40	C	2	H	4	CL	2	0	G	1
C2H5	TRC[2]	25.91	58.87	12.44	15.05	17.47	19.60	23.13	25.90	30.37	C	2	H	5		0	0	G	1
	90SANDIA[42]	28.02	60.14	11.32	13.60	15.59	18.29	22.58	25.50	29.56	C	2	H	5		0	0	G	1
	90CHEN[43]		59.30	12.11	14.91	17.39	19.58	23.20	25.98	30.41	C	2	H	5		0	0	G	1
	86TSANG[49]		59.37	12.13	14.66	17.18	19.22	22.84	25.65	30.24	C	2	H	5		0	0	G	1
	94BURCAT[34]	28.36	59.06	12.07							C	2	H	5		0	0	G	1
	92COHEN[38]		59.23	12.18	14.80	17.24	19.42	23.01	25.82	30.33	C	2	H	5		0	0	G	1
	LAY/BOZ95[16]	28.80	57.42	11.89	14.57	16.95	19.09	22.76	25.66		C	2	H	5		0	0	G	1
	Seet98[9]	28.85									C	2	H	5		0	0	G	1
	SEAKINS92[20]	28.92+ 0.36									C	2	H	5		0	0	G	1
	CIO/LIU97[12]	29.30	(this study)								C	2	H	5		0	0	G	1
	CIO/LIU97[12]	29.49	B3LYP(adjusted)								C	2	H	5		0	0	G	1
	MELIUS93[7]	28.80									C	2	H	5		0	0	G	1
	NICOVICH91[22]	29.10									C	2	H	5		0	0	G	1
	RUSS/SEET88[25]	28.68	62.14								C	2	H	5		0	0	G	1
	NJIT99	29.30	57.42	11.89	14.57	16.95	19.09	22.76	25.66		C	2	H	5		0	0	G	1
C2H5CL	JANAF[3]	-26.80	66.01	15.03	18.57	21.61	24.22	28.37	31.44	36.16	C	2	H	5	CL	1	0	G	1
	TRC[2]	-26.84	65.94	15.04	18.54	21.66	24.28	28.38	31.43	36.17	C	2	H	5	CL	1	0	G	1
	HO/BAR92[19]	-26.83	66.03	15.06		21.67		28.43	31.47	36.27	C	2	H	5	CL	1	0	G	1
	CHAO74[31]	-26.83	65.91	14.97							C	2	H	5	CL	1	0	G	1
	88LIAS[47]	-26.79	65.96								C	2	H	5	CL	1	0	G	1
	71FLET/PIL[67]	-26.83									C	2	H	5	CL	1	0	G	1
	83KOL/PAP[55]	-26.8+ 0.2									C	2	H	5	CL	1	0	G	1
	MELIUS93[7]	-27.20									C	2	H	5	CL	1	0	G	1
	NJIT99	-26.80	66.01	15.03	18.57	21.61	24.22	28.37	31.44	36.16	C	2	H	5	CL	1	0	G	1

Table 2.2 (Continued)																						
SPECIES	REFERENCE []	Hf° ₂₉₈	S° ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰	ELEMENTS											
C2H6	JANAF[3]	-20.20	54.81	12.54	15.78	18.70	21.33	25.78	29.29	34.87	C	2	H	6		0	0	G	1			
	83KOL/PAP[55]	-20.1 +/- 0.1									C	2	H	6		0	0	G	1			
	MELIUS93[7]	-20.80	(staggered)									C	2	H	6		0	0	G	1		
	73CHAO/WIL[64]	-20.24									C	2	H	6		0	0	G	1			
	NJIT99	-20.20	54.81	12.54	15.78	18.70	21.33	25.78	29.29	34.87	C	2	H	6		0	0	G	1			
CH3CF3	ZAC/TSANG96[15]	-180.54									C	2	H	3	F	3	0	G	1			
	CHEN/ROD75[32]	-178.20									C	2	H	3	F	3	0	G	1			
	MELIUS93[7]	-180.53									C	2	H	3	F	3	0	G	1			
	PEDLEY86[27]	-177.94									C	2	H	3	F	3	0	G	1			
	SWS[4]	-178.20									C	2	H	3	F	3	0	G	1			
CH2CF3	ZAC/TSANG96[15]	-125.86									C	2	H	2	F	3	0	G	1			
	78RODGERS[60]	-123.59									C	2	H	2	F	3	0	G	1			
	MELIUS93[7]	-125.90									C	2	H	2	F	3	0	G	1			
CH3CF2CL	MELIUS93[7]	-128.70									C	2	H	3	F	2	CL	1	G	1		
	78PAP/KOL[61]	-126.60									C	2	H	3	F	2	CL	1	G	1		
	THERM[6]	-127.51									C	2	H	3	F	2	CL	1	G	1		
CH2CF2CL	MELIUS93[7]	-75.40									C	2	H	2	F	2	CL	1	G	1		
CH3CFCL2	MELIUS93[7]	-79.67									C	2	H	3	F	1	CL	2	G	1		
CH2CFCL2	MELIUS93[7]	-25.80									C	2	H	2	F	1	CL	2	G	1		

Table 2.3 (Continued)												ELEMENTS										
SPECIES	REFERENCE []	Hf ^o ₂₉₈	S ^o ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰												
CCL2CH	MELIUS93[7]	62.30										C	2	H	1	CL	2	0	G	0		
	MOPAC[5]		71.28	16.75	18.60	19.82	20.70	21.91	22.75	24.02		C	2	H	1	CL	2	0	G	0		
C2HCL3	TRC[2]	-2.29	77.72	19.23	21.80	23.68	25.07	26.95	28.16	29.79		C	2	H	1	CL	3	0	G	0		
CHCL2CCL2	CIO/LIU97[12]	6.55	G2(isodesmic)											C	2	H	1	CL	4	0	G	1
(1,1,2,2)	TRC[2]		90.65	23.88	26.74	28.78	30.23	32.15	33.32	34.89		C	2	H	1	CL	4	0	G	1		
CCL3CHCL	CIO/LIU97[12]	11.28	G2(isodesmic)											C	2	H	1	CL	4	0	G	1
(1,2,2,2)	TRC[2]	12.19	88.26	25.57	28.51	30.38	31.62	33.13	34.03	35.25		C	2	H	1	CL	4	0	G	1		
CHCL2CCL3	TRC[2]	-34.80	91.18	28.30	31.96	34.52	36.34	38.64	40.17	41.99		C	2	H	1	CL	5	0	G	1		
CH2CCL	MELIUS93[7]	61.40										C	2	H	2	CL	1	0	G	0		
	MOPAC[5]		62.77	13.00	14.82	16.27	17.44	19.26	20.61	22.76		C	2	H	2	CL	1	0	G	0		
CHCHCL	MELIUS93[7]	64.80										C	2	H	2	CL	1	0	G	0		
	MOPAC[5]		65.60	13.72	15.55	16.94	18.03	19.67	20.90	22.88		C	2	H	2	CL	1	0	G	0		
CH2CCL2	TRC[2]	0.57	68.83	16.06	18.77	20.83	22.41	24.69	26.28	28.63		C	2	H	2	CL	2	0	G	0		
CHCLCHCL	AVG[2,7,69]	-0.45										C	2	H	2	CL	2	0	G	0		
(trans)	SWS[4]		69.29	15.99	18.58	20.65	22.28	24.62	26.24			C	2	H	2	CL	2	0	G	0		
Z_CHCLCHCL	TRC[2]	-0.67	69.24	15.59	18.38	20.54	22.21	24.59	26.22	28.61		C	2	H	2	CL	2	0	G	0		
(cis)																						
CHCL2CHCL	CIO/LIU97[12]	11.53	G2(isodesmic)											C	2	H	2	CL	3	0	G	1
(1,2,2)	TRC[2]		84.51	21.49	24.59	26.84	28.49	30.64	32.05	34.08		C	2	H	2	CL	3	0	G	1		
CH2CLCCL2	CIO/LIU97[12]	7.65	G2(isodesmic)											C	2	H	2	CL	3	0	G	1
(1,1,2)	TRC[2]		84.56	21.39	24.09	26.15	27.70	29.95	31.50	33.77		C	2	H	2	CL	3	0	G	1		
CCL3CH2	CIO/LIU97[12]	18.39	G2(isodesmic)											C	2	H	2	CL	3	0	G	1
(2,2,2)	TRC[2]		80.50	22.01	24.86	26.86	28.35	30.40	31.83	33.94		C	2	H	2	CL	3	0	G	1		
CH2CLCCL3	TRC[2]	-35.71	85.07	24.67	28.36	31.16	33.28	36.24	38.17	40.70		C	2	H	2	CL	4	0	G	1		
(1,1,1,2)																						
C2H2CL4	MELIUS93[7]	-36.00										C	2	H	2	CL	4	0	G	1		
(CHCL2CHCL2)	TRC[2]		84.86	23.74	27.67	30.65	32.89	35.99	38.01	40.66		C	2	H	2	CL	4	0	G	1		
(1,1,2,2)																						
C2H3	LAY/BOZ95[16]	71.64	53.79	10.10	11.93	13.57	14.97	17.22	18.95			C	2	H	3		0	0	G	0		
CH2CHCL	COL/THOM97[11]	5.00										C	2	H	3	CL	1	0	G	0		
	SWS[4]		63.08	12.89	15.56	17.80	19.61	22.35	24.35			C	2	H	3	CL	1	0	G	0		

Table 2.3 (Continued)																			
SPECIES	REFERENCE []	Hf° ₂₉₈	S° ₂₉₈	Cp ³⁰⁰	Cp ⁴⁰⁰	Cp ⁵⁰⁰	Cp ⁶⁰⁰	Cp ⁸⁰⁰	Cp ¹⁰⁰⁰	Cp ¹⁵⁰⁰	ELEMENTS								
CH2CLCHCL	CIO/LIU97[12]	14.65	G2(isodesmic)								C	2	H	3	CL	2	0	G	1
(1,2) a,b	TRC[2]		78.56	18.33	21.15	23.40	25.19	27.82	29.73	32.70	C	2	H	3	CL	2	0	G	1
CH3CCL2	CIO/LIU97[12]	12.43	G2(isodesmic)								C	2	H	3	CL	2	0	G	1
(1,1) a,a	CHEN/ROUX92[18]		75.18	18.17	20.75	22.91	24.70	27.48	29.51	32.60	C	2	H	3	CL	2	0	G	1
CHCL2CH2	CIO/LIU97[12]	20.31	G2(isodesmic)								C	2	H	3	CL	2	0	G	1
(2,2) b,b	TRC[2]		74.64	18.95	21.99	24.28	26.05	28.54	30.31	33.01	C	2	H	3	CL	2	0	G	1
CH2CLCHCL2	TRC[2]	-34.80	79.71	20.40	24.47	27.74	30.29	33.85	36.15	39.29	C	2	H	3	CL	3	0	G	1
(1,1,2)																			
CH3CCL3	TRC[2]	-34.01	76.51	22.14	25.72	28.52	30.68	33.75	35.81	38.80	C	2	H	3	CL	3	0	G	1
(1,1,1)																			
C2H4	JANAF[3]	12.54	52.40	10.29	12.68	14.93	16.89	20.04	22.44	26.29	C	2	H	4		0	0	G	0
CH3CHCL	CIO/LIU97[12]	19.18	G2(isodesmic)								C	2	H	4	CL	1	0	G	1
a	CHEN/ROUX92[18]		68.86	14.84	17.57	20.00	22.05	25.29	27.72	31.51	C	2	H	4	CL	1	0	G	1
CH2CLCH2	CIO/LIU97[12]	23.20	G2(isodesmic)								C	2	H	4	CL	1	0	G	1
b	CHEN/ROUX92[18]		69.07	15.51	18.09	20.37	22.30	25.37	27.71	31.44	C	2	H	4	CL	1	0	G	1
CH2CLCH2CL	AVG[33,55]	-31.22									C	2	H	4	CL	2	0	G	1
	TRC[2]		73.12	18.54	21.95	24.96	27.45	31.16	33.78	37.64	C	2	H	4	CL	2	0	G	1
CH3CHCL2	TRC[2]	-31.09	72.94	18.32	21.84	24.79	27.18	30.79	33.40	37.40	C	2	H	4	CL	2	0	G	1
C2H5	CIO/LIU97[12]	29.30	(this study)								C	2	H	5		0	0	G	1
	LAY/BOZ95[16]		57.42	11.89	14.57	16.95	19.09	22.76	25.66		C	2	H	5		0	0	G	1
C2H5CL	JANAF[3]	-26.80	66.01	15.03	18.57	21.61	24.22	28.37	31.44	36.16	C	2	H	5	CL	1	0	G	1
C2H6	JANAF[3]	-20.20	54.81	12.54	15.78	18.70	21.33	25.78	29.29	34.87	C	2	H	6		0	0	G	1

REFERENCES (PART TWO)

1. Benson, S. W. *Thermochemical Kinetics* ; 2nd ed. Wiley-Interscience : New York, 1976.
2. Rodgers, A. S. *Selected Values for Properties of Chemical Compounds* ; Thermodynamic Research Center, Texas A&M University : College Station, TX, 1982.
3. Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables* ; 2nd Ed.(NSRDS-NBS37). U.S.Government Printing Office : Washington D.C., 1970.
4. Stull, D. R.; Westrum, E. F. Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds* ; Robert E. Krieger Publishing : Malabar, FL, 1987.
5. Stewart, J. J. *MOPAC 6.0*, Frank J. Seiler Research Lab., US Air Force Academy, Colorado, 1990.
6. Ritter, E. R. *J. Chem. Inf. Comput. Sci.* 1991, 31, 400.
7. Melius, C. F. *BAC-MP4 Heats of Formation and Free Energies* ; Sandia National Laboratories : Livermore, CA, 1993.
8. Chen, C. J.; Wong, D.; Bozzelli, J. W. *J. Phys. Chem. A.* 1998, 102, 4551-4558.
9. Seetula, J. A. *J. Chem. Soc., Faraday Trans.* 1998, 94(7), 891-898.
10. Seetula, J. A. *J. Chem. Soc., Faraday Trans.* 1996, 92, 3069-3078.
11. Colegrove, B. T.; Thompson, T. B. *J. Chem. Phys.* 1997, 106 (4), 22.
12. Cioslowski, J.; Guanghua Liu, G.; Moncrieff, D. *J. Am. Chem. Soc.* 1997, 119(47), 11452-11457(ENG).
13. Glukhovtsev, M. N.; Bach, R. D. *J. Phys. Chem. A*, 1997, 101(19), 3574-3579.
14. Rodriguez, C. F.; Bohme, D. K.; Hopkinson, A. C. *J. Phys. Chem.* 1996, 100, 2942-2949.
15. Zachariah, M. R.; Westmoreland, P. R.; Burgess Jr., D. R.; Tsang, W.; Melius, C. F. *J. Phys. Chem.* 1996, 100, 8737-8747.

16. Lay, T. H.; Bozzelli, J. W.; Dean, A. M.; Ritter, E. R. *J. Phys. Chem.* 1995, 99(39), 14514-14527.
17. Rayez, M. T.; Rayez, J. C.; Sawerysyn, J. P. *J. Phys. Chem.* 1994, 98(44), 11342-11352.
18. Chen, Y.; Tschuikow-Roux, E. *J. Phys. Chem.* 1992, 96, 7266-7272.
19. Ho, W.; Barat, R. B.; Bozzelli, J. W. *Combustion and Flame* 1992, 88, 265-295.
20. Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* 1992, 96, 9847-9855.
21. Taylor, P. H.; Dellinger, B.; Tirey, D. A. *Int. J. Chem. Kinet.* 1991, 23, 1051-1074.
22. Nicovich, J. M.; Van Dijk, C. A.; Kreutter, K.D.; Wine, P. H. *J. Phys. Chem.* 1991, 95, 9890-9896.
23. Miyokawa, K.; Tschuikow-Roux, E. *J. Phys. Chem.* 1990, 94, 715-717.
24. Kafafi, S. A.; Hudgens, J. W. *J. Phys. Chem.* 1989, 93, 3474-3479.
25. Russell, J. J.; Seetula, J. A.; Gutman, D. *J. Am. Chem. Soc.* 1988, 110, 3092-3099.
26. Tschuikow-Roux, E.; Paddison, S. *Int. J. Chem. Kinet.* 1987, 19, 15-24.
27. Pedley, J. B.; Naylor, R. O.; Kirby, S. P. *Thermodynamic Data of Organic Compounds*; 2nd ed. Chapman and Hall : London, 1986.
28. Orlov, Y. D.; Lebedev, Y. A.; Korsunskii, B. L. Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Kalinin State University. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, 1984(July), 7, 1550-1555.
29. McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* 1982, 33, 493-532.
30. DeFrees, D. J.; McIver, Jr., R. T.; Hehre, W. J. *J. Am. Chem. Soc.* 1980, 102, 3334.
31. Chao, J.; Rodgers, A. S.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* 1974, 3, 141.
32. Chen, S. S.; Rodgers, A. S.; Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* 1975, 4(2), 441-456.
33. Lide, D. R. (Ed.) *CRC Handbook of Chemistry and Physics* (1913-1995); 75th ed. CRC Press : Boca Raton, FL, 1994, pp 5-9.

34. Burcat, A.; McBride, B. *1994 Ideal Gas Thermodynamic Data for Combustion and Air-Pollution Use* ; Israel Institute of Technology : Haifa, 1993.
35. Born, M.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Chem. Soc.* 1994, 116, 7210.
36. (a) Cohen, N.; Benson, S. W. *Chem. Rev.* 1993, 93, 2419. (b) Cohen, N. *J. Phys. Chem. Ref. Data* 1996, 25(6), 1411.
37. Kohn, D. W.; Robles, E. S. J.; Logan, C. F.; Chen, P. *J. Phys. Chem.* 1993, 97, 4936.
38. Cohen, N. *J. Phys. Chem.* 1992, 96, 9052.
39. Hudgens, J. W.; Johnson, R. D.; Timonen, R. S.; Seetula, J. A.; Gutman, D. *J. Phys. Chem.* 1991, 95, 4400.
40. Grev, R. S.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* 1991, 95, 5128.
41. Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* 1991, 113, 5773.
42. *Thermodynamic data base of ideal gas* ; Sandia National Laboratory : 1990.
43. Chen, Y.; Rauk, A.;Tschuikow-Roux, E. *J. Chem. Phys.* 1990, 93, 1187.
44. Cox, J. D.; Wagman, D. D.; Medvedev, V. A. (Eds.) *CODATA Key Values for Thermodynamics* ; Hemisphere Publishing Corp. : New York, 1989.
45. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, Jr., R. F.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data (Suppl. III)*, 1989, 18, 881.
46. Tschuikow-Roux, E.; Chen, Y. *J. Am. Chem. Soc.* 1989, 111, 9030.
47. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data (Suppl. I)*, 1988, 17.
48. Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* 1988, 110, 7343.
49. Tsang, W. *J. Phys. Chem. Ref. Data* 1986, 15, 1087.
50. Tsang, W, "Single Pulse Shock Tube Study on the stability of Perfluorobromomethane" to be published.
51. Chase, Jr., M. W.; Davis, C.A.; Downey, Jr., J. R.; Frurip, D. J.; McDonald, R.A.; Syverud, A. N. *J. Phys. Chem. Ref. Data (Suppl.)*, 1985, 14.
52. Lias, S. G.; Karpas, Z.; Liebman, J. F. *J. Am. Chem. Soc.* 1985, 107, 6089.

53. Leopold, D. G.; Murray, K. K.; Miller, A. E. S.; Lineberger, W. C. *J. Chem. Phys.* 1985, 83, 4849.
54. Weissman, M.; Benson, S. W. *J. Phys. Chem.*, 1983, 87, 243.
55. Kolesov, V. P.; Papina, T. S. *Russ.Chem.Rev.* 1983, 52, 425, and references cited therein.
56. Heneghan, S. P.; Knoot, P. A.; Benson, S. W. *Int. J. Chem.Kinet.* 1981, 13, 677.
57. Weissman, M.; Benson, S. W. *Int. J. Chem. Kinet.* 1980, 12, 403.
58. Rossi, M.; Golden, D. M. *J. Am.Chem. Soc.*, 1979, 101, 1230.
59. Lengel, R. K.; Zare, R.N. *J. Am. Chem. Soc.* 1978, 100, 7495.
60. Rodgers, A. S. *ACS Symp. Ser.* 1978, 66, 296.
61. Papina, T. S.; Kolesov, V. P. *Vestn. Mosk. Univ. Ser. 2 Khim.* 1978, 19, 500.
62. Rodgers, A. S.; Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* 1974, 3, 117.
63. Mendenhall, G. D.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* 1973, 77, 2707.
64. Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* 1973, 2, 427.
65. Chao, J.; Rodgers, A. S.; Wilhoit, R. C.; Zwolinski, B. J. *Ideal Gas Chemical Thermodynamic Properties of the Six Chloroethanes with Symmetric Top* ; NBS: Washington, DC, 1972.
66. Mansson, M.; Ringner, B.; Sunner, S. *J. Chem. Thermodyn.* 1971, 3, 547.
67. Fletcher, R. A.; Pilcher, G. *Trans. Faraday Society.* 1971, 67, 3191.
68. Benson, S. W.; O'neal, H. E. *Kinetic Data on Gas Phase, Unimolecular Reactions* ; U.S. Government Printing Office : Washington,D.C., 1970.
69. Stull, D. R.; Westrum, Jr., E .F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds* ; John Wiley & Sons Inc : NY, 1969.
70. Herzberg, G.; Jones, J. W. *Astrophys. J.* 1969, 158, 399.
71. Dibeler, V. H.; Krauss, M.; Reese, R. M.; Harllee, F. N. *J. Chem. Phys.* 1965, 42, 3791

72. Ritter, E. R.; Bozzelli, J. W. *Chemical & Physical Processes in Combustion* 1993, 103, 459.
73. (a) Ho, W.; Yu, Q. R.; Bozzelli, J. W. *Combust. Sci. Technol.* 1992, 85, 23. (b) Ho, W.; Bozzelli, J. W. *24th Symp. (Int.) Combust., Combust. Inst.* 1992, 743. (c) Wang, H.; Hahn, T. O.; Sung, C. J.; Law, C. K. *Combust. Flame* 1996, 105, 291. (d) Yang, G.; Kennedy, I. A. *Combust. Flame* 1993, 92, 187.
74. Westbrook, C. K. *19th Symp. (Int.) Combust. Combust. Inst.* 1982, 126.
75. Karra, D.; Senkan, S. M. *Combust. Sci. Technol.* 1987, 54, 333.
76. Chang, W. D.; Kara, S. D.; Senkan, S. M. *Combust. Sci. Technol.* 1986, 49, 107.

PART III
THERMOCHEMICAL AND KINETIC ANALYSIS
ON CH₃CjO + O₂ REACTION

CHAPTER 1

ABSTRACT FOR PART THREE

Reaction pathways and kinetics are analyzed on $\text{CH}_3\text{CjO} + \text{O}_2$ reaction system using density functional and *ab initio* calculations to determine thermodynamic properties of reactants, intermediate radicals, and transition state (TS) structures. Enthalpies of formation ($\Delta H_f^\circ_{298}$) are determined using the CBSQ composite method and also by density functional calculations with isodesmic reactions for radical species. Entropies (S°_{298}) and heat capacities ($C_p^\circ(T)$ 300–1500 K) are determined using geometric parameters and vibrational frequencies obtained at the HF/6-31G(d') level of theory. Quantum Rice-Ramsperger-Kassel (QRRK) analysis is used to calculate energy dependent rate constants, $k(E)$. The acetyl radical CH_3CjO adds to O_2 to form a CCOQj peroxy radical ($\Delta H_f^\circ_{298} = -38.75$ kcal/mole in CBSQ). The peroxy radical can undergo dissociation back to reactants, decompose to products, $\text{CH}_2\text{CO} + \text{HO}_2$ via HO_2 elimination ($E_{a,\text{rxn}} = 28.01$ kcal/mole in CBSQ) or isomerize via hydrogen shift ($E_{a,\text{rxn}} = 26.93$ kcal/mole in CBSQ) to form a CjCOQ isomer ($\Delta H_f^\circ_{298} = -32.35$ kcal/mole in CBSQ). This isomer CjCOQ can undergo β -scission to products, $\text{CH}_2\text{CO} + \text{HO}_2$ ($E_{a,\text{rxn}} = 31.53$ kcal/mole in CBSQ) or decompose to $\text{CyCOC=O} + \text{OH}$ via OH elimination ($E_{a,\text{rxn}} = 23.08$ kcal/mole in CBSQ). Rate constants are estimated as function of pressure and temperature using QRRK analysis for $k(E)$ and modified strong collision analysis for fall-off. Important reactions are stabilization of CCOQj peroxy adduct at low temperature and $\text{CH}_2\text{CO} + \text{HO}_2$ and oxirane aldehyde +

OH at high temperature. Rate constants at 1atm pressure are ($k=A(T/K)^n \exp(-E_a/RT)$,
 A in $\text{cm}^3/(\text{mole}\cdot\text{s})$, E_a in kcal/mole): $k_1=(6.93 \times 10^{43})(T/K)^{-10.29} e^{-8.28/RT}$ for $\text{CH}_3\text{CjO} +$
 $\text{O}_2 \Rightarrow \text{CCOQj}$; $k_6=(3.65 \times 10^{18})(T/K)^{-1.78} e^{-6.29/RT}$ for $\text{CH}_3\text{CjO} + \text{O}_2 \Rightarrow \text{CH}_2\text{CO} + \text{HO}_2$
 ; $k_7=(2.09 \times 10^{27})(T/K)^{-4.45} e^{-13.44/RT}$ for $\text{CH}_3\text{CjO} + \text{O}_2 \Rightarrow \text{CyCOC=O} + \text{OH}$;
 $k_8=(8.42 \times 10^{40})(T/K)^{-9.17} e^{-12.47/RT}$ for $\text{CH}_3\text{CjO} + \text{O}_2 \Rightarrow \text{CjCOQ}$

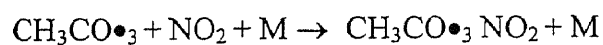
CHAPTER 2

INTRODUCTION FOR PART THREE

Important initial products from pyrolysis, oxidation, or photochemical reactions of saturated and unsaturated hydrocarbons are the corresponding radicals. The subsequent reactions of the hydrocarbon radicals with molecular oxygen are complex and difficult to study experimentally and present a source of controversy with regard to both pathway and reactions rates. These reactions, furthermore, represent the principal pathways of the radical conversion in many hydrocarbon oxidation and combustion processes^{1,2} and also in atmosphere.

The currently accepted OH radical chain mechanism for oxidation of volatile organic compounds (VOC) during night-time conditions requires a source of RC•O radicals to form RCO₃ or RO₂ radicals.^{3,4} The formation / pathways and kinetics of RC•O radical formation is not fully understood. Atmospheric researchers are active in areas of both experimental and modeling studies relating to these kinetic processes. Areas of focus are primarily those relative to secondary pathways, specifically the reactions of O₂ and NO with radicals formed in the primary OH abstraction or addition steps. The rate and extent of formation of secondary pollutants and photochemical oxidant, including ozone, are largely determined by these reactions. The product distributions in the photo-oxidation of VOCs under simulated troposphere conditions can be influenced by the varied reaction rates and channels (pathways) of RC•O radical interaction with oxygen.

RC•O radicals can be produced from emitted organic precursor species such as CH₃CHO, in several ways, by reactions with OH, or NO₃ radicals or by photolysis. CH₃CHO is of particular interest in atmospheric chemistry since it is formed as a product of the reaction of O₃ and / or OH radicals with naturally occurring, non-methane hydrocarbons, especially higher olefins such as isoprene and terpene. The photo-oxidation of hydrocarbons in photochemical smog also produces acetaldehyde as a major intermediate product. Acetylperoxy radicals CCOQj (often represented as CH₃CO•₃) are formed as a result of CH₃CjO radical reaction with O₂ in the photo-oxidation of higher carbonyl compounds (acetaldehyde, acetone, methylvinylketone, methylglyoxal, etc..) play an important role in atmospheric photo-oxidation processes. In the polluted atmosphere they react with NO_x and in the clean troposphere with other peroxy radicals. Acetylperoxy radicals are the precursor of peroxyacetylnitrate (PAN) an important constituent of photochemical smog and an air pollutant having important physiological effects. PAN is formed by combination with NO₂:



Because of its thermal stability at lower temperatures and its photochemical inertness under tropospheric conditions, PAN can act as a temporary reservoir for NO_x and serve as a carrier for transport in colder regions of the troposphere.

Peroxy radicals (ROO•), particularly CH₃CO•₃, are important intermediates in the oxidation of organic compounds in the troposphere^{3,4}. Their loss processes are one of the major factors influencing chain length in forming of ozone. Their reactions with NO are primarily chain propagating reactions resulting in the formation of NO₂,

which, on photolysis, yields O_3 . NO_2 , HO_2 and other peroxy radicals are, in contrast, mainly chain terminating. Hydro and alkyl - peroxy radicals are important in remote continental and marine atmospheres; they undergo reactions resulting in aldehydes, alcohols, organic acids, and hydroperoxides. There exists a need to establish structure-reactivity relationships for the different classes of radicals, due to different major reaction paths of the variety of peroxy radicals formed from VOCs and their oxidized derivatives. These relationships will allow estimation of kinetic pathways and rate constants, without required experimental data on each reactions of each molecule in a series.

Several studies have illustrated that the reactions of ethyl⁵⁻¹⁰ and isopropyl¹¹ radicals at pressures from 1 to 6000 torr and temperatures from 300 to 900 K, exhibit significant negative temperature dependence (NTD) and complex fall-off with pressure. The ethyl reaction is the best characterized and is shown to produce $C_2H_4 + HO_2$. The rate of ethyl radical loss decreases significantly with temperature⁵ and increases with pressure; this is explained by invoking reversible formation of a weakly bound adduct. The adduct, $C_2H_5OO\bullet$ is readily stabilized at low temperatures and atmospheric pressure; but dissociates back to reactants at higher temperatures. This rapid dissociation of the adduct is the origin of the observed NTD regime in hydrocarbon oxidation.

Analysis of the $C_2H_5 + O_2$ reaction system^{12, 13} invokes formation of a chemically activated adduct, which can be stabilized or, before stabilization, can dissociate back to $C_2H_5 + O_2$, react through a cyclic five-member ring intermediate to form a primary hydroperoxy alkyl radical, which can be stabilized or undergo elimination to $C_2H_4 +$

HO₂. The ethyl peroxy C₂H₅OO can also react directly via HO₂ elimination to C₂H₄ + HO₂. The formation of epoxide + OH in this system is limited by a lower Arrhenius A factors due to the isomerization and epoxide formation transition states combined with a low E_a for direct HO₂ elimination. The results of modeling studies for loss of ethyl and production of ethylene show good agreement with experimental data^{8,9}.

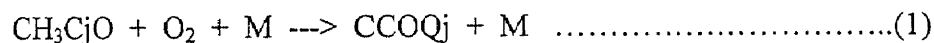
Important conclusions from the modeling indicate that well depth is often critical to the further reaction to new products. A deeper well provides more energy in the initially formed chemically activated adduct for forward reaction, before stabilization can occur. Isomerization, HO₂ elimination and epoxide + OH reaction A factors are much lower than that for dissociation of the complex to reactants, but the isomerization barrier height is often lower. At higher temperatures increased isomerization relative to stabilization of the activated complex leads to higher C₂H₄ + HO₂ formation rates in these systems. Similar results are reported on analysis of reactions of allyl, vinyl and formyl radicals reaction with oxygen.^{14,15}

There is however very little information on the important reaction of CH₃CjO radicals with O₂¹⁶. The oxidation process involves formation of chemically activated peroxyacetyl radical, CH₃CO•₃, which, similar to the ethyl peroxy system. The adduct can dissociate back to reactants, undergo reaction to new products or be collisionally stabilized.

Acetaldehyde and the corresponding radical species that result via loss of hydrogen atoms from the two different carbon sites in CH₃CHO are also common products (intermediates) from oxidation processes of higher molecular weight hydrocarbon species in both combustion and in atmospheric photochemistry. The acetaldehyde and

its two radicals are also produced by molecular weight growth from C₁ carbon combustion and mild oxidation processes where the slow reaction of methyl radical with O₂ to CH₃O + O or CH₂O + OH. The slow conversion of CH₃OO• (methyl peroxy radical) to products, results in an equilibrium between CH₃ + O₂ and CH₃OO• where entropy favors the reactants at higher temperatures. As a result methyl radicals often buildup in the radical pool until combination occurs forming ethane and ethyl + H. Acetaldehyde is one of the important oxidation products of ethane and ethylene. Acetaldehyde and acetyl radicals are important intermediates in the overall breakdown processes of higher molecular weight and C₁ hydrocarbons to CH₂O, CO, CO₂ and H₂O. The radical reactions with oxygen also serve as model reactions for larger aldehydic molecule systems.

This study focuses on reaction mechanism of acetyl radical association with O₂. Thermodynamic properties are estimated for reactants, intermediate, products and transition states along the reaction pathway. The thermodynamic parameters are used to calculate high-pressure limit rate constants using canonical Transition State Theory. Rate constants as a function of temperature and pressure are estimated using a multi frequency Quantum RRK analysis with modified strong collision analysis of Gilbert et. al¹⁷⁻¹⁹ for fall off. The data at relevant pressures and temperatures should be useful to both atmospheric and combustion modelers.



One absolute measurement of k₁ has been reported in the literature. McDade et al.³⁶ determined k₁ = (1.2 ± 0.2) * 10¹² cm³/(mole-s) in 1-4 torr total pressure of He at 298K. The high-pressure limiting value of k₁ = (3.01 ± 1.5) * 10¹² cm³/(mole-s)

recommended by the IUPAC panel is based on the absolute measurements of McDade et al.³⁶ and the pressure dependence of the $C_2H_5 + O_2$ reaction³⁷. The results from two studies, one of the relative reactivity of CH_3CjO with O_2 and Cl_2 ³⁸, the other of the rate constant for the reaction of CH_3CjO with Cl_2 ³⁹, have been combined to give a high-pressure limiting rate constant of $k_1 = (1.9 \pm 0.4) * 10^{12} \text{ cm}^3/(\text{mole-s})$ at room temperature.

Recently, Sehested et al.³⁵ report on $k_1 = (2.65 \pm 0.4) * 10^{12} \text{ cm}^3/(\text{mole-s})$ at 295K and 1000 mbar total pressure of SF_6 .

Tyndall et al.⁴⁰ studied the reaction of OH radical with methyl glyoxal and acetaldehyde in a low pressure (c.a. 3 torr) flow reactor at temperatures from 260 to 333 K. They report rate constants for OH abstractions from the parent molecules and also report data on further reactions of the radicals formed from the abstractions by OH. They infer that only the acetyl radical is formed and further reaction of acetyl radical with O_2 leads to noticeable regeneration of OH; from observations showing reduced loss of the OH versus time. Some chamber experiments with FTIR monitoring showed no evidence of OH radical production.

Absolute rate constants of Fluorine atom reaction with acetaldehyde were studied by Sehested and coworkers³⁵ using pulse radiolysis combined with transient ultraviolet absorption. They report production of two radicals - formyl methyl at 35% and acetyl at 65% (both $\pm 9\%$). We note that for reactions where chlorine atom is abstracting hydrogen atoms. Chlorine atoms usually have similar A factors and similar or lower E_a 's when the reactions are exothermic which they are in all cases in this study. In the case of acetaldehyde, for example, k_{298} for Cl atom abstraction is reported as $4.58 \times$

10^{13} [41] at 298K, while abstraction by F atom is 5.00×10^{13} [42]. The H--Cl bond is 103 kcal/mole, while the carbonyl C--H and methyl C--H bonds on acetaldehyde are 88 and 94 kcal/mole respectively. Chlorine should, therefore, readily abstract from both hydrogen sites of acetaldehyde.

Michael et al.⁴³ studied the reaction of OH with acetaldehyde in a low pressure discharge flow reactor with resonance fluorescence monitoring. He also studied the reaction of radical(s) generated via the OH reaction with O₂. The total reaction rate constant for OH with acetaldehyde was $A = 3.3 \times 10^{12}$, with a small negative energy of activation of 610 cal/mole. Michael et al. report near complete regeneration of OH radical in the OH + acetaldehyde experiments when O₂ was present to further react with the indicated acetyl radical formed. In separate studies with Cl atom reacting with acetaldehyde, they observed production of OH radical on further radical reaction(s) with O₂. They considered and rejected possible formation of formyl methyl radicals based on work of Gutman's research group and an assumed bond energy of the H--C bond on the methyl group of 98 kcal/mole.

Slagle and Gutman⁴⁴ studied formation of acetyl radical from acetaldehyde in reaction of Cl atoms from 1082 cm⁻¹ IR multiphoton decomposition of CF₂Cl₂ of C₆F₅Cl. They monitored the radical profiles with photoionization mass spectrometry. Verification of CH₃CjO radical versus formyl methyl was by use of deuterated acetaldehyde, CH₃CHO. They observed CH₃CjO and could not detect CjCHO; but did not estimate lower limits of its detection.

Reaction kinetics of acetylperoxy radicals with nitric oxide and nitrogen dioxide were studies by Maricq and Szenté³⁹, where the peroxy radicals were generated via

reaction of acetyl radical with O₂. Acetyl radicals were generated by reaction of acetaldehyde with Cl atoms and Cl atoms were produced by 351 nm eximer laser pulses ca 300 mJ/pulse. Maricq and Szente provide data on nitric oxide plus acetyl and methyl peroxy radical decay and NO₂ formation versus time for modeling comparisons.

Formyl methyl radicals, the other possible radical that may be formed by abstraction of H atoms from acetaldehyde, were generated by photodissociations of methyl-vinyl ether by Zhu and Johnston⁴⁵. $\text{CH}_3\text{-O-C}_2\text{H}_3 + h\nu \rightleftharpoons \text{CH}_3 + \text{C}_2\text{H}_3\text{O}$. Here the vinoxy radical undergoes rapid electron rearrangement to the lower energy form (ca 18 kcal/mole lower in energy) formyl methyl radical. Kinetic studies on this formyl methyl radical with O₂ show slower reaction, $k_2 = 1.2 \times 10^{11} \text{ cm}^3/\text{mole-sec}$, than rate constants reported for acetyl radical $k_1 = 1 \times 10^{12} \text{ cm}^3/\text{mole-sec}$. They suggest that if formyl methyl radicals are produced in reactions of Cl atoms or OH with acetaldehyde, they will react about one tenth as fast with O₂, probably leading to small or no corrections to the faster acetyl + O₂ reactions.

Photo dissociation of PAN, (PeroxyAcetylNitrate) was used by Villalta and Howard¹¹ to generate acetylperoxy radicals for study of reaction kinetics with nitric oxide. Rate constants determined by this method agreed well with other reported values. This agreement of kinetic data where acetylperoxy radicals are generated by a very different and positive mechanism supports the assumption of Maricq and Szente⁴³, Sehested et al.³⁵, Tyndall et al.⁴⁰, Michael et al.⁴³, and Slagle and Gutman⁴⁴, that primarily acetyl radicals are generated by reaction with OH, or Cl atoms.

CHAPTER 3

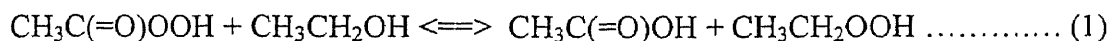
CALCULATION METHOD FOR PART THREE

3.1 Determination of Enthalpies of Formation

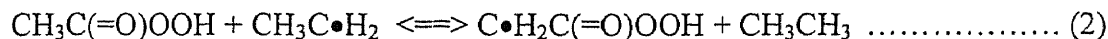
Enthalpies of formation ($\Delta H_f^\circ_{298}$) for reactants, intermediate radicals, transition states and products are calculated using CBS-Q composite method and density functionals. The initial structure of each compound or transition state is determined using ROHF or UHF/PM3 in MOPAC²⁰, followed by optimization and vibrational frequency calculation at HF/6-31G(d') level of theory using GAUSSIAN 94²¹. Transition State (TS) geometries are identified by the existence of only one imaginary frequency, structure information and the TST reaction coordinate vibration information. Zero-point vibrational energies (ZPVE), vibrational frequencies and thermal contributions to enthalpy from harmonic frequencies are scaled by 0.91844 as recommended by Petersson et. al²². Single point energy calculation are carried out at the B3LYP/6-31G(d'). The complete basis set (CBS-Q) method of Petersson and coworkers for computing accurate energies²³⁻²⁵ are chosen as our primary for determining enthalpies.

The CBS-Q calculation sequence is performed on the MP2/6-31G(d') geometry and followed by single point calculations at the theory level of QCISD(T)/6-31+G(d'), MP4(SDQ)/CbsB4 and MP2/CBSB3 CBSExtrap=(Nmin=10,Pop).

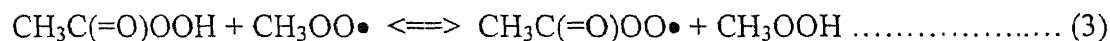
The isodesmic reactions are used to determine the heat of formation ($\Delta H_f^\circ_{298}$) for intermediate radicals. For estimation of $\text{CH}_3\text{C}(=\text{O})\text{OOH}$ [defined CCOQ, Q=OOH (hydroperoxy group)]



For estimation of $\text{C}\cdot\text{H}_2\text{C}(=\text{O})\text{OOH}$ [defined CjCOQ, j : radical site]



For estimation of $\text{CH}_3\text{C}(=\text{O})\text{OO}\cdot$ [defined CCOQj, Qj : -OO \cdot]



The method of isodesmic reactions relies upon the similarity of bonding environment in the reactants and products that leads to cancellation of systematic errors in the *ab initio* MO calculations.²⁶ The basic requirement of the isodesmic reaction is that the number of bonds of each formal chemical bond type is conserved in the reaction. In reaction (1), *ab initio* calculations with ZPVE and thermal correction are performed for all of four compounds. Since $\Delta H_f^\circ_{298}$ of three compounds excepting CCOQ have been experimentally or theoretically calculated, the unknown $\Delta H_f^\circ_{298}$ of CCOQ is obtained. The remaining two radicals are calculated in the same manner.

The $\Delta H_f^\circ_{298}$ of transition state compounds are estimated by evaluation of $\Delta H_f^\circ_{298}$ of the stable radical adducts plus difference of total energies with ZPVE and thermal correction between these radical species and the transition state (TS).

TCCOQjS : A peroxy radical CCOQj isomerize to form a CjCOQ isomer via hydrogen shift.

TCCOXQE : A peroxy radical CCOQj decompose to products, $\text{CH}_2\text{CO} + \text{HO}_2$ via HO_2 elimination.

TCjCOXQ : A CjCOQ isomer undergo β -scission to products, $\text{CH}_2\text{CO} + \text{HO}_2$

TYCOCDOXOH : A CjCOQ isomer decompose to products, $\text{CyCOC}=\text{O} + \text{OH}$ via
OH elimination.

3.2 Determination of Entropy and Heat Capacity

The contributions of external rotation and vibrations to entropies and heat capacities are calculated from scaled vibration frequencies and moments of inertia for the optimized HF/6-31G(d') structures. Contributions from frequencies corresponding to hindered internal rotation are replaced with contributions calculated from the method of Pitzer and Gwinn²⁷ for S and $C_p(T)$. Number of optical isomers and spin degeneracy of unpaired electrons are also incorporated.

3.3 High-Pressure Limit A Factors (A_∞) and Rate Constants (k_∞) Determination

For the reactions where thermodynamic properties of TS are calculated by *ab initio* or density functional methods, k_∞ s are fit by three parameters A_∞ , n, and E_a over temperature range from 298 to 2000K, $k_\infty = A_\infty(T)^n \exp(-E_a/RT)$ Entropy differences between reactant and TS are used to determine the pre-exponential factor, A, via conventional transition state theory (TST) for unimolecular and bimolecular reactions $A = (k_b T/h_p) \exp(\Delta S^\ddagger/R)$ and $A = (ek_b T/h_p) \exp(\Delta S^\ddagger/R)$, respectively. h_p is Plank's constant and k_b is the Boltzman constant.

3.4 Kinetic Analysis

Once the potential energy surface and thermochemical properties are evaluated, forward or reverse rate for each, elementary reaction step are determined, Multi-frequency Quantum Rice-Ramsperger-Kassel (QRRK) analysis is then used for $k(E)$ and modified strong collision analysis of Gilbert et. al¹⁷⁻¹⁹ used for fall-off; to obtain rate constants as a function of temperature and pressure. Reactions which incur a change in number of moles, such as unimolecular dissociation, have energy of activation calculated as ΔU_{rxn} plus an E_a for the reverse addition, where U is internal energy.

A modified QRRK analysis we use in this study is described by Zhong and Bozzelli.³⁴ It is shown to yield reasonable results and provides a framework by which the effects of temperature and pressure can be evaluated in complex reaction systems. The current version of the QRRK computer code utilizes a reduced set of vibration frequencies which accurately reproduce the molecule (adduct) heat capacity data, with inclusion of one external rotation to calculate density of states $\rho(E)$.

Comparisons of ratios of these $\rho(E)/Q$ (partition function Q) with direct count $\rho(E)/Q$ are shown to be in good agreement.³⁴ Nonlinear Arrhenius effects resulting from changes in the thermodynamic properties of the respective TST's relative to the adduct with temperature are incorporated using a two parameter Arrhenius pre-exponential factor (A, n) in AT^n .

CHAPTER 4

RESULT AND DISCUSSION FOR PART THREE

4.1 Geometries of Two Intermediate Radicals and Transition States

Figure 3.1 to 3.5 show MP2/6-31G(d') determined geometries of CCOQj, CjCOQ, TCCOQjS, TCCOXQE and TYCOCDOXOH respectively. [names are defined in section 3.1] Figure 3.1 and Figure 3.2 show the optimized geometries of two intermediate radicals, CCOQj and CjCOQ, respectively. Figure 3.3 shows TCCOQjS structure for isomerization (H shift) reaction. The H₆ atom is in a bridge structure shifting from C₁ to radical site O₅. The leaving bond length H₆-C₁ is calculated as 1.27Å with MP2/6-31G(d') determined geometry; where the H-C bond length in CCOQj is calculated as 1.09Å. The forming bond length H₆-O₅ is calculated as 1.25Å. All bond lengths are from MP2/6-31G(d') determined geometries. The normal bond length H-O in CjCOQ is calculated as 0.97Å. Figure 3.4 shows TCCOXQE structure, HO₂ elimination of CCOQj --> CH₂CO + HO₂. The leaving bond length of C₁-H₃ is calculated as 1.23Å and the C-H bond length in CCOQj is calculated as 1.09Å. The leaving bond length of C₂-O₆ is calculated as 2.02Å and the C-O bond length in CjCOQ is calculated as 1.38Å. The leaving O₆-O₇ bond length is calculated as 1.28Å and the O-O bond length in CjCOQ is calculated as 1.46Å. Again all bond lengths are from MP2/6-31G(d') determined geometries.

Figure 3.5 shows TYCOCDOXOH structure, OH elimination of CjCOQ --> CyCOC=O + OH. The leaving bond length O₄-O₇ is calculated as 1.84Å and the O-O

CCOQj [Qj = OO. (peroxy) , j : radical site]

CH₃C=O(OO.)

Geometry optimization at the MP2/6-31G(d') level of theory.

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C2-C1	1.50				
O3-C2	1.44	O3-C2-C1	115.7		
O4-O3	1.31	O4-O3-O2	113.2	O4-O3-O2-C1	0.0
O5-O2	1.19	O5-C2-C1	129.0	O5-C2-C1-O3	-180.0
H6-C1	1.09	H6-C1-C2	107.2	H6-C1-C2-O3	-180.0
H7-C1	1.09	H7-C1-C2	110.7	H7-C1-C2-O3	59.5
H8-C1	1.09	H8-C1-C2	110.7	H8-C1-C2-O3	-59.5

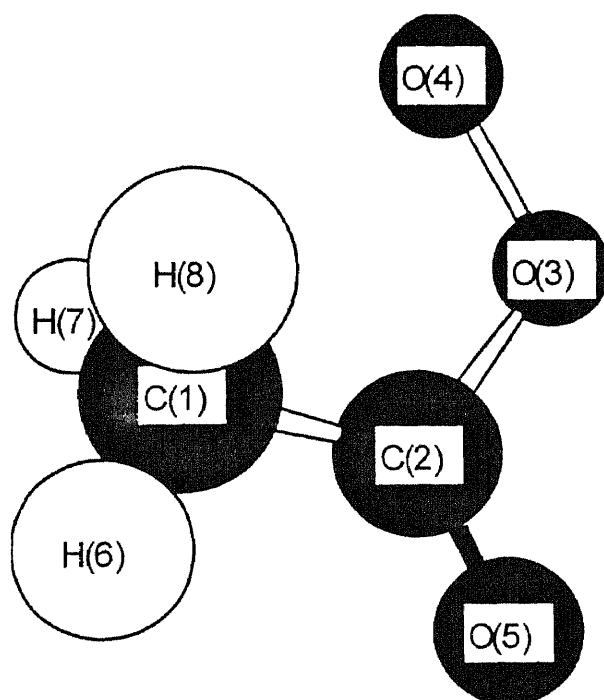


Figure 3.1 Structure for CCOQj

C_jCOQ [Q = OOH (hydroperoxy group), j : radical site]

C₂H₂C=O(OOH)

Geometry optimization at the MP2/6-31G(d') level of theory.

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C2-C1	1.48				
O3-C2	1.38	O3-C2-C1	118.0		
O4-O3	1.46	O4-O3-O2	111.8	O4-O3-O2-C1	1.4
O5-O2	1.19	O5-C2-C1	125.4	O5-C2-C1-O3	-179.2
H6-C1	1.08	H6-C1-C2	123.6	H6-C1-C2-O3	2.5
H7-C1	1.08	H7-C1-C2	115.1	H7-C1-C2-O3	-179.1
H8-C4	0.97	H8-O4-O3	98.2	H8-O4-O3-C2	141.4

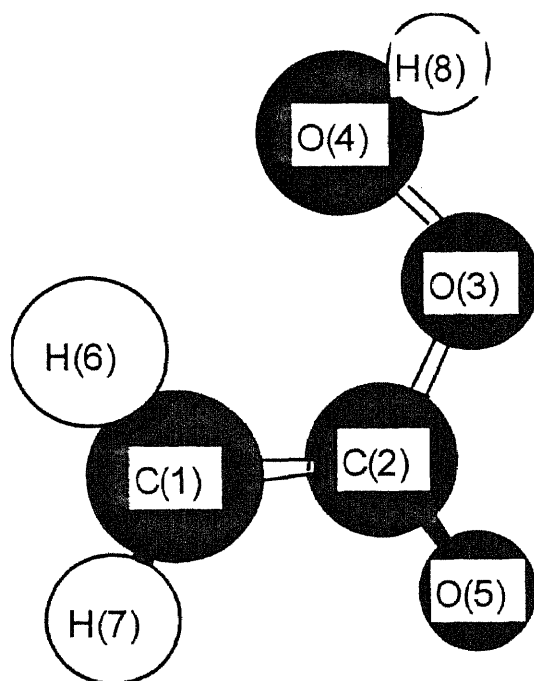
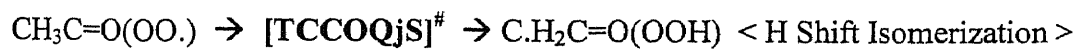


Figure 3.2 Structure for C_jCOQ

TCCOQjS

Geometry optimization at the MP2/6-31G(d') level of theory.

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C2-C1	1.52				
O3-C2	1.20	O3-C2-C1	128.6		
O4-C2	1.38	O4-C2-C1	108.8	O4-C2-C1-O3	180.0
O5-O4	1.42	O5-O4-C2	108.2	O5-O4-C2-C1	0.0
H6-O5	1.25	O6-O5-O4	98.2	O6-O5-O4-C2	0.0
H7-C1	1.09	O7-C1-C2	114.8	O7-C1-C2-O3	-67.3
H8-C1	1.09	H8-C1-C2	114.8	H8-C1-C2-O3	67.3

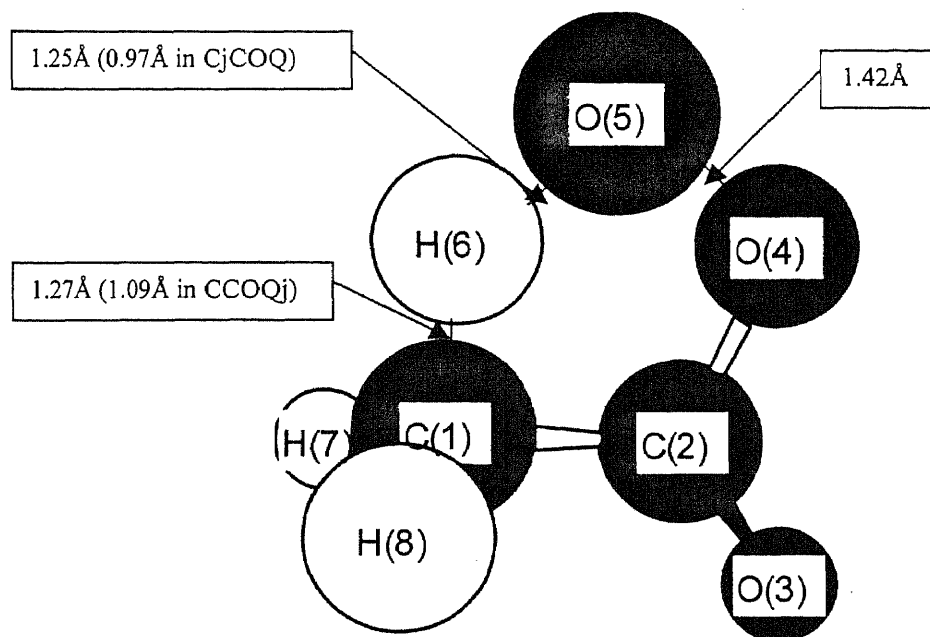
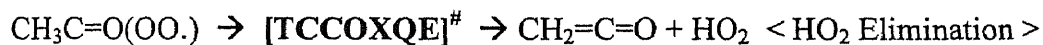


Figure 3.3 Structure for TCCOQjS

TCCOXQE

Geometry optimization at the MP2/6-31G(d') level of theory.

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C2-C1	1.42				
H3-C1	1.09	H3-C1-C2	110.6		
H4-C1	1.09	H4-C1-C2	112.3	H4-C1-C2-H3	127.2
O5-C2	1.17	O5-C2-C1	157.6	O5-C2-C1-H3	-86.4
O6-O2	2.02	O6-C2-C1	95.3	O6-C2-C1-H3	99.8
O7-O6	1.28	O7-O6-C2	105.8	O7-O6-C2-C1	9.4
H8-C1	1.23	H8-C1-C2	99.3	H8-C1-C2-H3	-110.8

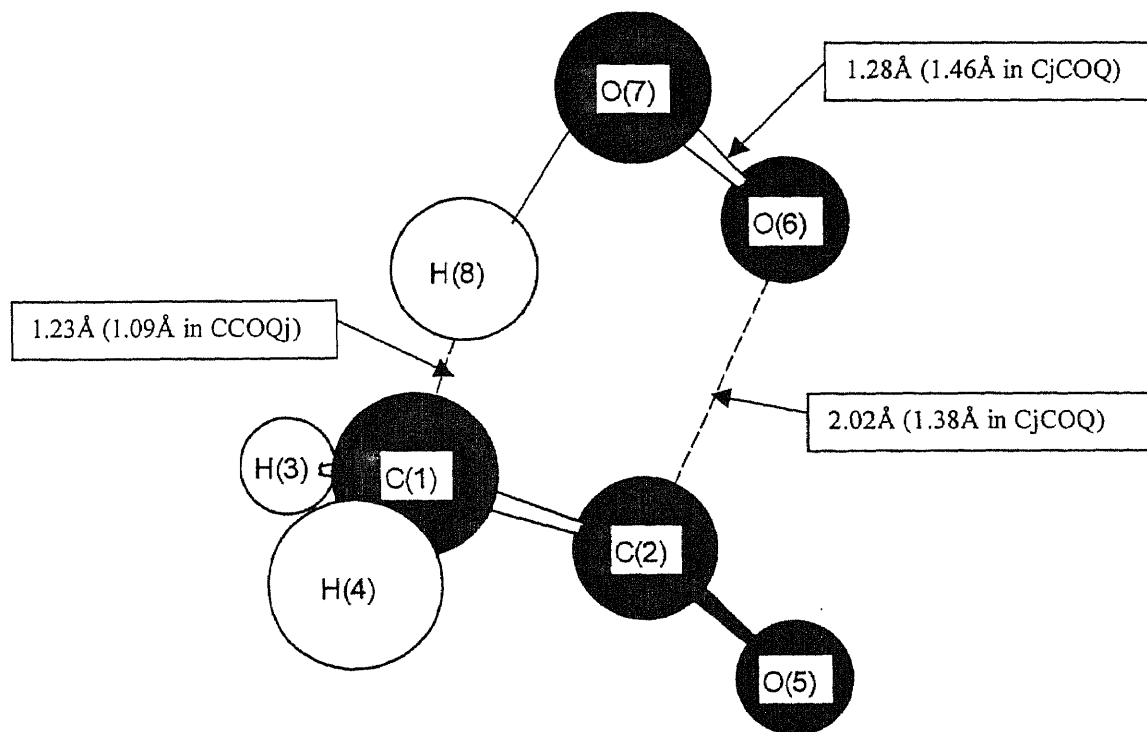
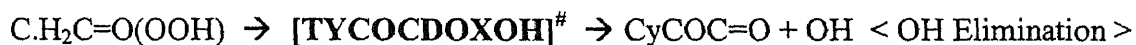


Figure 3.4 Structure for TCCOXQE

TYCOCDOXOH



Geometry optimization at the MP2/6-31G(d') level of theory.

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C2-O1	1.21				
C3-C2	1.47	C3-C2-O1	138.9		
O4-C2	1.31	O4-C2-O1	132.3	O4-C2-O1-C3	-180.0
H5-C3	1.08	H5-C3-C2	120.2	H5-C3-C2-O1	93.8
H6-C3	1.08	H6-C3-C2	120.2	H6-C3-C2-O1	-93.8
O7-O4	1.84	O7-O4-C2	109.1	O7-O4-C2-O1	0.0
H8-O7	0.98	H8-O7-O4	93.7	H8-O7-O4-C2	0.0

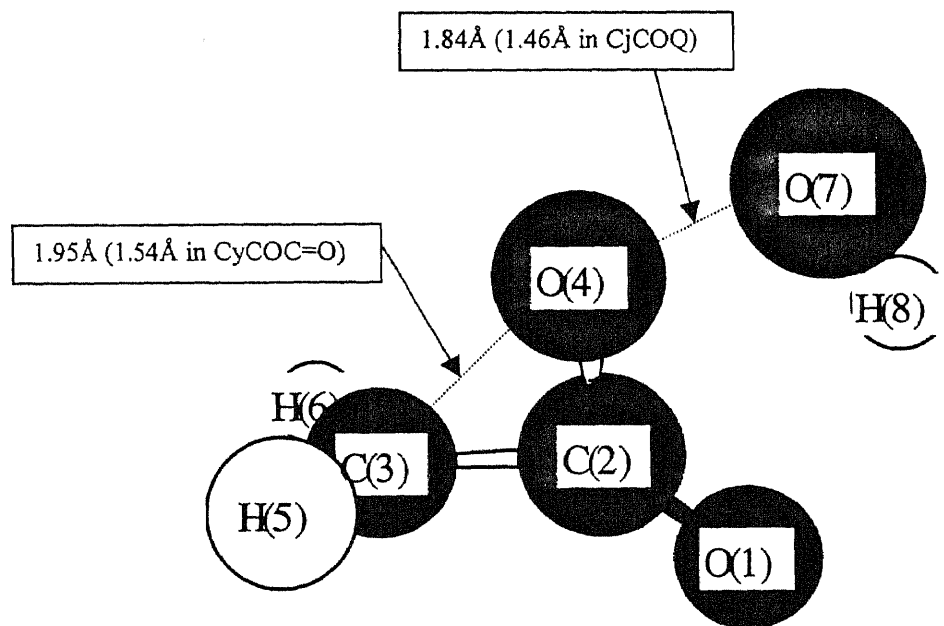


Figure 3.5 Structure for TYCOCDOXOH

bond length in CjCOQ is calculated as 1.46Å. The forming C₃-O₄ bond is calculated as 1.95Å and the C-O bond length in CyCOC=O is calculated as 1.54Å.

4.2 Estimation of Entropy ($S^0_{(298)}$) and Heat Capacity ($C_p(T)$'s, 300 - 1500K)

$S^0_{(298)}$ and $C_p(T)$'s are calculated based on vibration frequencies and moments of inertia of the optimized HF/6-31G(d') structures. (Table 3.1 and Table 3.2)

The calculation results using MP2/6-31G(d') determined geometries and HF/6-31G(d') determined frequencies are summarized in Table 3.3. TVR represents the sum of the contributions from translations, vibrations and external rotations for $S^0_{(298)}$ and $C_p(T)$'s. Symmetry, optical isomer and electronic spin are incorporated in estimation of $S^0_{(298)}$ as described in Table 3.3. Contributions of internal rotation for $S^0_{(298)}$ and $C_p(T)$'s are calculated based on rotational barrier heights, moments of inertia of the rotors using the method of Pitzer and Gwinn's²⁶. (Table 3.4)

4.3 Estimation of Enthalpy of Formation ($\Delta H_f^\circ_{298}$) using Total Energies and Isodesmic Reactions

The overall energy diagram for the CH₃CjO + O₂ reaction system is illustrated in Figure 3.6.

CBSQ calculations are performed on the MP2/6-31G(d') determined geometries and HF/6-31G(d') determined frequencies. Density functionals are performed on the B3LYP/6-31G(d) determined geometries and frequencies.

Isodesmic reactions are applied to accurately estimate $\Delta H_f^\circ_{298}$ of CCOQ and two intermediate radicals, CjCOQ and CCOQj. Zero point Vibration energies (ZPVE's) and thermal corrections to 298.15 K are taken into account. The total energies at 0 K

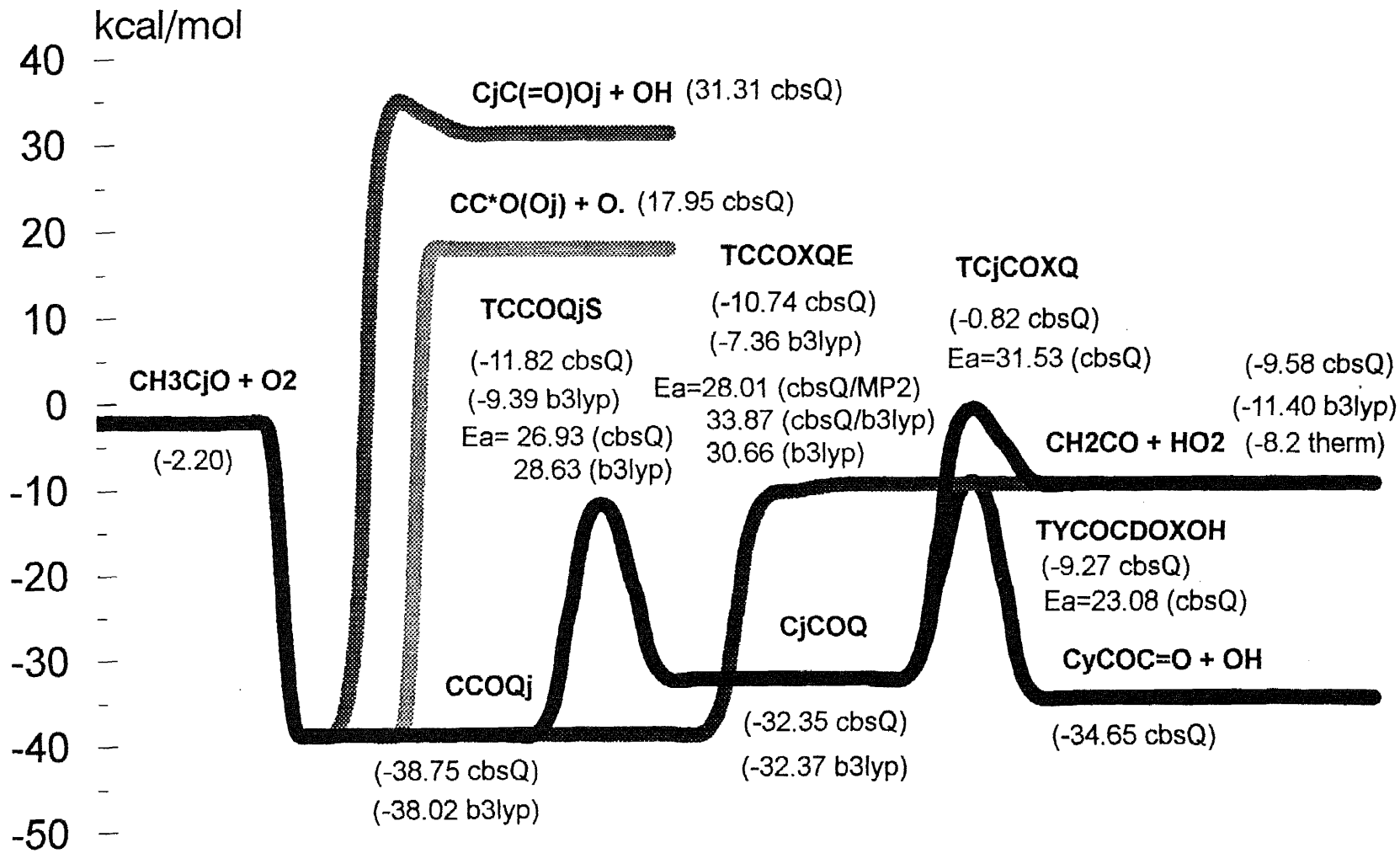


Figure 3.6 Potential Energy Diagram $\text{CH}_3\text{C}_j\text{O} + \text{O}_2$

[Q=OOH, Qj=OO., j=radical site]

Table 3.1 Vibrational Frequencies^a (ν cm⁻¹) HF/6-31G(d') level of calculation

Species	Vibrational Frequencies																	
CH3CHO	160	543	847	956	1223	1256	1519	1556	1598	1607	2029	3123	3190	3251	3309			
CH3CjO	107	506	920	1040	1154	1502	1595	1596	2141	3199	3289	3293						
CCOQ	35	175	318	346	475	672	714	998	1190	1173	1192	1425	1548	1602	1607	1677	2009	3222
	3297	3336	3962															
CCOQj	107	167	340	459	628	714	954	1094	1166	1252	1323	1545	1601	1607	2103	3219	3292	3337
CjCOQ	106	129	368	371	536	624	627	774	915	1096	1202	1371	1577	1631	1809	3365	3495	4113
CH2CO	492	632	690	1102	1264	1554	2381	3363	3466									
TCCOQjS ^b	-1669 ^f	139	274	485	543	601	690	846	934	1017	1032	1070	1165	1435	1727	1881	3136	3224
TCCOXQE ^c	-1596 ^f	81	226	375	452	513	566	771	1012	1063	1182	1460	1507	1533	1868	2435	3259	3340
TCjCOXQ ^d	-877.6 ^f	98	182	228	290	408	514	554	731	1015	1096	1143	1545	1626	2192	3327	3435	4059
CC*O(Oj)	52	428	594	634	933	1050	1170	1384	1534	1604	1606	2018	3214	3287	3331			
CyCOC=O	542	596	839	1060	1104	1172	1257	1349	1622	2216	3315	3418						
TYCOCDOXOH ^e	-671 ^f	152	194	270	326	387	613	634	804	985	1012	1017	1211	1459	1898	3191	3307	3611

^a non-scaled. ^{b,c,d,e} Transition State Structure described in results section.

^f Transition State, one imaginary frequency.

Table 3.2 Moments of Inertia (amu-Bohr²) HF/6-31G(d') level of calculation

Species	I _A	I _B	I _C	Species	I _A	I _B	I _C
CH3CHO	31.09	175.54	195.57	TCCOQjS	177.19	371.70	536.83
CH3CjO	20.77	180.48	190.17	TCCOXQE	194.75	477.79	660.74
CCOQ	191.62	383.50	562.14	TCjCOXQ	202.06	443.62	609.40
CCOQj	165.45	396.96	551.32	CC*O(Oj)	147.47	182.32	318.64
CjCOQ	170.86	382.43	553.29	CyCOC=O	67.39	218.08	273.37
CH2CO	6.30	171.66	177.96	TYCOCDOXOH	194.30	421.08	602.79

Table 3.3 Ideal Gas Phase Thermodynamic Properties Obtained
by CBSQ Calculation^a and by Therm^{*}

Species (s, e, OI) ^g		ΔH_f° ₂₉₈ ^b	S° ₂₉₈ ^c	C_{p300} ^c	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
CH3CHO	TVR ^d		57.97 ^g	11.58	14.29	16.88	19.20	22.98	25.80	30.10
(CH3-C(=O)H)	Internal Rotor 1 ^f		5.16	1.44	1.30	1.23	1.17	1.10	1.07	1.03
(3,0,1)	Total		63.13	13.02	15.59	18.11	20.37	24.08	26.87	31.13
	THERM	-39.10	63.11	12.49	15.83	18.59	20.85	24.22	26.50	29.76
CH3CjO**	TVR		58.82	11.12	13.24	15.24	17.01	19.90	22.06	25.39
(CH3-C(=O))	Internal Rotor 1		5.24	1.62	1.41	1.29	1.21	1.12	1.08	1.03
(3,1/2,1)	Total		64.06	12.74	14.65	16.53	18.22	21.02	23.14	26.42
	THERM	-2.20	62.71	11.10	13.92	16.23	18.11	20.89	22.75	25.35
CCOQ***	TVR		66.79	15.22	18.93	22.24	25.05	29.40	32.54	37.27
(CH3-C(=O)OOH)	Internal Rotor 1,2,3		9.65	5.53	6.06	6.27	6.30	6.06	5.64	4.70
(3,0,2)	Total	-84.70	76.44	20.75	24.99	28.51	31.35	35.46	38.18	41.97
	THERM	-80.48	77.23	20.53	24.34	27.65	30.39	34.52	37.41	
CCOQj***	TVR		66.86	15.33	18.81	21.84	24.36	28.18	30.87	34.77
(CH3-C(=O)OO.)	Internal Rotor 1,2		12.69	2.72	2.46	2.30	2.21	2.12	2.08	2.03
(3,1/2,1)	Total	-38.75	79.55	18.05	21.27	24.14	26.57	30.30	32.95	36.80
	THERM	-44.38	77.45	18.48	21.50	24.10	26.30	29.80	32.44	
CjCOQ	TVR		70.45	15.79	19.14	21.85	24.01	27.19	29.43	32.85
(CH2-C(=O)OOH)	Internal Rotor 1,2,3		8.80	6.00	6.39	6.50	6.46	6.15	5.69	4.72
(1,1/2,2)	Total	-32.35	79.25	21.79	25.53	28.35	30.47	33.34	35.12	37.57
	THERM	-38.18	74.50	20.23	23.94	26.87	29.16	32.40	34.56	
CH2CO (2,0,1)	TVR		57.57	12.26	14.10	15.61	16.85	18.81	20.29	22.61
(CH2=C=O)	Total		57.57	12.26	14.10	15.61	16.85	18.81	20.29	22.61
	THERM	-11.70	57.81	12.68	14.77	16.43	17.75	19.65	20.92	22.91
TCCOQjS	TVR		72.15	19.92	23.97	27.10	29.51	32.90	35.12	38.15
(1,1/2,2)	Total	-11.82	72.15	19.92	23.97	27.10	29.51	32.90	35.12	38.15
TCCOXQE	TVR		74.97	20.04	23.37	26.14	28.41	31.83	34.20	37.57
(1,1/2,2)	Total	-10.74	74.97	20.04	23.37	26.14	28.41	31.83	34.20	37.57
TcjCOXQ	TVR		74.11	18.14	20.96	23.20	25.00	27.76	29.80	33.03
(1,1/2,2)	Internal Rotor 1,2		5.07	3.83	4.19	4.41	4.52	4.47	4.20	3.47
	Total	-0.82	79.18	21.97	25.15	27.61	29.52	32.23	34.00	36.50
CC*O(Oj)	TVR		62.80	12.71	15.42	17.91	21.10	23.58	26.16	30.15
(CH3-C(=O)O.)	Internal Rotor 1		5.62	1.08	1.05	1.03	1.02	1.01	1.00	1.00
(3,1/2,1)	Total	-41.61	68.42	13.79	16.47	18.94	22.12	24.59	27.16	31.15
	THERM	-51.38	63.56	14.78	17.67	20.28	22.42	25.81	28.19	
CyCOC=O	TVR		62.29	11.95	14.65	17.06	19.06	22.10	24.24	27.42
(1,0,1)	Total	-44.14	62.29	11.95	14.65	17.06	19.06	22.10	24.24	27.42
TYCOCDOXOH	TVR		73.08	18.74	21.97	24.50	26.48	29.39	31.47	34.77
(1,1/2,1)	Internal Rotor 1		4.31	1.46	1.30	1.20	1.14	1.08	1.05	1.02
	Total	-9.27	77.39	20.20	23.27	25.70	27.62	30.47	32.52	35.79

* : therm values for stable species are included for comparison

** j : radical site, *** Q = OOH (hydroperoxy group), Qj = OO.(peroxy)

a : Thermodynamic properties are referred to a standard state of an ideal gas of pure enantiomer at 1 atm.

b : Units in kcal/mol c : Units in cal/mol-K

d : Sum of contributions from translations, vibrations, and external rotations.

f : Contribution from internal rotation

g : Symmetry number, optical isomer and electronic spin are taken into account, -Rln(s), Rln2, Rln2, respectively.

s = number of symmetry, e = electronic spin, OI = number of optical isomer

Table 3.4 Moments of Inertia ($\text{amu}\cdot\text{A}^2$) and Rotational Barriers (kcal/mole)
for Internal Rotors

Species	Rotor	I_A	I_B	V	n^a
CH ₃ CHO	CH ₃ --C(=O)H	3.12	18.90	1.20	6
CH ₃ CjO ^b	CH ₃ --C.(=O)	3.12	23.81	1.20	3
CCOQ ^c	CH ₃ --C(=O)OOH	3.12	130.14	3.18	6
	CH ₃ C(=O)--OOH	44.19	1.56	5.46	2
	CH ₃ C(=O)O--OH	100.00	0.92	7.15	1
CCOQj ^d	CH ₃ --C(=O)OO.	3.12	126.74	0.70	6
	CH ₃ C(=O)--OO.	44.19	30.84	1.00	2
CjCOQ	C.H ₂ --C(=O)OOH	1.75	130.14	3.18	2
	C.H ₂ C(=O)--OOH	42.44	1.56	5.46	2
	C.H ₂ C(=O)O--OH	100.00	0.92	7.15	1
TCjCOXQ	C.H ₂ C(=O)--OOH	42.44	1.56	5.46	2
	C.H ₂ C(=O)O--OH	100.00	0.92	7.15	1
CC*O(Oj) ^e	CH ₃ --C(=O)O.	3.12	38.12	0.48	6
TYCOCDXOH	OH--CyCOC=O	0.98	61.8	1	2

^a n : foldness

^b "j" stands for radical site.

^c "Q" stands for hydroperoxy group(OOH).

^d "Qj" stands for peroxy (OO.).

^e "*" stands for double bonding(C=O).

Table 3.5 List of Total Energy, ZPVE, and Thermal Correction of CBSQ Calculation^a

Species	Total Energy at 0K ^b	ZPVE ^c	Thermal Correction ^d	Total Energy at 298K ^b
CH3CHO	-153.5808040	0.0596140	0.0047500	-153.5760540
CH3CjO ^e	-152.9409014	0.0463440	0.0048310	-152.9360704
CCOQ ^f	-303.8036387	0.0701660	0.0066110	-303.7970277
CCOQj ^g	-303.1591877	0.0569790	0.0059440	-303.1532437
CjCOQ	-303.1472163	0.0546810	0.0058250	-303.1413913
CH2CO	-152.3751740	0.0340450	0.0043090	-152.3708650
TCCOQjS	-303.1150471	0.0492970	0.0055420	-303.1095051
TCCOXQE	-303.1140266	0.0492960	0.0062490	-303.1077776
TCjCOXQ	-303.0980978	0.0511300	0.0069470	-303.0911508
CC*O(Oj) ^h	-228.0835228	0.0520300	0.0053120	-228.0782108
CyCOC=O	-227.5038475	0.0421240	0.0042990	-227.4995485
TYCOCDOXOH	-303.1112666	0.0480010	0.0066610	-303.1046056

^a Unit in Hartree 1 HF=627.51 kcal/mol.

^b Scaled ZPVE are included. Scaling factor is recommended as 0.91844 by Petersson et.al [22]

^c Non-scaled.

^d Non-scaled.

^e "j" stands for radical site.

^f "Q" stands for hydroperoxy group(OOH).

^g "Qj" stands for peroxy(OO.).

^h "*" stands for double bonding(C=O).

including scaled ZPVE's, nonscaled ZPVE's, thermal corrections to 298.15 K, and total energies at 298 K including scaled ZPVE's are shown in Table 3.5 for CBSQ calculations. Frequencies are scaled by 0.91844 for HF/6-31G(d') determined frequencies as recommended by Petersson et al.²²

Table 3.6 Molecule Considered to Have Known $\Delta H_f^\circ_{298}$ for Use in Isodesmic Reactions.

Compounds	$\Delta H_f^\circ_{298}$ (kcal/mole)
CH ₃ CH ₂ OH	-56.17 [30]
CH ₃ C(=O)OH	-103.56 (Avg. of [30],[31],[32])
CH ₃ CH ₂ OOH	-39.9 [33]

The evaluated enthalpies of formation for the molecules considered to have known $\Delta H_f^\circ_{298}$ values, for use in the isodesmic reaction, are : -56.17[30], -103.56[average of 30, 31, 32], and -39.9[33] for CH₃CH₂OH, CH₃C(=O)OH, and CH₃CH₂OOH, respectively. A low or zero $\Delta H^\circ_{\text{frxn},298}$ supports the hypothesis of group additivity and increases credibility of the calculations.

The CBSQ and density functionals determined enthalpy of reaction (1) is -2.59 and -3.88 kcal/mole, respectively. $\Delta H_f^\circ_{298}[\text{CCOQ}]$ is evaluated from

$$\begin{aligned} \Delta H^\circ_{\text{frxn},298} &= \Delta H_f^\circ_{298} [\text{CH}_3\text{C(=O)OH}] + \Delta H_f^\circ_{298} [\text{CH}_3\text{CH}_2\text{OOH}] \\ &\quad - \Delta H_f^\circ_{298} [\text{CCOQ}] - \Delta H_f^\circ_{298} [\text{CH}_3\text{CH}_2\text{OH}] = -2.59 \text{ or } -3.88 \\ &= -103.56 + (-39.9) - X - (-56.17) \text{ kcal/mole} \dots\dots\dots(4) \end{aligned}$$

The enthalpy of formation of CCOQ obtained is -84.7 and -83.41 kcal/mole in CBSQ and density functionals calculations, respectively.

The enthalpy of formation of two intermediate radicals, C_jCOQ and $CCOQ_j$ by CBSQ and density functionals are obtained from use of isodesmic reactions (2) and (3) and bond dissociation energy of C_2H_5-H (101.6 kcal/mole) and CH_3OO-H (86.3 kcal/mole). The data results in enthalpy values are -32.35 and -32.37 for C_jCOQ , -38.75 and -38.02 for $CCOQ_j$, in CBSQ and density functionals calculations, respectively.

Formation of $CCOQ_j$ adduct has a well depth of 36.55 kcal/mole.

The activation energy for isomerization, $TCCOQ_jS$, is estimated from both the reactant $CCOQ_j$ and the product C_jCOQ . The averaged result is 26.93 and 28.63 kcal/mole in CBSQ and density functionals, respectively. The activation energy for direct HO_2 elimination, $TCCOXQE$, is estimated by taking the difference of total energy with ZPVE and thermal correction between transition state(TS) and peroxy reactant, resulting in 28.01 and 30.66 kcal/mole in CBSQ and density functionals, respectively. The activation energy for HO_2 elimination from the hydroperoxide isomer, TC_jCOXQ , is estimated by taking the difference of total energy with ZPVE and thermal correction between transition state(TS) and reactant, resulting in 31.53 kcal/mole via CBSQ. The activation energy for epoxide formation via OH elimination, $TYCOCDOXOH$, is estimated by taking the difference of total energy with ZPVE and thermal correction between transition state(TS) and hydroperoxide isomer, resulting in 23.08 kcal/mole by CBSQ.

4.4 QRRK Calculation Results

QRRK calculations for $k(E)$ and modified strong collision analysis of Gilbert et. al¹⁷⁻¹⁹ for fall-off are performed on the $\text{CH}_3\text{CjO} + \text{O}_2$ reaction to obtain rate constants as a function of temperature and pressure and results are listed in Table 3.7. ΔE down of 400 cal/mole is used for bath gas N_2 .

Plots of rate constants at 1atm pressure versus $1000/T$ are illustrated in Figure 3.7.

Stabilization (CCOQj) is clearly important at lower temperatures, 1atm pressure, with reverse dissociation and ketene + HO_2 products via direct HO_2 elimination important at higher temperatures.

Plots of rate constants at 298 K versus pressure are illustrated in Figure 3.8.

The figure illustrates that stabilization is the dominant path at high pressures, while reverse dissociation and ketene + HO_2 products via direct HO_2 elimination channel are most important at low pressures.

Plots of rate constants at 1000 K versus pressure are illustrated in Figure 3.9.

The figure illustrates that stabilization decreases as pressure is decreased. Reverse dissociation and ketene + HO_2 products via direct HO_2 elimination are most important at both high and low pressures.

Table 3.7 Input Parameters^a and High-Pressure Limit Rate Constants (K_{∞})^b for QRRK Calculations^c and the Resulting Rate Constants (Temp=298K) : CBSQ Result (adjusted)

Input parameters for QRRK calculations			
High-pressure Limit Rate Constants			
Reaction	A[S ⁻¹ or cm ³ /(mole s)]	n	k_{∞}
			Ea (kcal/mole)
1 CH ₃ CjO + O ₂ => CCOQj ^d	2.65E+12	0.0	0.0
-1 CCOQj => CH ₃ CjO + O ₂ ^e	9.40E+13	0.0	34.66
2 CCOQj => CjCOQ ^f	1.52E+5	2.22	26.25
3 CCOQj => CH ₂ CO + HO ₂ ^f	9.29E+5	2.14	27.30
4 CjCOQ => CyCOC=O + OH ^f	8.13E+8	0.98	23.09
5 CjCOQ => CH ₂ CO + HO ₂ ^f	5.21E+10	0.81	31.77

Calculated Reaction Parameters at P = 1atm, $k=A(T/K)^n \exp(-Ea/RT)$ (T=298-2000K)

Reaction	A	n	Ea (kcal/mole)	$k_{298}(s^{-1}$ or cm ³ /(mole s)
1 CH ₃ CjO + O ₂ => CCOQj	6.93E+43	-10.29	8.28	2.03E+12
6 CH ₃ CjO + O ₂ => CH ₂ CO + HO ₂	3.65E+18	-1.78	6.29	3.51E+09
7 CH ₃ CjO + O ₂ => CyCOC=O + OH	2.09E+27	-4.45	13.44	2.83E+06
8 CH ₃ CjO + O ₂ => CjCOQ	8.42E+40	-9.17	12.47	1.23E+09
2 CCOQj => CjCOQ	2.61E+40	-9.10	36.50	1.00E-09
3 CCOQj => CH ₂ CO + HO ₂	1.07E+36	-7.53	35.97	1.00E-09
4 CjCOQ => CyCOC=O + OH	1.97E+31	-6.27	29.39	1.68E-08
5 CjCOQ => CH ₂ CO + HO ₂	4.18E+34	-7.11	37.76	2.16E-11

^aGeometric mean frequency (from CPFIT, Ref.[34]: 389.7 cm⁻¹(5.993); 1292.8 cm⁻¹ (7.788); 2889.0 cm⁻¹ (3.279). Lennard-Jones parameters: $\sigma_{ij}=5.19\text{\AA}$, $\epsilon/k=533.08$

^bThe units of A factors and rate constants k are s⁻¹ for unimolecular reactions and cm³/(mole s) for bimolecular reactions.

^c ΔE down of 400 cal/mole is used.

^d $k_{\infty,1}$: Sehested et al. [35]

^e $k_{\infty,-1}$: thermodynamics and microscopic reversibility <MR>

^fA is calculated using TST and entropy of transition state, ΔS^*_{298} from HF/6-31G(d') (see Table 3.3); Ea is from CBSQ calculation (see Table 3.3 and description for determination of Ea in Results section). All parameters A, n, Ea, are fit over the temperature range of 298-2000K.

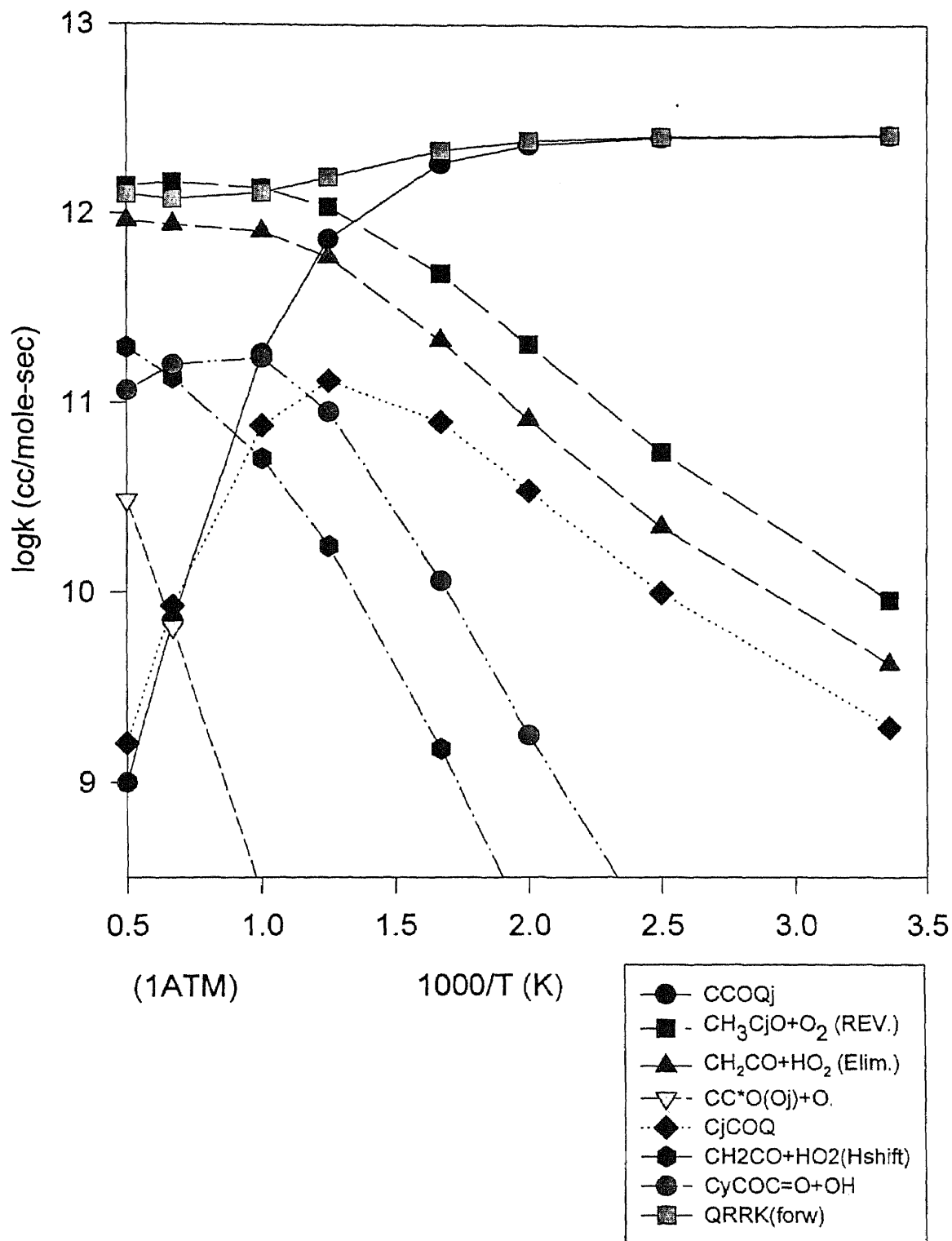


Figure 3.7 k vs. Temperature at 1atm CH₃C_jO + O₂

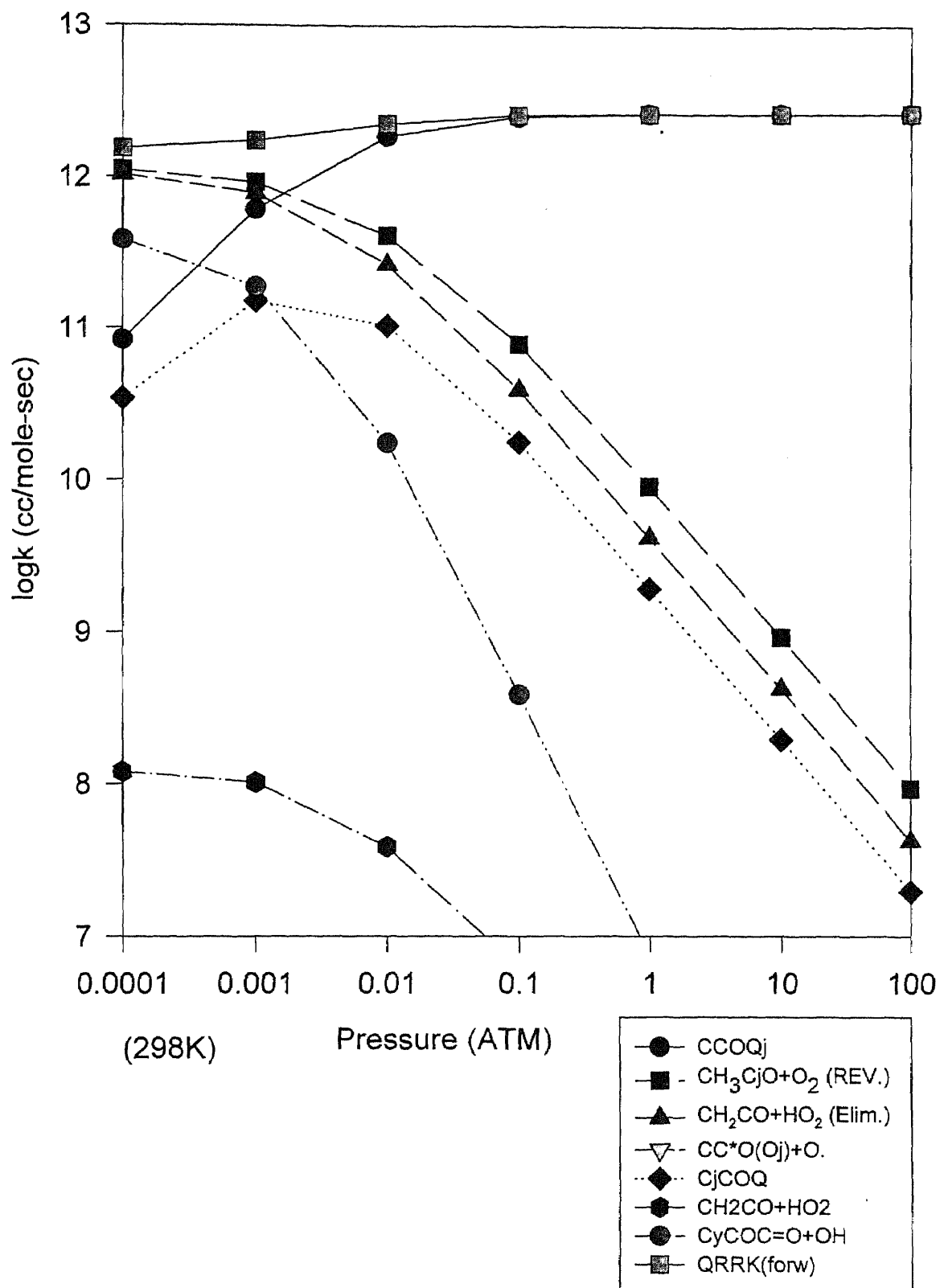


Figure 3.8 k vs. Pressure at 298K $\text{CH}_3\text{CjO} + \text{O}_2$

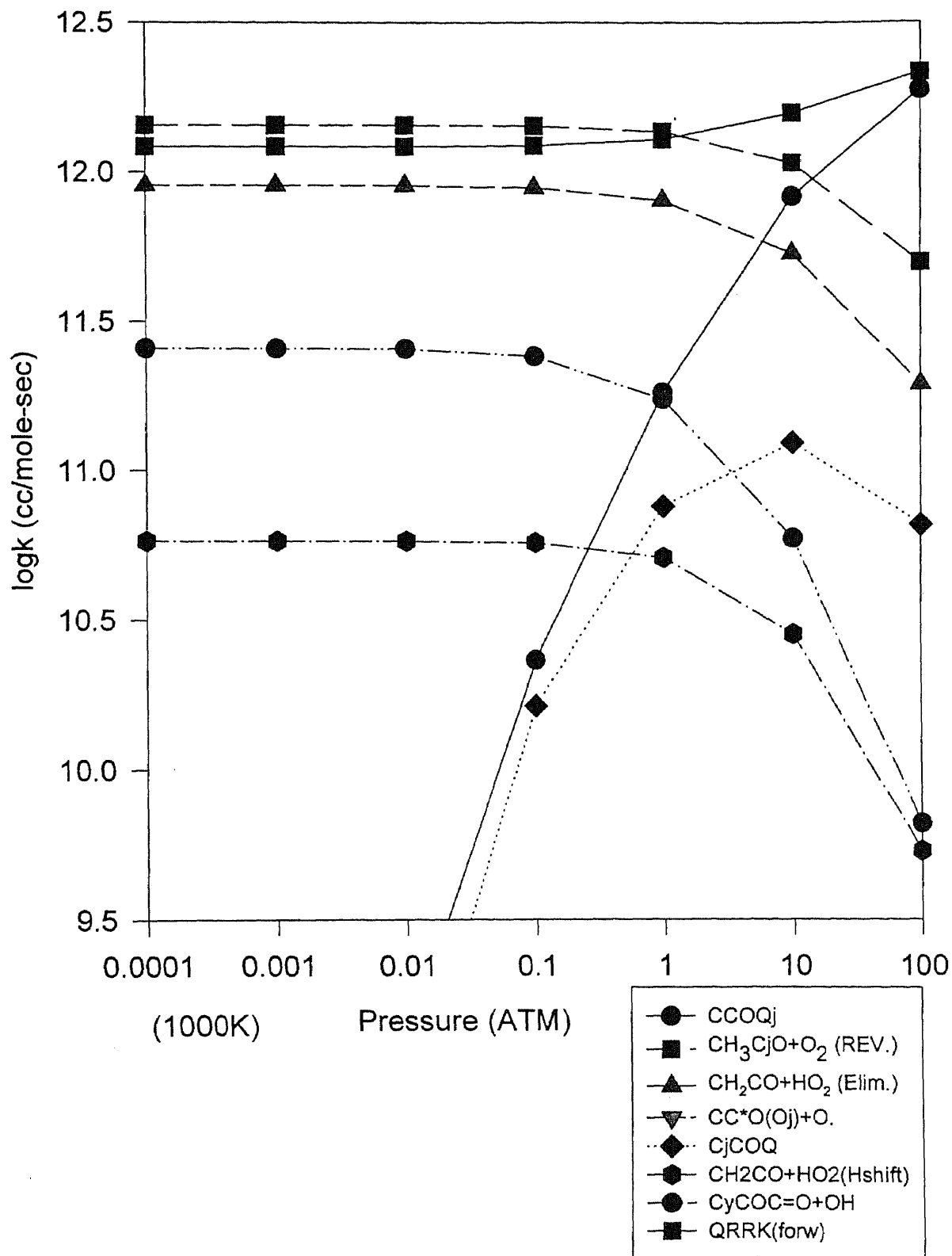


Figure 3.9 k vs. Pressure at 1000K CH₃C_jO + O₂

CHAPTER 5

SUMMARY FOR PART THREE

Thermodynamic properties of stable radicals and transition states on $\text{CH}_3\text{CjO} + \text{O}_2$ reaction system are calculated using density functional and *ab initio* methods.

Enthalpies of formation ($\Delta H_f^\circ_{298}$) are determined using the CBSQ composite method and density functional calculations with isodesmic reactions. Entropies (S°_{298}) and heat capacities ($C_p(T)$ 300 –1500 K) are determined using geometric parameters and vibrational frequencies obtained at the HF/6-31G(d') level of theory.

Reaction pathways and kinetics are analyzed on $\text{CH}_3\text{CjO} + \text{O}_2$ reaction system using QRRK for $k(E)$ and modified strong collision analysis of Gilbert et. al¹⁷⁻¹⁹ for fall-off.

Major reaction paths at 1atm pressure are stabilization of CCOQj peroxy adduct at low temperature and $\text{CH}_2\text{CO} + \text{HO}_2$ via HO_2 elimination and $\text{CyCOC=O} + \text{OH}$ via OH elimination at high temperature.

APPENDIX 3.1

THERMODYNAMIC ANALYSIS FOR CH₃CJO + O₂ REACTION

THERMODYNAMIC ANALYSIS for REACTION

Rx CH3CJO + O2 = CCOQJ
Hf {Kcal/mol} -2.200 .000 -38.750
S {cal/mol K} 64.060 46.630 79.550

dHr {kcal/mol} (298K) = -36.55 dHr avg (298., 1500. K) = -36.45
dU (dE) {kcal/mol} (") = -35.96 dUr avg (298., 1500. K) = -34.66
dSr {cal/mol K} (") = -31.14 dSr avg (298., 1500. K) = -31.35
dGr {kcal/mol} (") = -27.27 dGr avg (298., 1500. K) = -8.26
Af/Ar (") = 1.039E-02 Af/Ar avg (298., 1500. K) = 2.823E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-3.655E+01	-3.596E+01	-3.116E+01	1.037E-02	-2.721E+01
400.00	-3.675E+01	-3.596E+01	-3.174E+01	1.032E-02	-2.406E+01
500.00	-3.686E+01	-3.587E+01	-3.198E+01	1.140E-02	-2.087E+01
600.00	-3.691E+01	-3.572E+01	-3.207E+01	1.313E-02	-1.767E+01
800.00	-3.687E+01	-3.528E+01	-3.202E+01	1.793E-02	-1.126E+01
1000.00	-3.675E+01	-3.476E+01	-3.188E+01	2.398E-02	-4.867E+00
1200.00	-3.660E+01	-3.421E+01	-3.174E+01	3.088E-02	1.496E+00
1500.00	-3.634E+01	-3.336E+01	-3.155E+01	4.244E-02	1.099E+01
2000.00	-3.591E+01	-3.193E+01	-3.130E+01	6.415E-02	2.670E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx CCOQJ = CC*O(OJ) + O
Hf {Kcal/mol} -38.750 -41.590 59.560
S {cal/mol K} 79.550 68.420 38.470

dHr {kcal/mol} (298K) = 56.72 dHr avg (298., 1500. K) = 56.45
dU (dE) {kcal/mol} (") = 56.13 dUr avg (298., 1500. K) = 54.66
dSr {cal/mol K} (") = 27.34 dSr avg (298., 1500. K) = 27.12
dGr {kcal/mol} (") = 48.57 dGr avg (298., 1500. K) = 32.07
Af/Ar (") = 1.422E+01 Af/Ar avg (298., 1500. K) = 4.217E+00

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	5.672E+01	5.613E+01	2.735E+01	1.417E+01	4.852E+01
400.00	5.677E+01	5.598E+01	2.750E+01	1.150E+01	4.577E+01
500.00	5.678E+01	5.579E+01	2.752E+01	9.278E+00	4.302E+01
600.00	5.676E+01	5.556E+01	2.747E+01	7.556E+00	4.027E+01
800.00	5.665E+01	5.506E+01	2.732E+01	5.246E+00	3.479E+01
1000.00	5.651E+01	5.452E+01	2.717E+01	3.882E+00	2.934E+01
1200.00	5.637E+01	5.399E+01	2.704E+01	3.034E+00	2.392E+01
1500.00	5.618E+01	5.320E+01	2.690E+01	2.261E+00	1.584E+01
2000.00	5.594E+01	5.197E+01	2.676E+01	1.580E+00	2.426E+00

APPENDIX 3.2

KINETIC ANALYSIS FOR CH₃CjO + O₂ REACTION

THERMODYNAMIC ANALYSIS for REACTION

Rx CCOQJ = TCCOQJS

Hf {Kcal/mol} -38.750 -11.820

S {cal/mol K} 79.550 72.150

dHr {kcal/mol} (298K) = 26.93 dHr avg (298., 1500. K) = 28.29

dU (dE) {kcal/mol} (") = 26.93 dUr avg (298., 1500. K) = 28.29

dSr {cal/mol K} (") = -7.40 dSr avg (298., 1500. K) = -5.46

dGr {kcal/mol} (") = 29.14 dGr avg (298., 1500. K) = 33.20

Af/Ar (") = 2.413E-02 Af/Ar avg (298., 1500. K) = 6.417E-02

Fit Af/Ar : A = 1.711E-06 n = 1.70 alpha = 6.111E-04 avg error 3.13 %

Fit Af/Ar w/ddU: A = 7.988E-10 n = 3.10 alpha = 1.720E-03 avg error 2.94 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.693E+01	2.693E+01	-7.388E+00	2.428E-02	2.915E+01
400.00	2.717E+01	2.717E+01	-6.726E+00	3.388E-02	2.986E+01
500.00	2.744E+01	2.744E+01	-6.119E+00	4.598E-02	3.050E+01
600.00	2.773E+01	2.773E+01	-5.592E+00	5.996E-02	3.108E+01
800.00	2.829E+01	2.829E+01	-4.779E+00	9.027E-02	3.211E+01
1000.00	2.878E+01	2.878E+01	-4.231E+00	1.189E-01	3.301E+01
1200.00	2.918E+01	2.918E+01	-3.865E+00	1.429E-01	3.382E+01
1500.00	2.965E+01	2.965E+01	-3.513E+00	1.706E-01	3.492E+01
2000.00	3.016E+01	3.016E+01	-3.216E+00	1.982E-01	3.659E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{prime} * T^n * \exp(-E_a/RT)$

$A_{prime} = 1.5209E+05$ $n = 2.21722$ $E_a = 2.6246E+04$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.518E+11	3.107E+05	3.618E-09	3.570E-09
400.00	2.824E+11	5.879E+05	4.048E-04	4.075E-04
500.00	4.791E+11	9.643E+05	4.858E-01	4.935E-01
600.00	7.496E+11	1.445E+06	5.949E+01	6.040E+01
800.00	1.505E+12	2.734E+06	2.806E+04	2.807E+04
1000.00	2.478E+12	4.484E+06	1.270E+06	1.251E+06
1200.00	3.574E+12	6.718E+06	1.731E+07	1.694E+07
1500.00	5.333E+12	1.102E+07	2.550E+08	2.511E+08
2000.00	8.260E+12	2.085E+07	4.178E+09	4.295E+09

THERMODYNAMIC ANALYSIS for REACTION

Rx CJCOQ = TCCOQS

Hf {Kcal/mol} -32.350 -11.820

S {cal/mol K} 84.120 72.150

dHr {kcal/mol} (298K) = 20.53 dHr avg (298., 1500. K) = 21.74

dU (dE) {kcal/mol} (") = 20.53 dUr avg (298., 1500. K) = 21.74

dSr {cal/mol K} (") = -11.97 dSr avg (298., 1500. K) = -10.61

dGr {kcal/mol} (") = 24.10 dGr avg (298., 1500. K) = 31.28

Af/Ar (") = 2.420E-03 Af/Ar avg (298., 1500. K) = 4.794E-03

Fit Af/Ar : A = 1.553E-04 n = .43 alpha = -6.148E-04 avg error 7.45 %

Fit Af/Ar w/ddU: A = 4.668E-06 n = 1.03 alpha = -5.410E-04 avg error 13.51 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.053E+01	2.053E+01	-1.197E+01	2.416E-03	2.412E+01
400.00	2.054E+01	2.054E+01	-1.195E+01	2.441E-03	2.532E+01
500.00	2.064E+01	2.064E+01	-1.173E+01	2.733E-03	2.650E+01
600.00	2.081E+01	2.081E+01	-1.143E+01	3.182E-03	2.766E+01
800.00	2.125E+01	2.125E+01	-1.079E+01	4.381E-03	2.988E+01
1000.00	2.175E+01	2.175E+01	-1.023E+01	5.804E-03	3.198E+01
1200.00	2.225E+01	2.225E+01	-9.776E+00	7.300E-03	3.398E+01
1500.00	2.296E+01	2.296E+01	-9.252E+00	9.500E-03	3.683E+01
2000.00	2.394E+01	2.394E+01	-8.683E+00	1.265E-02	4.130E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$ A_{prime} = 3.8474E+04 n = 2.01928 E_a = 1.9703E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.510E+10	1.005E+05	1.669E-05	1.708E-05
400.00	2.034E+10	1.796E+05	1.218E-01	1.184E-01
500.00	2.847E+10	2.818E+05	2.701E+01	2.645E+01
600.00	3.978E+10	4.073E+05	1.047E+03	1.042E+03
800.00	7.302E+10	7.280E+05	1.141E+05	1.160E+05
1000.00	1.209E+11	1.142E+06	2.128E+06	2.171E+06
1200.00	1.825E+11	1.651E+06	1.615E+07	1.638E+07
1500.00	2.969E+11	2.591E+06	1.342E+08	1.342E+08
2000.00	5.272E+11	4.631E+06	1.276E+09	1.252E+09

THERMODYNAMIC ANALYSIS for REACTION

Rx CCOQJ = TCCOXQE
 Hf {Kcal/mol} -38.750 -10.740
 S {cal/mol K} 79.550 74.970

dHr {kcal/mol} (298K) = 28.01 dHr avg (298., 1500. K) = 29.39
 dU (dE) {kcal/mol} (") = 28.01 dUr avg (298., 1500. K) = 29.39
 dSr {cal/mol K} (") = -4.58 dSr avg (298., 1500. K) = -2.77
 dGr {kcal/mol} (") = 29.38 dGr avg (298., 1500. K) = 31.88
 Af/Ar (") = 9.976E-02 Af/Ar avg (298., 1500. K) = 2.478E-01
 Fit Af/Ar : A = 2.310E-04 n = 1.06 alpha = -8.875E-05 avg error 1.41 %
 Fit Af/Ar w/ddU: A = 1.484E-06 n = 1.97 alpha = 3.886E-04 avg error 1.27 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.801E+01	2.801E+01	-4.567E+00	1.004E-01	2.938E+01
400.00	2.822E+01	2.822E+01	-3.971E+00	1.355E-01	2.981E+01
500.00	2.843E+01	2.843E+01	-3.511E+00	1.708E-01	3.018E+01
600.00	2.864E+01	2.864E+01	-3.125E+00	2.075E-01	3.051E+01
800.00	2.909E+01	2.909E+01	-2.474E+00	2.879E-01	3.107E+01
1000.00	2.958E+01	2.958E+01	-1.932E+00	3.782E-01	3.151E+01
1200.00	3.007E+01	3.007E+01	-1.482E+00	4.742E-01	3.185E+01
1500.00	3.077E+01	3.077E+01	-9.647E-01	6.154E-01	3.221E+01
2000.00	3.184E+01	3.184E+01	-3.463E-01	8.401E-01	3.253E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$
 $A_{\text{prime}} = 9.2883E+05$ $n = 2.14429$ $E_a = 2.7300E+04$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	6.277E+11	2.050E+05	2.443E-09	2.455E-09
400.00	1.130E+12	3.798E+05	4.290E-04	4.269E-04
500.00	1.780E+12	6.129E+05	6.666E-01	6.631E-01
600.00	2.594E+12	9.061E+05	9.579E+01	9.557E+01
800.00	4.799E+12	1.679E+06	5.405E+04	5.425E+04
1000.00	7.881E+12	2.709E+06	2.701E+06	2.716E+06
1200.00	1.186E+13	4.006E+06	3.951E+07	3.965E+07
1500.00	1.923E+13	6.464E+06	6.324E+08	6.317E+08
2000.00	3.501E+13	1.198E+07	1.160E+10	1.156E+10

THERMODYNAMIC ANALYSIS for REACTION

Rx CJCOQ = TCJCOXQ
 Hf {Kcal/mol} -32.350 -820
 S {cal/mol K} 84.120 82.960

dHr {kcal/mol} (298K) = 31.53 dHr avg (298., 1500. K) = 31.28
 dU (dE) {kcal/mol} (") = 31.53 dUr avg (298., 1500. K) = 31.28
 dSr {cal/mol K} (") = -1.16 dSr avg (298., 1500. K) = -1.33
 dGr {kcal/mol} (") = 31.88 dGr avg (298., 1500. K) = 32.47
 Af/Ar (") = 5.578E-01 Af/Ar avg (298., 1500. K) = 5.127E-01
 Fit Af/Ar : A = 1.473E-01 n = .27 alpha = 5.187E-04 avg error 2.71 %
 Fit Af/Ar w/ddU: A = 9.832E-02 n = .36 alpha = 8.149E-04 avg error 5.71 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	3.153E+01	3.153E+01	-1.155E+00	5.592E-01	3.188E+01
400.00	3.159E+01	3.159E+01	-9.790E-01	6.110E-01	3.198E+01
500.00	3.161E+01	3.161E+01	-9.297E-01	6.263E-01	3.208E+01
600.00	3.161E+01	3.161E+01	-9.430E-01	6.222E-01	3.217E+01
800.00	3.153E+01	3.153E+01	-1.048E+00	5.903E-01	3.237E+01
1000.00	3.141E+01	3.141E+01	-1.181E+00	5.518E-01	3.259E+01
1200.00	3.127E+01	3.127E+01	-1.314E+00	5.163E-01	3.284E+01
1500.00	3.102E+01	3.102E+01	-1.495E+00	4.712E-01	3.326E+01
2000.00	3.059E+01	3.059E+01	-1.745E+00	4.156E-01	3.408E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$
 $A_{\text{prime}} = 5.2099E+10$ $n = .80559$ $E_a = 3.1773E+04$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	3.496E+12	9.898E+01	3.723E-11	3.664E-11
400.00	5.092E+12	1.248E+02	2.784E-05	2.830E-05
500.00	6.525E+12	1.494E+02	9.894E-02	1.005E-01
600.00	7.778E+12	1.730E+02	2.386E+01	2.403E+01
800.00	9.839E+12	2.181E+02	2.390E+04	2.371E+04
1000.00	1.150E+13	2.611E+02	1.568E+06	1.546E+06
1200.00	1.291E+13	3.024E+02	2.608E+07	2.572E+07
1500.00	1.473E+13	3.619E+02	4.447E+08	4.424E+08
2000.00	1.732E+13	4.563E+02	7.868E+09	8.014E+09

THERMODYNAMIC ANALYSIS for REACTION

Rx CJCOQ = TYCOCDOXO

Hf {Kcal/mol} -32.350 -9.270

S {cal/mol K} 84.120 77.390

dHr {kcal/mol} (298K) = 23.08 dHr avg (298., 1500. K) = 23.05

dU (dE) {kcal/mol} (") = 23.08 dUr avg (298., 1500. K) = 23.05

dSr {cal/mol K} (") = -6.73 dSr avg (298., 1500. K) = -6.77

dGr {kcal/mol} (") = 25.09 dGr avg (298., 1500. K) = 29.14

Af/Ar (") = 3.381E-02 Af/Ar avg (298., 1500. K) = 3.308E-02

Fit Af/Ar : A = 3.270E-02 n = .01 alpha = 4.184E-05 avg error .61 %

Fit Af/Ar w/ddU: A = 3.015E-02 n = .02 alpha = 7.455E-05 avg error 1.19 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.308E+01	2.308E+01	-6.731E+00	3.380E-02	2.510E+01
400.00	2.307E+01	2.307E+01	-6.762E+00	3.327E-02	2.577E+01
500.00	2.306E+01	2.306E+01	-6.775E+00	3.304E-02	2.645E+01
600.00	2.306E+01	2.306E+01	-6.781E+00	3.295E-02	2.713E+01
800.00	2.306E+01	2.306E+01	-6.783E+00	3.292E-02	2.849E+01
1000.00	2.306E+01	2.306E+01	-6.785E+00	3.288E-02	2.984E+01
1200.00	2.305E+01	2.305E+01	-6.793E+00	3.276E-02	3.120E+01
1500.00	2.302E+01	2.302E+01	-6.817E+00	3.236E-02	3.324E+01
2000.00	2.290E+01	2.290E+01	-6.882E+00	3.132E-02	3.666E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$ A_{prime} = 8.1299E+08 n = .97757 E_a = 2.3089E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.113E+11	2.640E+02	3.235E-06	3.234E-06
400.00	2.773E+11	3.497E+02	6.879E-02	6.876E-02
500.00	3.443E+11	4.349E+02	2.852E+01	2.853E+01
600.00	4.120E+11	5.198E+02	1.639E+03	1.640E+03
800.00	5.487E+11	6.886E+02	2.751E+05	2.753E+05
1000.00	6.851E+11	8.565E+02	6.256E+06	6.255E+06
1200.00	8.190E+11	1.024E+03	5.192E+07	5.185E+07
1500.00	1.012E+12	1.273E+03	4.481E+08	4.473E+08
2000.00	1.305E+12	1.687E+03	4.102E+09	4.110E+09

APPENDIX 3.3

KINETIC DATA FOR $\text{CH}_3\text{CjO} + \text{O}_2$ REACTIONS ARRHENIUS FORM

Chemical Activation CH₃CjO + O₂

CH3CO+O2	<=>	CCOQJ	4.57E+36	-9.52	2923.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	13% err,	1.00 x N2
CH3CO+O2	<=>	CCOQJ	3.85E+38	-9.79	3460.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	15% err,	1.00 x N2
CH3CO+O2	<=>	CCOQJ	3.13E+42	-10.62	5330.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	19% err,	1.00 x N2
CH3CO+O2	<=>	CCOQJ	3.61E+45	-11.16	7568.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	17% err,	1.00 x N2
CH3CO+O2	<=>	CCOQJ	6.93E+43	-10.29	8278.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	24% err,	1.00 x N2
CH3CO+O2	<=>	CCOQJ	2.06E+37	-8.02	7092.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	35% err,	1.00 x N2
CH3CO+O2	<=>	CCOQJ	2.53E+28	-5.10	4760.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	32% err,	1.00 x N2
CH3CO+O2	<=>	CH3CO+O2	2.10E+12	-.04	254.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	3% err,	1.00 x N2
CH3CO+O2	<=>	CH3CO+O2	8.45E+12	-.22	590.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	1% err,	1.00 x N2
CH3CO+O2	<=>	CH3CO+O2	2.04E+15	-.90	1977.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	4% err,	1.00 x N2
CH3CO+O2	<=>	CH3CO+O2	8.76E+18	-1.92	4461.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	6% err,	1.00 x N2
CH3CO+O2	<=>	CH3CO+O2	2.30E+20	-2.27	6608.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	11% err,	1.00 x N2
CH3CO+O2	<=>	CH3CO+O2	8.34E+16	-1.18	7088.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	36% err,	1.00 x N2
CH3CO+O2	<=>	CH3CO+O2	8.02E+08	1.24	5735.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	60% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	1.52E+12	-.07	-38.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	3% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	1.09E+13	-.32	449.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	5% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	8.79E+15	-1.15	2232.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	10% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	1.05E+19	-2.00	4747.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	8% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	3.65E+18	-1.78	6293.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	18% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	1.82E+13	-.15	6053.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	44% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	1.49E+04	2.57	4223.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	60% err,	1.00 x N2
CH3CO+O2	<=>	CC*OOJ+O.	9.55E+12	-.04	20844.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	45% err,	1.00 x N2
CH3CO+O2	<=>	CC*OOJ+O.	9.57E+12	-.04	20845.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	45% err,	1.00 x N2
CH3CO+O2	<=>	CC*OOJ+O.	9.80E+12	-.04	20852.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	45% err,	1.00 x N2
CH3CO+O2	<=>	CC*OOJ+O.	1.23E+13	-.07	20916.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	45% err,	1.00 x N2
CH3CO+O2	<=>	CC*OOJ+O.	7.07E+13	-.28	21429.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	45% err,	1.00 x N2
CH3CO+O2	<=>	CC*OOJ+O.	4.53E+15	-.77	23096.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	56% err,	1.00 x N2
CH3CO+O2	<=>	CC*OOJ+O.	3.77E+13	-.09	23979.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	91% err,	1.00 x N2
CH3CO+O2	<=>	CJCOQ	2.46E+33	-8.48	2472.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	18% err,	1.00 x N2
CH3CO+O2	<=>	CJCOQ	5.33E+36	-9.15	3859.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	23% err,	1.00 x N2
CH3CO+O2	<=>	CJCOQ	2.50E+43	-10.75	7786.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	28% err,	1.00 x N2
CH3CO+O2	<=>	CJCOQ	3.80E+46	-11.26	11605.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	20% err,	1.00 x N2
CH3CO+O2	<=>	CJCOQ	8.42E+40	-9.17	12465.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	43% err,	1.00 x N2
CH3CO+O2	<=>	CJCOQ	6.51E+27	-4.95	10292.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	78% err,	1.00 x N2
CH3CO+O2	<=>	CJCOQ	3.75E+11	.08	6449.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	85% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	2.78E+11	.13	5058.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	5% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	8.52E+11	-.01	5335.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	4% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	5.22E+14	-.81	6982.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	2% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	3.01E+20	-2.43	10960.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	6% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	2.16E+23	-3.14	15002.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	23% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	2.79E+17	-1.26	16212.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	77% err,	1.00 x N2
CH3CO+O2	<=>	CH2CO+HO2	6.55E+02	3.13	13930.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	137% err,	1.00 x N2
CH3CO+O2	<=>	OCYCO+OH	1.26E+16	-1.48	1158.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	2% err,	1.00 x N2
CH3CO+O2	<=>	OCYCO+OH	1.79E+18	-2.10	2400.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	4% err,	1.00 x N2
CH3CO+O2	<=>	OCYCO+OH	1.33E+24	-3.77	6154.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	11% err,	1.00 x N2
CH3CO+O2	<=>	OCYCO+OH	1.25E+29	-5.12	10758.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	12% err,	1.00 x N2

CH3CO+O2	<=>	OCYCO+OH	2.09E+27	-4.45	13442.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	46% err,	1.00 x N2
CH3CO+O2	<=>	OCYCO+OH	7.34E+16	-1.24	12904.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	108% err,	1.00 x N2
CH3CO+O2	<=>	OCYCO+OH	1.57E+00	3.71	9664.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	151% err,	1.00 x N2

Dissociation

CCOQJ	<=>	CH3CO+O2	7.32E+38	-9.73	37889.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	15% err,	1.00 x N2
CCOQJ	<=>	CH3CO+O2	5.72E+40	-9.99	38408.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	17% err,	1.00 x N2
CCOQJ	<=>	CH3CO+O2	4.19E+44	-10.80	40248.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	21% err,	1.00 x N2
CCOQJ	<=>	CH3CO+O2	4.84E+47	-11.35	42481.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	19% err,	1.00 x N2
CCOQJ	<=>	CH3CO+O2	9.49E+45	-10.47	43193.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	24% err,	1.00 x N2
CCOQJ	<=>	CH3CO+O2	2.85E+39	-8.21	42008.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	33% err,	1.00 x N2
CCOQJ	<=>	CH3CO+O2	3.50E+30	-5.29	39676.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	30% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	3.02E+45	-11.70	34786.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	16% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	4.69E+47	-11.99	36613.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	16% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	1.57E+47	-11.50	37697.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	21% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	1.30E+43	-9.94	37458.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	32% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	1.07E+36	-7.53	35972.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	42% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	2.56E+27	-4.71	33715.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	41% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	8.21E+18	-1.98	31283.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	29% err,	1.00 x N2
CCOQJ	<=>	CC*OOJ+O.	3.03E+26	-6.06	57367.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	40% err,	1.00 x N2
CCOQJ	<=>	CC*OOJ+O.	3.04E+27	-6.06	57368.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	40% err,	1.00 x N2
CCOQJ	<=>	CC*OOJ+O.	3.11E+28	-6.07	57374.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	40% err,	1.00 x N2
CCOQJ	<=>	CC*OOJ+O.	3.84E+29	-6.09	57436.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	40% err,	1.00 x N2
CCOQJ	<=>	CC*OOJ+O.	1.93E+31	-6.29	57925.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	40% err,	1.00 x N2
CCOQJ	<=>	CC*OOJ+O.	5.79E+33	-6.68	59462.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	50% err,	1.00 x N2
CCOQJ	<=>	CC*OOJ+O.	7.71E+31	-5.77	60018.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	76% err,	1.00 x N2
CCOQJ	<=>	CJCOQ	1.05E+57	-15.58	37127.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	13% err,	1.00 x N2
CCOQJ	<=>	CJCOQ	4.20E+58	-15.66	39020.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	17% err,	1.00 x N2
CCOQJ	<=>	CJCOQ	3.69E+55	-14.34	39378.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	29% err,	1.00 x N2
CCOQJ	<=>	CJCOQ	3.08E+49	-12.15	38558.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	46% err,	1.00 x N2
CCOQJ	<=>	CJCOQ	2.61E+40	-9.10	36498.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	58% err,	1.00 x N2
CCOQJ	<=>	CJCOQ	6.24E+29	-5.63	33648.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	53% err,	1.00 x N2
CCOQJ	<=>	CJCOQ	5.33E+19	-2.40	30739.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	35% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	8.71E+32	-8.02	42632.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	11% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	3.14E+34	-8.18	42959.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	11% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	3.28E+38	-9.04	44828.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	15% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	2.52E+44	-10.39	48777.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	18% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	2.34E+44	-9.95	51548.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	34% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	5.07E+34	-6.70	50827.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	73% err,	1.00 x N2
CCOQJ	<=>	CH2CO+HO2	1.66E+19	-1.85	47457.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	93% err,	1.00 x N2
CCOQJ	<=>	OCYCO+OH	7.42E+45	-11.96	36987.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	19% err,	1.00 x N2
CCOQJ	<=>	OCYCO+OH	1.01E+52	-13.39	40909.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	21% err,	1.00 x N2
CCOQJ	<=>	OCYCO+OH	1.20E+55	-13.87	44624.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	21% err,	1.00 x N2
CCOQJ	<=>	OCYCO+OH	2.14E+51	-12.35	46148.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	45% err,	1.00 x N2
CCOQJ	<=>	OCYCO+OH	7.01E+40	-8.89	45045.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	84% err,	1.00 x N2
CCOQJ	<=>	OCYCO+OH	1.61E+26	-4.28	42025.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	113% err,	1.00 x N2
CCOQJ	<=>	OCYCO+OH	3.68E+10	.50	38140.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	106% err,	1.00 x N2

CJCOQ	<=>	CCOQJ	1.32E+57	-16.22	30001.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	17% err,	1.00 x N2
CJCOQ	<=>	CCOQJ	7.20E+59	-16.61	32351.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	16% err,	1.00 x N2
CJCOQ	<=>	CCOQJ	1.23E+57	-15.33	32965.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	25% err,	1.00 x N2
CJCOQ	<=>	CCOQJ	4.92E+50	-13.00	32199.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	43% err,	1.00 x N2
CJCOQ	<=>	CCOQJ	1.03E+41	-9.73	30078.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	56% err,	1.00 x N2
CJCOQ	<=>	CCOQJ	4.20E+29	-6.00	27076.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	53% err,	1.00 x N2
CJCOQ	<=>	CCOQJ	9.32E+18	-2.58	24025.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	36% err,	1.00 x N2
CJCOQ	<=>	CH3CO+O2	3.15E+34	-8.78	30087.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	23% err,	1.00 x N2
CJCOQ	<=>	CH3CO+O2	5.71E+37	-9.43	31424.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	29% err,	1.00 x N2
CJCOQ	<=>	CH3CO+O2	2.60E+44	-11.02	35301.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	34% err,	1.00 x N2
CJCOQ	<=>	CH3CO+O2	8.76E+47	-11.64	39219.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	22% err,	1.00 x N2
CJCOQ	<=>	CH3CO+O2	5.99E+42	-9.69	40265.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	37% err,	1.00 x N2
CJCOQ	<=>	CH3CO+O2	8.33E+29	-5.54	38210.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	69% err,	1.00 x N2
CJCOQ	<=>	CH3CO+O2	5.13E+13	-.51	34401.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	77% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	7.53E+46	-12.34	30200.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	28% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	1.33E+49	-12.60	33278.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	19% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	2.09E+48	-11.97	35644.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	18% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	2.85E+42	-9.85	36297.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	41% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	1.10E+31	-6.14	34752.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	75% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	1.30E+16	-1.46	31555.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	97% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	2.52E+00	3.33	27616.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	89% err,	1.00 x N2
CJCOQ	<=>	CC*OOJ+O.	3.79E+22	-5.37	49300.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	22% err,	1.00 x N2
CJCOQ	<=>	CC*OOJ+O.	3.89E+23	-5.38	49307.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	22% err,	1.00 x N2
CJCOQ	<=>	CC*OOJ+O.	5.03E+24	-5.41	49373.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	22% err,	1.00 x N2
CJCOQ	<=>	CC*OOJ+O.	4.08E+26	-5.67	49925.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	24% err,	1.00 x N2
CJCOQ	<=>	CC*OOJ+O.	7.63E+30	-6.59	52203.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	27% err,	1.00 x N2
CJCOQ	<=>	CC*OOJ+O.	4.08E+33	-6.99	55300.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	17% err,	1.00 x N2
CJCOQ	<=>	CC*OOJ+O.	4.32E+26	-4.53	55490.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	32% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	1.12E+27	-6.21	32810.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	21% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	2.88E+28	-6.32	33048.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	22% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	3.87E+31	-6.93	34351.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	27% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	2.50E+35	-7.70	36706.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	23% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	4.18E+34	-7.11	37759.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	15% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	2.91E+28	-4.95	36702.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	21% err,	1.00 x N2
CJCOQ	<=>	CH2CO+HO2	1.88E+20	-2.27	34547.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	18% err,	1.00 x N2
CJCOQ	<=>	OCYCO+OH	5.56E+36	-9.27	26773.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	32% err,	1.00 x N2
CJCOQ	<=>	OCYCO+OH	2.34E+40	-9.99	29023.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	28% err,	1.00 x N2
CJCOQ	<=>	OCYCO+OH	1.38E+41	-9.85	30565.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	18% err,	1.00 x N2
CJCOQ	<=>	OCYCO+OH	7.67E+37	-8.54	30670.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	18% err,	1.00 x N2
CJCOQ	<=>	OCYCO+OH	1.97E+31	-6.27	29392.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	26% err,	1.00 x N2
CJCOQ	<=>	OCYCO+OH	1.65E+23	-3.62	27305.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	26% err,	1.00 x N2
CJCOQ	<=>	OCYCO+OH	8.08E+15	-1.27	25205.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	16% err,	1.00 x N2

APPENDIX 3.4

LOG RATE CONSTANTS VS PRESSURE AND TEMPERATURE FOR $\text{CH}_3\text{CjO} + \text{O}_2$ REACTION

Chemical Activation Reaction (CH₃CjO + O₂) Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	10.923	12.046	12.015	-2.203	10.537	8.081	11.585	12.187
1.00E-04	400.	2.50E+00	10.281	12.062	12.027	1.201	10.009	8.997	11.603	12.175
1.00E-04	500.	2.00E+00	9.709	12.089	12.013	3.545	9.492	9.559	11.579	12.153
1.00E-04	600.	1.67E+00	9.183	12.112	11.997	5.441	8.994	9.950	11.548	12.133
1.00E-04	800.	1.25E+00	8.230	12.140	11.972	7.328	8.073	10.458	11.482	12.103
1.00E-04	1000.	1.00E+00	7.387	12.156	11.955	8.412	7.297	10.764	11.409	12.085
1.00E-04	1500.	6.67E-01	5.861	12.166	11.943	9.817	6.009	11.137	11.218	12.074
1.00E-04	2000.	5.00E-01	5.002	12.144	11.961	10.487	5.233	11.294	11.068	12.100
P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	11.786	11.964	11.893	-2.203	11.176	8.012	11.272	12.238
1.00E-03	400.	2.50E+00	11.237	12.043	11.991	1.200	10.875	8.977	11.501	12.189
1.00E-03	500.	2.00E+00	10.693	12.084	12.002	3.545	10.441	9.553	11.545	12.157
1.00E-03	600.	1.67E+00	10.177	12.110	11.993	5.441	9.974	9.948	11.536	12.134
1.00E-03	800.	1.25E+00	9.229	12.140	11.971	7.328	9.069	10.458	11.480	12.104
1.00E-03	1000.	1.00E+00	8.387	12.156	11.955	8.412	8.296	10.764	11.408	12.085
1.00E-03	1500.	6.67E-01	6.861	12.166	11.943	9.817	7.008	11.137	11.218	12.074
1.00E-03	2000.	5.00E-01	6.002	12.144	11.961	10.487	6.233	11.294	11.068	12.100
P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	12.268	11.613	11.422	-2.205	11.016	7.588	10.242	12.350
1.00E-02	400.	2.50E+00	11.979	11.919	11.781	1.200	11.221	8.818	10.986	12.260
1.00E-02	500.	2.00E+00	11.577	12.043	11.919	3.544	11.106	9.495	11.317	12.189
1.00E-02	600.	1.67E+00	11.126	12.097	11.962	5.441	10.813	9.927	11.443	12.146
1.00E-02	800.	1.25E+00	10.220	12.138	11.967	7.328	10.034	10.455	11.465	12.105
1.00E-02	1000.	1.00E+00	9.385	12.156	11.954	8.412	9.287	10.763	11.406	12.085
1.00E-02	1500.	6.67E-01	7.861	12.166	11.943	9.817	8.007	11.137	11.218	12.074
1.00E-02	2000.	5.00E-01	7.002	12.144	11.961	10.487	7.233	11.294	11.068	12.100
P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	12.400	10.895	10.594	-2.223	10.251	6.423	8.590	12.410
1.00E-01	400.	2.50E+00	12.321	11.504	11.209	1.190	10.825	8.148	9.809	12.368
1.00E-01	500.	2.00E+00	12.147	11.840	11.587	3.540	11.115	9.157	10.578	12.292
1.00E-01	600.	1.67E+00	11.875	12.008	11.793	5.439	11.168	9.773	11.025	12.212
1.00E-01	800.	1.25E+00	11.150	12.124	11.933	7.328	10.809	10.427	11.361	12.120
1.00E-01	1000.	1.00E+00	10.366	12.154	11.948	8.412	10.213	10.758	11.381	12.088
1.00E-01	1500.	6.67E-01	8.859	12.166	11.943	9.817	8.998	11.136	11.216	12.074
1.00E-01	2000.	5.00E-01	8.002	12.144	11.961	10.487	8.230	11.294	11.068	12.100
P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	12.421	9.963	9.626	-2.370	9.291	4.680	6.668	12.422
1.00E+00	400.	2.50E+00	12.409	10.747	10.350	1.108	10.001	6.784	8.127	12.414
1.00E+00	500.	2.00E+00	12.367	11.311	10.916	3.498	10.541	8.207	9.249	12.388
1.00E+00	600.	1.67E+00	12.269	11.685	11.331	5.424	10.903	9.178	10.063	12.336

1.00E+00	800.	1.25E+00	11.866	12.036	11.771	7.324	11.117	10.245	10.954	12.194
1.00E+00	1000.	1.00E+00	11.260	12.135	11.905	8.411	10.880	10.708	11.237	12.109
1.00E+00	1500.	6.67E-01	9.848	12.165	11.940	9.817	9.929	11.132	11.201	12.075
1.00E+00	2000.	5.00E-01	8.999	12.144	11.960	10.487	9.208	11.293	11.064	12.100
P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	12.423	8.972	8.630	-2.958	8.296	2.722	4.679	12.423
1.00E+01	400.	2.50E+00	12.422	9.800	9.376	.673	9.032	4.964	6.200	12.422
1.00E+01	500.	2.00E+00	12.416	10.477	10.015	3.216	9.658	6.643	7.488	12.418
1.00E+01	600.	1.67E+00	12.397	11.022	10.563	5.294	10.187	7.950	8.566	12.406
1.00E+01	800.	1.25E+00	12.256	11.728	11.344	7.292	10.883	9.632	10.052	12.325
1.00E+01	1000.	1.00E+00	11.919	12.031	11.728	8.403	11.092	10.453	10.773	12.198
1.00E+01	1500.	6.67E-01	10.786	12.158	11.925	9.816	10.668	11.096	11.113	12.083
1.00E+01	2000.	5.00E-01	9.983	12.142	11.958	10.487	10.102	11.283	11.041	12.101
P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	12.423	7.973	7.630	-3.884	7.296	.727	2.680	12.423
1.00E+02	400.	2.50E+00	12.423	8.807	8.379	-.191	8.036	2.992	4.209	12.423
1.00E+02	500.	2.00E+00	12.422	9.507	9.031	2.456	8.676	4.740	5.535	12.423
1.00E+02	600.	1.67E+00	12.420	10.118	9.620	4.757	9.253	6.210	6.716	12.421
1.00E+02	800.	1.25E+00	12.392	11.096	10.614	7.076	10.213	8.411	8.620	12.402
1.00E+02	1000.	1.00E+00	12.274	11.697	11.287	8.330	10.818	9.729	9.821	12.333
1.00E+02	1500.	6.67E-01	11.577	12.113	11.848	9.808	11.077	10.905	10.800	12.131
1.00E+02	2000.	5.00E-01	10.913	12.132	11.940	10.484	10.797	11.214	10.919	12.112

Chemical Activation Reaction (CH₃CjO + O₂) Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	10.923	12.046	12.015	-2.203	10.537	8.081	11.585	12.187
298.	3.36E+00	1.00E-03	11.786	11.964	11.893	-2.203	11.176	8.012	11.272	12.238
298.	3.36E+00	1.00E-02	12.268	11.613	11.422	-2.205	11.016	7.588	10.242	12.350
298.	3.36E+00	1.00E-01	12.400	10.895	10.594	-2.223	10.251	6.423	8.590	12.410
298.	3.36E+00	1.00E+00	12.421	9.963	9.626	-2.370	9.291	4.680	6.668	12.422
298.	3.36E+00	1.00E+01	12.423	8.972	8.630	-2.958	8.296	2.722	4.679	12.423
298.	3.36E+00	1.00E+02	12.423	7.973	7.630	-3.884	7.296	.727	2.680	12.423
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	10.281	12.062	12.027	1.201	10.009	8.997	11.603	12.175
400.	2.50E+00	1.00E-03	11.237	12.043	11.991	1.200	10.875	8.977	11.501	12.189
400.	2.50E+00	1.00E-02	11.979	11.919	11.781	1.200	11.221	8.818	10.986	12.260
400.	2.50E+00	1.00E-01	12.321	11.504	11.209	1.190	10.825	8.148	9.809	12.368
400.	2.50E+00	1.00E+00	12.409	10.747	10.350	1.108	10.001	6.784	8.127	12.414
400.	2.50E+00	1.00E+01	12.422	9.800	9.376	.673	9.032	4.964	6.200	12.422
400.	2.50E+00	1.00E+02	12.423	8.807	8.379	-.191	8.036	2.992	4.209	12.423
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	9.709	12.089	12.013	3.545	9.492	9.559	11.579	12.153
500.	2.00E+00	1.00E-03	10.693	12.084	12.002	3.545	10.441	9.553	11.545	12.157
500.	2.00E+00	1.00E-02	11.577	12.043	11.919	3.544	11.106	9.495	11.317	12.189
500.	2.00E+00	1.00E-01	12.147	11.840	11.587	3.540	11.115	9.157	10.578	12.292
500.	2.00E+00	1.00E+00	12.367	11.311	10.916	3.498	10.541	8.207	9.249	12.388
500.	2.00E+00	1.00E+01	12.416	10.477	10.015	3.216	9.658	6.643	7.488	12.418
500.	2.00E+00	1.00E+02	12.422	9.507	9.031	2.456	8.676	4.740	5.535	12.423
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	9.183	12.112	11.997	5.441	8.994	9.950	11.548	12.133
600.	1.67E+00	1.00E-03	10.177	12.110	11.993	5.441	9.974	9.948	11.536	12.134
600.	1.67E+00	1.00E-02	11.126	12.097	11.962	5.441	10.813	9.927	11.443	12.146
600.	1.67E+00	1.00E-01	11.875	12.008	11.793	5.439	11.168	9.773	11.025	12.212
600.	1.67E+00	1.00E+00	12.269	11.685	11.331	5.424	10.903	9.178	10.063	12.336
600.	1.67E+00	1.00E+01	12.397	11.022	10.563	5.294	10.187	7.950	8.566	12.406
600.	1.67E+00	1.00E+02	12.420	10.118	9.620	4.757	9.253	6.210	6.716	12.421
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	8.230	12.140	11.972	7.328	8.073	10.458	11.482	12.103
800.	1.25E+00	1.00E-03	9.229	12.140	11.971	7.328	9.069	10.458	11.480	12.104
800.	1.25E+00	1.00E-02	10.220	12.138	11.967	7.328	10.034	10.455	11.465	12.105
800.	1.25E+00	1.00E-01	11.150	12.124	11.933	7.328	10.809	10.427	11.361	12.120
800.	1.25E+00	1.00E+00	11.866	12.036	11.771	7.324	11.117	10.245	10.954	12.194
800.	1.25E+00	1.00E+01	12.256	11.728	11.344	7.292	10.883	9.632	10.052	12.325
800.	1.25E+00	1.00E+02	12.392	11.096	10.614	7.076	10.213	8.411	8.620	12.402

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	7.387	12.156	11.955	8.412	7.297	10.764	11.409	12.085
1000.	1.00E+00	1.00E-03	8.387	12.156	11.955	8.412	8.296	10.764	11.408	12.085
1000.	1.00E+00	1.00E-02	9.385	12.156	11.954	8.412	9.287	10.763	11.406	12.085
1000.	1.00E+00	1.00E-01	10.366	12.154	11.948	8.412	10.213	10.758	11.381	12.088
1000.	1.00E+00	1.00E+00	11.260	12.135	11.905	8.411	10.880	10.708	11.237	12.109
1000.	1.00E+00	1.00E+01	11.919	12.031	11.728	8.403	11.092	10.453	10.773	12.198
1000.	1.00E+00	1.00E+02	12.274	11.697	11.287	8.330	10.818	9.729	9.821	12.333
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	5.861	12.166	11.943	9.817	6.009	11.137	11.218	12.074
1500.	6.67E-01	1.00E-03	6.861	12.166	11.943	9.817	7.008	11.137	11.218	12.074
1500.	6.67E-01	1.00E-02	7.861	12.166	11.943	9.817	8.007	11.137	11.218	12.074
1500.	6.67E-01	1.00E-01	8.859	12.166	11.943	9.817	8.998	11.136	11.216	12.074
1500.	6.67E-01	1.00E+00	9.848	12.165	11.940	9.817	9.929	11.132	11.201	12.075
1500.	6.67E-01	1.00E+01	10.786	12.158	11.925	9.816	10.668	11.096	11.113	12.083
1500.	6.67E-01	1.00E+02	11.577	12.113	11.848	9.808	11.077	10.905	10.800	12.131
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	5.002	12.144	11.961	10.487	5.233	11.294	11.068	12.100
2000.	5.00E-01	1.00E-03	6.002	12.144	11.961	10.487	6.233	11.294	11.068	12.100
2000.	5.00E-01	1.00E-02	7.002	12.144	11.961	10.487	7.233	11.294	11.068	12.100
2000.	5.00E-01	1.00E-01	8.002	12.144	11.961	10.487	8.230	11.294	11.068	12.100
2000.	5.00E-01	1.00E+00	8.999	12.144	11.960	10.487	9.208	11.293	11.064	12.100
2000.	5.00E-01	1.00E+01	9.983	12.142	11.958	10.487	10.102	11.283	11.041	12.101
2000.	5.00E-01	1.00E+02	10.913	12.132	11.940	10.484	10.797	11.214	10.919	12.112

Adduct (CCOQj) Dissociation Reaction Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	-13.040	-8.998	-30.463	-8.752	-18.173	-10.896	-8.555
1.00E-04	400.	2.50E+00	-7.159	-3.973	-20.822	-3.850	-11.229	-5.423	-3.600
1.00E-04	500.	2.00E+00	-3.925	-1.259	-15.220	-1.234	-7.313	-2.501	-.933
1.00E-04	600.	1.67E+00	-1.921	.376	-11.079	.285	-4.817	-.755	.652
1.00E-04	800.	1.25E+00	.274	2.054	-6.617	1.690	-1.950	1.050	2.244
1.00E-04	1000.	1.00E+00	1.312	2.719	-4.206	2.112	-.468	1.815	2.869
1.00E-04	1500.	6.67E-01	2.302	3.113	-1.260	2.034	1.167	2.373	3.269
1.00E-04	2000.	5.00E-01	2.709	3.191	.205	1.619	1.900	2.492	3.397

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	-12.172	-8.850	-29.463	-8.661	-17.256	-11.160	-8.443
1.00E-03	400.	2.50E+00	-6.202	-3.593	-19.822	-3.559	-10.258	-5.187	-3.269
1.00E-03	500.	2.00E+00	-2.941	-.683	-14.220	-.735	-6.323	-1.945	-.394
1.00E-03	600.	1.67E+00	-.927	1.083	-10.079	.957	-3.821	.000	1.348
1.00E-03	800.	1.25E+00	1.273	2.906	-5.617	2.611	-.951	1.985	3.123
1.00E-03	1000.	1.00E+00	2.312	3.648	-3.206	3.159	.531	2.797	3.827
1.00E-03	1500.	6.67E-01	3.302	4.100	-.260	3.124	2.167	3.371	4.265
1.00E-03	2000.	5.00E-01	3.709	4.188	1.205	2.704	2.900	3.491	4.397

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	-11.682	-8.822	-28.465	-8.644	-16.760	-11.923	-8.422
1.00E-02	400.	2.50E+00	-5.455	-3.452	-18.823	-3.450	-9.479	-5.535	-3.146
1.00E-02	500.	2.00E+00	-2.055	-.363	-13.221	-.459	-5.418	-1.896	-.095
1.00E-02	600.	1.67E+00	.023	1.577	-9.080	1.413	-2.861	.356	1.826
1.00E-02	800.	1.25E+00	2.264	3.638	-4.617	3.344	.041	2.714	3.860
1.00E-02	1000.	1.00E+00	3.310	4.501	-2.206	4.069	1.529	3.690	4.702
1.00E-02	1500.	6.67E-01	4.302	5.060	.740	4.246	3.166	4.355	5.247
1.00E-02	2000.	5.00E-01	4.709	5.175	2.205	3.894	3.900	4.487	5.393

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	-11.547	-8.818	-27.483	-8.642	-17.071	-12.877	-8.420
1.00E-01	400.	2.50E+00	-5.110	-3.421	-17.832	-3.426	-9.337	-6.303	-3.118
1.00E-01	500.	2.00E+00	-1.483	-.246	-12.225	-.354	-4.923	-2.357	.020
1.00E-01	600.	1.67E+00	.773	1.834	-8.082	1.657	-2.134	.220	2.084
1.00E-01	800.	1.25E+00	3.194	4.186	-3.617	3.898	.972	3.094	4.416
1.00E-01	1000.	1.00E+00	4.292	5.243	-1.206	4.846	2.510	4.366	5.460
1.00E-01	1500.	6.67E-01	5.300	5.986	1.740	5.285	4.164	5.274	6.194
1.00E-01	2000.	5.00E-01	5.708	6.150	3.205	5.048	4.899	5.459	6.381

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	-11.526	-8.818	-26.629	-8.641	-17.903	-13.871	-8.419
1.00E+00	400.	2.50E+00	-5.022	-3.417	-16.913	-3.423	-9.902	-7.248	-3.113
1.00E+00	500.	2.00E+00	-1.263	-.220	-11.271	-.331	-5.145	-3.157	.051
1.00E+00	600.	1.67E+00	1.168	1.922	-7.101	1.742	-2.012	-.348	2.187

1.00E+00	800.	1.25E+00	3.911	4.506	-2.622	4.232	1.601	3.044	4.766
1.00E+00	1000.	1.00E+00	5.185	5.808	-.208	5.449	3.370	4.716	6.054
1.00E+00	1500.	6.67E-01	6.288	6.852	2.739	6.263	5.141	6.052	7.085
1.00E+00	2000.	5.00E-01	6.706	7.103	4.205	6.195	5.891	6.365	7.351

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	-11.523	-8.818	-26.214	-8.641	-18.880	-14.871	-8.419
1.00E+01	400.	2.50E+00	-5.009	-3.416	-16.345	-3.422	-10.809	-8.240	-3.113
1.00E+01	500.	2.00E+00	-1.213	-.216	-10.570	-.328	-5.895	-4.110	.057
1.00E+01	600.	1.67E+00	1.295	1.941	-6.255	1.760	-2.524	-1.194	2.217
1.00E+01	800.	1.25E+00	4.301	4.642	-1.666	4.373	1.644	2.584	4.944
1.00E+01	1000.	1.00E+00	5.845	6.155	.779	5.823	3.842	4.670	6.455
1.00E+01	1500.	6.67E-01	7.227	7.603	3.738	7.113	6.003	6.594	7.874
1.00E+01	2000.	5.00E-01	7.689	8.006	5.204	7.294	6.837	7.131	8.280

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	-11.523	-8.818	-26.139	-8.641	-19.877	-15.871	-8.419
1.00E+02	400.	2.50E+00	-5.007	-3.416	-16.209	-3.422	-11.797	-9.240	-3.113
1.00E+02	500.	2.00E+00	-1.207	-.216	-10.345	-.328	-6.851	-5.103	.057
1.00E+02	600.	1.67E+00	1.319	1.944	-5.845	1.762	-3.399	-2.162	2.222
1.00E+02	800.	1.25E+00	4.437	4.680	-.937	4.412	1.113	1.800	5.005
1.00E+02	1000.	1.00E+00	6.200	6.316	1.672	5.997	3.746	4.217	6.669
1.00E+02	1500.	6.67E-01	8.018	8.181	4.723	7.755	6.550	6.805	8.509
1.00E+02	2000.	5.00E-01	8.619	8.812	6.199	8.251	7.609	7.662	9.124

Adduct (CCOQj) Dissociation Reaction Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	-13.040	-8.998	-30.463	-8.752	-18.173	-10.896	-8.555
298.	3.36E+00	1.00E-03	-12.172	-8.850	-29.463	-8.661	-17.256	-11.160	-8.443
298.	3.36E+00	1.00E-02	-11.682	-8.822	-28.465	-8.644	-16.760	-11.923	-8.422
298.	3.36E+00	1.00E-01	-11.547	-8.818	-27.483	-8.642	-17.071	-12.877	-8.420
298.	3.36E+00	1.00E+00	-11.526	-8.818	-26.629	-8.641	-17.903	-13.871	-8.419
298.	3.36E+00	1.00E+01	-11.523	-8.818	-26.214	-8.641	-18.880	-14.871	-8.419
298.	3.36E+00	1.00E+02	-11.523	-8.818	-26.139	-8.641	-19.877	-15.871	-8.419
T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	-7.159	-3.973	-20.822	-3.850	-11.229	-5.423	-3.600
400.	2.50E+00	1.00E-03	-6.202	-3.593	-19.822	-3.559	-10.258	-5.187	-3.269
400.	2.50E+00	1.00E-02	-5.455	-3.452	-18.823	-3.450	-9.479	-5.535	-3.146
400.	2.50E+00	1.00E-01	-5.110	-3.421	-17.832	-3.426	-9.337	-6.303	-3.118
400.	2.50E+00	1.00E+00	-5.022	-3.417	-16.913	-3.423	-9.902	-7.248	-3.113
400.	2.50E+00	1.00E+01	-5.009	-3.416	-16.345	-3.422	-10.809	-8.240	-3.113
400.	2.50E+00	1.00E+02	-5.007	-3.416	-16.209	-3.422	-11.797	-9.240	-3.113
T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	-3.925	-1.259	-15.220	-1.234	-7.313	-2.501	-.933
500.	2.00E+00	1.00E-03	-2.941	-.683	-14.220	-.735	-6.323	-1.945	-.394
500.	2.00E+00	1.00E-02	-2.055	-.363	-13.221	-.459	-5.418	-1.896	-.095
500.	2.00E+00	1.00E-01	-1.483	-.246	-12.225	-.354	-4.923	-2.357	.020
500.	2.00E+00	1.00E+00	-1.263	-.220	-11.271	-.331	-5.145	-3.157	.051
500.	2.00E+00	1.00E+01	-1.213	-.216	-10.570	-.328	-5.895	-4.110	.057
500.	2.00E+00	1.00E+02	-1.207	-.216	-10.345	-.328	-6.851	-5.103	.057
T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	-1.921	.376	-11.079	.285	-4.817	-.755	.652
600.	1.67E+00	1.00E-03	-.927	1.083	-10.079	.957	-3.821	.000	1.348
600.	1.67E+00	1.00E-02	.023	1.577	-9.080	1.413	-2.861	.356	1.826
600.	1.67E+00	1.00E-01	.773	1.834	-8.082	1.657	-2.134	.220	2.084
600.	1.67E+00	1.00E+00	1.168	1.922	-7.101	1.742	-2.012	-.348	2.187
600.	1.67E+00	1.00E+01	1.295	1.941	-6.255	1.760	-2.524	-1.194	2.217
600.	1.67E+00	1.00E+02	1.319	1.944	-5.845	1.762	-3.399	-2.162	2.222
T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	.274	2.054	-6.617	1.690	-1.950	1.050	2.244
800.	1.25E+00	1.00E-03	1.273	2.906	-5.617	2.611	-.951	1.985	3.123
800.	1.25E+00	1.00E-02	2.264	3.638	-4.617	3.344	.041	2.714	3.860
800.	1.25E+00	1.00E-01	3.194	4.186	-3.617	3.898	.972	3.094	4.416
800.	1.25E+00	1.00E+00	3.911	4.506	-2.622	4.232	1.601	3.044	4.766
800.	1.25E+00	1.00E+01	4.301	4.642	-1.666	4.373	1.644	2.584	4.944
800.	1.25E+00	1.00E+02	4.437	4.680	-.937	4.412	1.113	1.800	5.005

T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	1.312	2.719	-4.206	2.112	-.468	1.815	2.869
1000.	1.00E+00	1.00E-03	2.312	3.648	-3.206	3.159	.531	2.797	3.827
1000.	1.00E+00	1.00E-02	3.310	4.501	-2.206	4.069	1.529	3.690	4.702
1000.	1.00E+00	1.00E-01	4.292	5.243	-1.206	4.846	2.510	4.366	5.460
1000.	1.00E+00	1.00E+00	5.185	5.808	-.208	5.449	3.370	4.716	6.054
1000.	1.00E+00	1.00E+01	5.845	6.155	.779	5.823	3.842	4.670	6.455
1000.	1.00E+00	1.00E+02	6.200	6.316	1.672	5.997	3.746	4.217	6.669
T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	2.302	3.113	-1.260	2.034	1.167	2.373	3.269
1500.	6.67E-01	1.00E-03	3.302	4.100	-.260	3.124	2.167	3.371	4.265
1500.	6.67E-01	1.00E-02	4.302	5.060	.740	4.246	3.166	4.355	5.247
1500.	6.67E-01	1.00E-01	5.300	5.986	1.740	5.285	4.164	5.274	6.194
1500.	6.67E-01	1.00E+00	6.288	6.852	2.739	6.263	5.141	6.052	7.085
1500.	6.67E-01	1.00E+01	7.227	7.603	3.738	7.113	6.003	6.594	7.874
1500.	6.67E-01	1.00E+02	8.018	8.181	4.723	7.755	6.550	6.805	8.509
T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	2.709	3.191	.205	1.619	1.900	2.492	3.397
2000.	5.00E-01	1.00E-03	3.709	4.188	1.205	2.704	2.900	3.491	4.397
2000.	5.00E-01	1.00E-02	4.709	5.175	2.205	3.894	3.900	4.487	5.393
2000.	5.00E-01	1.00E-01	5.708	6.150	3.205	5.048	4.899	5.459	6.381
2000.	5.00E-01	1.00E+00	6.706	7.103	4.205	6.195	5.891	6.365	7.351
2000.	5.00E-01	1.00E+01	7.689	8.006	5.204	7.294	6.837	7.131	8.280
2000.	5.00E-01	1.00E+02	8.619	8.812	6.199	8.251	7.609	7.662	9.124

Adduct (CjCOQ) Dissociation Reaction Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	-5.046	-9.369	-5.876	-26.948	-12.441	-5.943	-4.941
1.00E-04	400.	2.50E+00	-1.500	-4.732	-1.703	-18.298	-6.983	-1.936	-1.200
1.00E-04	500.	2.00E+00	.277	-2.257	.474	-13.389	-3.959	.142	.797
1.00E-04	600.	1.67E+00	1.210	-.775	1.706	-10.233	-2.070	1.327	1.947
1.00E-04	800.	1.25E+00	1.848	.756	2.792	-6.521	.037	2.451	2.991
1.00E-04	1000.	1.00E+00	1.799	1.444	3.095	-4.454	1.127	2.888	3.327
1.00E-04	1500.	6.67E-01	1.112	2.128	3.134	-1.771	2.463	3.268	3.563
1.00E-04	2000.	5.00E-01	.408	2.362	3.018	-.422	3.099	3.378	3.692
P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	-4.928	-8.715	-6.488	-25.949	-11.501	-5.717	-4.852
1.00E-03	400.	2.50E+00	-1.146	-3.859	-1.884	-17.299	-6.002	-1.463	-.924
1.00E-03	500.	2.00E+00	.863	-1.305	.612	-12.390	-2.966	.821	1.257
1.00E-03	600.	1.67E+00	1.984	.206	2.076	-9.233	-1.073	2.149	2.554
1.00E-03	800.	1.25E+00	2.876	1.752	3.473	-5.521	1.037	3.407	3.802
1.00E-03	1000.	1.00E+00	2.939	2.443	3.946	-3.454	2.127	3.877	4.247
1.00E-03	1500.	6.67E-01	2.266	3.128	4.106	-.771	3.463	4.267	4.552
1.00E-03	2000.	5.00E-01	1.550	3.362	4.011	.578	4.099	4.378	4.690
P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	-4.904	-8.850	-7.366	-24.967	-10.848	-5.661	-4.833
1.00E-02	400.	2.50E+00	-1.005	-3.491	-2.432	-16.305	-5.151	-1.264	-.803
1.00E-02	500.	2.00E+00	1.200	-.624	.417	-11.392	-2.026	1.210	1.543
1.00E-02	600.	1.67E+00	2.519	1.055	2.166	-8.234	-.098	2.719	3.006
1.00E-02	800.	1.25E+00	3.714	2.720	3.937	-4.522	2.032	4.228	4.496
1.00E-02	1000.	1.00E+00	3.969	3.435	4.625	-2.454	3.126	4.811	5.080
1.00E-02	1500.	6.67E-01	3.507	4.127	5.008	.229	4.463	5.259	5.517
1.00E-02	2000.	5.00E-01	2.860	4.362	4.977	1.578	5.099	5.376	5.683
P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	-4.901	-9.601	-8.344	-24.114	-10.641	-5.653	-4.830
1.00E-01	400.	2.50E+00	-.972	-3.860	-3.273	-15.363	-4.699	-1.214	-.773
1.00E-01	500.	2.00E+00	1.335	-.584	-.158	-10.417	-1.350	1.366	1.662
1.00E-01	600.	1.67E+00	2.819	1.438	1.891	-7.245	.732	3.029	3.264
1.00E-01	800.	1.25E+00	4.355	3.511	4.150	-3.524	2.992	4.837	5.040
1.00E-01	1000.	1.00E+00	4.848	4.368	5.133	-1.455	4.115	5.611	5.813
1.00E-01	1500.	6.67E-01	4.671	5.119	5.826	1.229	5.461	6.217	6.445
1.00E-01	2000.	5.00E-01	4.151	5.360	5.905	2.578	6.099	6.365	6.664
P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	-4.901	-10.557	-9.341	-23.794	-10.611	-5.653	-4.830
1.00E+00	400.	2.50E+00	-.967	-4.671	-4.238	-14.743	-4.591	-1.207	-.769
1.00E+00	500.	2.00E+00	1.368	-1.134	-1.004	-9.614	-1.091	1.402	1.688
1.00E+00	600.	1.67E+00	2.931	1.203	1.254	-6.343	1.185	3.138	3.357

1.00E+00	800.	1.25E+00	4.758	3.849	4.004	-2.549	3.767	5.199	5.377
1.00E+00	1000.	1.00E+00	5.545	5.057	5.378	- .463	5.033	6.210	6.386
1.00E+00	1500.	6.67E-01	5.765	6.057	6.525	2.228	6.449	7.090	7.305
1.00E+00	2000.	5.00E-01	5.425	6.340	6.769	3.577	7.095	7.319	7.619

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	-4.901	-11.552	-10.341	-24.243	-10.608	-5.653	-4.830
1.00E+01	400.	2.50E+00	-.966	-5.636	-5.233	-14.875	-4.577	-1.206	-.769
1.00E+01	500.	2.00E+00	1.373	-2.009	-1.968	-9.428	-1.042	1.407	1.692
1.00E+01	600.	1.67E+00	2.957	.503	.381	-5.880	1.313	3.159	3.375
1.00E+01	800.	1.25E+00	4.938	3.640	3.495	-1.741	4.178	5.342	5.517
1.00E+01	1000.	1.00E+00	5.988	5.295	5.272	.470	5.707	6.562	6.741
1.00E+01	1500.	6.67E-01	6.714	6.812	7.016	3.216	7.365	7.803	8.036
1.00E+01	2000.	5.00E-01	6.629	7.241	7.506	4.573	8.064	8.185	8.509

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	-4.901	-12.551	-11.341	-25.138	-10.608	-5.653	-4.830
1.00E+02	400.	2.50E+00	-.966	-6.632	-6.233	-15.645	-4.575	-1.206	-.769
1.00E+02	500.	2.00E+00	1.373	-2.988	-2.964	-10.007	-1.037	1.407	1.692
1.00E+02	600.	1.67E+00	2.961	-.426	-.593	-6.210	1.333	3.161	3.378
1.00E+02	800.	1.25E+00	4.990	2.984	2.693	-1.525	4.299	5.374	5.551
1.00E+02	1000.	1.00E+00	6.196	5.039	4.794	1.074	6.031	6.698	6.892
1.00E+02	1500.	6.67E-01	7.419	7.238	7.205	4.117	8.070	8.284	8.567
1.00E+02	2000.	5.00E-01	7.650	7.947	8.027	5.530	8.920	8.882	9.264

Adduct (CjCOQ) Dissociation Reaction Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	-5.046	-9.369	-5.876	-26.948	-12.441	-5.943	-4.941
298.	3.36E+00	1.00E-03	-4.928	-8.715	-6.488	-25.949	-11.501	-5.717	-4.852
298.	3.36E+00	1.00E-02	-4.904	-8.850	-7.366	-24.967	-10.848	-5.661	-4.833
298.	3.36E+00	1.00E-01	-4.901	-9.601	-8.344	-24.114	-10.641	-5.653	-4.830
298.	3.36E+00	1.00E+00	-4.901	-10.557	-9.341	-23.794	-10.611	-5.653	-4.830
298.	3.36E+00	1.00E+01	-4.901	-11.552	-10.341	-24.243	-10.608	-5.653	-4.830
298.	3.36E+00	1.00E+02	-4.901	-12.551	-11.341	-25.138	-10.608	-5.653	-4.830
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	-1.500	-4.732	-1.703	-18.298	-6.983	-1.936	-1.200
400.	2.50E+00	1.00E-03	-1.146	-3.859	-1.884	-17.299	-6.002	-1.463	-.924
400.	2.50E+00	1.00E-02	-1.005	-3.491	-2.432	-16.305	-5.151	-1.264	-.803
400.	2.50E+00	1.00E-01	-.972	-3.860	-3.273	-15.363	-4.699	-1.214	-.773
400.	2.50E+00	1.00E+00	-.967	-4.671	-4.238	-14.743	-4.591	-1.207	-.769
400.	2.50E+00	1.00E+01	-.966	-5.636	-5.233	-14.875	-4.577	-1.206	-.769
400.	2.50E+00	1.00E+02	-.966	-6.632	-6.233	-15.645	-4.575	-1.206	-.769
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	.277	-2.257	.474	-13.389	-3.959	.142	.797
500.	2.00E+00	1.00E-03	.863	-1.305	.612	-12.390	-2.966	.821	1.257
500.	2.00E+00	1.00E-02	1.200	-.624	.417	-11.392	-2.026	1.210	1.543
500.	2.00E+00	1.00E-01	1.335	-.584	-.158	-10.417	-1.350	1.366	1.662
500.	2.00E+00	1.00E+00	1.368	-1.134	-1.004	-9.614	-1.091	1.402	1.688
500.	2.00E+00	1.00E+01	1.373	-2.009	-1.968	-9.428	-1.042	1.407	1.692
500.	2.00E+00	1.00E+02	1.373	-2.988	-2.964	-10.007	-1.037	1.407	1.692
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	1.210	-.775	1.706	-10.233	-2.070	1.327	1.947
600.	1.67E+00	1.00E-03	1.984	.206	2.076	-9.233	-1.073	2.149	2.554
600.	1.67E+00	1.00E-02	2.519	1.055	2.166	-8.234	-.098	2.719	3.006
600.	1.67E+00	1.00E-01	2.819	1.438	1.891	-7.245	.732	3.029	3.264
600.	1.67E+00	1.00E+00	2.931	1.203	1.254	-6.343	1.185	3.138	3.357
600.	1.67E+00	1.00E+01	2.957	.503	.381	-5.880	1.313	3.159	3.375
600.	1.67E+00	1.00E+02	2.961	-.426	-.593	-6.210	1.333	3.161	3.378
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	1.848	.756	2.792	-6.521	.037	2.451	2.991
800.	1.25E+00	1.00E-03	2.876	1.752	3.473	-5.521	1.037	3.407	3.802
800.	1.25E+00	1.00E-02	3.714	2.720	3.937	-4.522	2.032	4.228	4.496
800.	1.25E+00	1.00E-01	4.355	3.511	4.150	-3.524	2.992	4.837	5.040
800.	1.25E+00	1.00E+00	4.758	3.849	4.004	-2.549	3.767	5.199	5.377
800.	1.25E+00	1.00E+01	4.938	3.640	3.495	-1.741	4.178	5.342	5.517
800.	1.25E+00	1.00E+02	4.990	2.984	2.693	-1.525	4.299	5.374	5.551

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	1.799	1.444	3.095	-4.454	1.127	2.888	3.327
1000.	1.00E+00	1.00E-03	2.939	2.443	3.946	-3.454	2.127	3.877	4.247
1000.	1.00E+00	1.00E-02	3.969	3.435	4.625	-2.454	3.126	4.811	5.080
1000.	1.00E+00	1.00E-01	4.848	4.368	5.133	-1.455	4.115	5.611	5.813
1000.	1.00E+00	1.00E+00	5.545	5.057	5.378	-.463	5.033	6.210	6.386
1000.	1.00E+00	1.00E+01	5.988	5.295	5.272	.470	5.707	6.562	6.741
1000.	1.00E+00	1.00E+02	6.196	5.039	4.794	1.074	6.031	6.698	6.892
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	1.112	2.128	3.134	-1.771	2.463	3.268	3.563
1500.	6.67E-01	1.00E-03	2.266	3.128	4.106	-.771	3.463	4.267	4.552
1500.	6.67E-01	1.00E-02	3.507	4.127	5.008	.229	4.463	5.259	5.517
1500.	6.67E-01	1.00E-01	4.671	5.119	5.826	1.229	5.461	6.217	6.445
1500.	6.67E-01	1.00E+00	5.765	6.057	6.525	2.228	6.449	7.090	7.305
1500.	6.67E-01	1.00E+01	6.714	6.812	7.016	3.216	7.365	7.803	8.036
1500.	6.67E-01	1.00E+02	7.419	7.238	7.205	4.117	8.070	8.284	8.567
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	.408	2.362	3.018	-.422	3.099	3.378	3.692
2000.	5.00E-01	1.00E-03	1.550	3.362	4.011	.578	4.099	4.378	4.690
2000.	5.00E-01	1.00E-02	2.860	4.362	4.977	1.578	5.099	5.376	5.683
2000.	5.00E-01	1.00E-01	4.151	5.360	5.905	2.578	6.099	6.365	6.664
2000.	5.00E-01	1.00E+00	5.425	6.340	6.769	3.577	7.095	7.319	7.619
2000.	5.00E-01	1.00E+01	6.629	7.241	7.506	4.573	8.064	8.185	8.509
2000.	5.00E-01	1.00E+02	7.650	7.947	8.027	5.530	8.920	8.882	9.264

**REFERENCES
(PART THREE)**

1. Benson, S. W. *Thermochemical Kinetics* ; 2nd ed. John Wiley and Sons : New York, 1976.
2. Slagle, I. R.; Ratajczak, E.; Gutman, D. J. *J. Phys. Chem.*, 1986, 90, 402.
3. Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. *Atmospheric Environ.*, 1992, 266A, 1805-1964.
4. Atkinson, R. *A Review, Atmospheric Environ.* 1990, 24a, 1-41.
5. Slagle, I. R.; Feng, Q.; Gutman, D. *J. Phys. Chem.*, 1984, 88, 3648.
6. McAdam, G. K.; Walker, R. W. *J. Chem. Soc., Far. Trans. 2*, 1987, 83, 1509.
7. Plumb, I. C.; Ryan, K.R. *Int. J. Chem. Kinet.* 1981, 13, 1011.
8. Kaiser, E. W.; Rimai, L.; Wallington, T. J. *J. Phys. Chem.*, 1989, 93, 4094.
9. Kaiser, E. W.; Rimai, L.; Wallington, T. J. *J. Phys. Chem.*, 1990, 94, 3394.
10. Gutman, D. *J. Chim. Phys.*, 1987, 84, 409.
11. Gulati, S. K.; Walker, R. W. *J. Chem. Soc., Far. Trans. 2*, 1988, 84, 401.
12. Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem.* 1990, 94, 3313.
13. Wagner, A.F.; Slagle, I. R.; Sarzynski, D.; Gutman, D. *J. Phys. Chem.*, 1990, 94, 1853.
14. Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem.* 1993, 97, 4427.
15. (a) Bozzelli, J. W.; Pitz W. J. *25-th Symp. (Intern) on Comb.*, 1994, 783. (b) Mobil, A. M.; Dian, E. W. G.; Lin, M. C. ; Morokuma, K. *J. Am. Chem. Soc.* 1996, 118, 9673
16. McMillan, G. R.; Calvert, J. G. *Oxidation and Combustion Review*, 1965, 83.
17. Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions* ; Oxford Press : Boston, MA, 1990.

18. Gilbert, R. G.; Smith, S. C. UNIMOL, 1990.
19. Gilbert, R. G.; Luther, K.; Troe, J. *Ber. Bunsen-Gas. Phys. Chem.* 1983, 87, 169
20. Stewart, J. J. P. *MOPAC 6.0*, Frank J. Seiler Research Lab., US Air Force Academy, Colorado, 1990.
21. Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Pople, E. S.; Gromperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Eds., *Gaussian 94 Computer Program, Revision C 2*, Gaussian Inc.: Pittsburgh, 1995.
22. Ochterski, J. W.; Petersson, G. A.; Montgomery, Jr., J. A. *J. Chem. Phys.* 1996, 104, 2598.
23. Nyden, M. R. Petersson, G. A. *J. Chem. Phys.* 1991, 75, 1843.
24. Petersson, G. A. *J. Chem. Phys.* 1994, 94, 6081.
25. Montgomery, J. A.; Petersson, G. A. *J. Phys. Chem.* 1994, 101, 5900.
26. Hehre, W. J.; Random, L.; Schleyer, P. R.; Pople, J. A. *Ab-Initio Molecular Orbital Theory*; John Wiley & Sons : New York, NY, 1986.
27. Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* 1942, 10, 428.
28. Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids* ; 2nd ed., Wiley : London, England, 1963.
29. Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*; McGraw-Hill Co. : New York, NY, 1979.
30. Rodgers, A. S. *Selected Values for Properties of Chemical Compounds* ; Thermodynamic Research Center, Texas A&M University : College Station, TX, 1982.
31. Pedley, J. B.; Naylor, R. O.; Kirby, S. P. *Thermodynamic Data of Organic Compounds* ; 2nd ed. Chapman and Hall : London, 1986.
32. Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables* ; 2nd Ed. (NSRDS-NBS37). U.S. Government Printing Office : Washington D.C., 1970.
33. Lay, T. H.; Bozzelli, J. W. *J. Phys. Chem. A* 1997, 101, 9505-9510.

34. (a) Zhong, X.; Bozzelli, J. W. *J. Phys. Chem. A* 1998, 102, 3537. (b) Bozzelli, J. W.; Chang, A. Y.; Dean, A. M. *Int. J. Chem. Kinet.* 1997, 29, 161.
35. Sehested, I.; Christensen, L. K.; Nielsen, O. J.; Wallington, T.J. *Int. J. Chem. Kinet.* 1998, 30, 913.
36. McDade, C. E.; Lenhardt, T. M.; Bayes, K. D. *J. Photochem.* 1982, 20, 1.
37. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Chem. Phys. Ref. Data* 1997, 26, 521.
38. Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Hurley, M. D. *Int. J. Chem. Kinet.* 1997, 29, 655.
39. Maricq, M. M.; Szente, J. J. *J. Chem. Phys. Lett.* 1996, 253, 333.
40. Tyndall, G. S.; Staffelbach, T. A.; Orlando, J. J.; Calvert, J. G. *Int. J. Chem. Kinet.* 1995, 27, 1009.
41. Atkinson, R.; Baulch, D.L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data* 1989, 18, 881.
42. Bartels, M.; Hoyermann, K. *An. Asoc. Quim. Argent.* 1985, 73, 253.
43. Michael, J. V.; Keil, D. G.; Klemm, R. B. *J. Chem. Phys.* 1985, 83, 1630.
44. Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.*, 1982, 104, 4741.
45. Zhu, L.; Johnston, G. *J. Phys. Chem.* 1995, 99, 15114.
46. Villalta, P. W.; Howard, C. J. *J. Phys. Chem.* 1996, 100, 13624.

PART IV
THERMOCHEMICAL AND KINETIC ANALYSIS
ON C_jCHO + O₂ REACTION

CHAPTER 1

ABSTRACT FOR PART FOUR

Reaction pathways and kinetics are analyzed on $C_jCHO + O_2$ reaction system using density functional and *ab initio* calculations to determine thermodynamic properties of reactants, intermediate radicals, and transition state (TS) structures. Enthalpies of formation ($\Delta H_f^\circ_{298}$) are determined using the CBSQ composite method and also by density functional calculations with isodesmic reactions for radical species. Entropies (S°_{298}) and heat capacities ($C_p^\circ(T)$ 300 –1500 K) are determined using geometric parameters and vibrational frequencies obtained at the HF/6-31G(d') level of theory. Quantum Rice-Ramsperger-Kassel (QRRK) analysis is used to calculate energy dependent rate constants, $k(E)$. The formyl methyl radical C_jCHO adds to O_2 to form a CQ_jCHO peroxy radical ($\Delta H_f^\circ_{298} = -21.01$ kcal/mole in CBSQ). The peroxy radical can undergo dissociation back to reactants, decompose to products, $CH_2CO + HO_2$ via HO_2 elimination ($E_{a,rxn} = 48.2$ kcal/mole in CBSQ) or isomerize via hydrogen shift ($E_{a,rxn} = 19.39$ kcal/mole in CBSQ) to form a CQC_jO isomer ($\Delta H_f^\circ_{298} = -21.81$ kcal/mole in CBSQ). This isomer CQC_jO can undergo β -scission to products, $CH_2CO + HO_2$ ($E_{a,rxn} = 24.32$ kcal/mole in CBSQ) or decompose to $CO + CH_2O + OH$ ($E_{a,rxn} = 9.57$ kcal/mole in CBSQ). Rate constants are estimated as function of pressure and temperature using QRRK analysis for $k(E)$ and modified strong collision analysis for fall-off. Important reactions are stabilization of CQ_jCHO peroxy adduct at low temperature and $CO + CH_2O + OH$ products via H shift and ketene + HO_2

products via H shift at high temperature. Rate constants at 1 atm pressure are

($k=A(T/K)^n \exp(-E_a/RT)$, A in $\text{cm}^3/(\text{mole}\cdot\text{s})$, E_a in kcal/mole): $k_1=(2.87 \times 10^{37})(T/K)^{-$

$8.73 e^{-6.42/RT}$ for $\text{C}_j\text{CHO} + \text{O}_2 \Rightarrow \text{CQ}_j\text{CHO}$; $k_6=(2.68 \times 10^{-6})(T/K)^{5.46} e^{-21.76/RT}$ for

$\text{C}_j\text{CHO} + \text{O}_2 \Rightarrow \text{CH}_2\text{CO} + \text{HO}_2$; $k_7=(1.25 \times 10^{14})(T/K)^{-1.05} e^{-4.99/RT}$ for $\text{C}_j\text{CHO} + \text{O}_2$

$\Rightarrow \text{CO} + \text{CH}_2\text{O} + \text{OH}$; $k_8=(2.07 \times 10^{14})(T/K)^{-3.74} e^{-2.71/RT}$ for $\text{C}_j\text{CHO} + \text{O}_2 \Rightarrow \text{CQC}_j\text{O}$

CHAPTER 2

INTRODUCTION FOR PART FOUR

Important initial products from pyrolysis, oxidation, or photochemical reactions of saturated and unsaturated hydrocarbons are the corresponding radicals.

The subsequent reactions of the hydrocarbon radicals with molecular oxygen are complex and difficult to study experimentally and present a source of controversy with regard to both pathway and reactions rates. These reactions, furthermore, represent the principal pathways of the radical conversion in many hydrocarbon oxidation and combustion processes^{1,2} and also in atmosphere. Acetaldehyde and the corresponding radical species that result via loss of hydrogen atoms from the two different carbon sites in CH_3CHO are also common products (intermediates) from oxidation processes of higher molecular weight hydrocarbon species in both combustion and in atmospheric photochemistry. The acetaldehyde and its two radicals are also produced by molecular weight growth from C_1 carbon combustion and mild oxidation processes where the slow reaction of methyl radical with O_2 to $\text{CH}_3\text{O} + \text{O}$ or $\text{CH}_2\text{O} + \text{OH}$. The slow conversion of $\text{CH}_3\text{OO}\bullet$ (methyl peroxy radical) to products, results in an equilibrium between $\text{CH}_3 + \text{O}_2$ and $\text{CH}_3\text{OO}\bullet$ where entropy favors the reactants at higher temperatures. As a result methyl radicals often buildup in the radical pool until combination occurs forming ethane and ethyl + H.

Acetaldehyde is one of the important oxidation products of ethane and ethylene.

Acetaldehyde and acetyl radicals are important intermediates in the overall

breakdown processes of higher molecular weight and C₁ hydrocarbons to CH₂O, CO, CO₂ and H₂O. The radical reactions with oxygen also serve as model reactions for larger aldehydic molecule systems.

Tyndall et al.³ studied the reaction of OH radical with methyl glyoxal and acetaldehyde in a low pressure (c.a. 3 torr) flow reactor at temperatures from 260 to 333 K. They report rate constants for OH abstractions from the parent molecules and also report data on further reactions of the radicals formed from the abstractions by OH. They infer that only the acetyl radical is formed and further reaction of acetyl radical with O₂ leads to noticeable regeneration of OH; from observations showing reduced loss of the OH versus time. Some chamber experiments with FTIR monitoring showed no evidence of OH radical production. Absolute rate constants of Fluorine atom reaction with acetaldehyde were studied by Sehested and coworkers⁴ using pulse radiolysis combined with transient ultraviolet absorption. They report production of two radicals - formyl methyl at 35% and acetyl at 65% (both ± 9%). We note that for reactions where chlorine atom is abstracting hydrogen atoms. Chlorine atoms usually have similar A factors and similar or lower E_a's when the reactions are exothermic which they are in all cases in this study. In the case of acetaldehyde, for example, k₂₉₈ for Cl atom abstraction is reported as 4.58×10^{13} [5] at 298K, while abstraction by F atom is 5.00×10^{13} [6]. The H--Cl bond is 103 kcal/mole, while the carbonyl C--H and methyl C--H bonds on acetaldehyde are 88 and 94 kcal/mole respectively. Chlorine should, therefore, readily abstract from both hydrogen sites of acetaldehyde. Michael et al.⁷ studied the reaction of OH with acetaldehyde in a low pressure discharge flow reactor with resonance fluorescence

monitoring. He also studied the reaction of radical(s) generated via the OH reaction with O_2 . The total reaction rate constant for OH with acetaldehyde was $A = 3.3 \times 10^{12}$, with a small negative energy of activation of 610 cal/mole. Michael et al. report near complete regeneration of OH radical in the OH + acetaldehyde experiments when O_2 was present to further react with the indicated acetyl radical formed. In separate studies with Cl atom reacting with acetaldehyde, they observed production of OH radical on further radical reaction(s) with O_2 . They considered and rejected possible formation of formyl methyl radicals based on work of Gutman's research group and an assumed bond energy of the H--C bond on the methyl group of 98 kcal/mole. Slagle and Gutman⁸ studied formation of acetyl radical from acetaldehyde in reaction of Cl atoms from 1082 cm^{-1} IR multiphoton decomposition of CF_2Cl_2 of C_6F_5Cl . They monitored the radical profiles with photoionization mass spectrometry. Verification of CH_3CjO radical versus formyl methyl was by use of deuterated acetaldehyde, CH_3CHO . They observed CH_3CjO and could not detect $CjCHO$; but did not estimate lower limits of its detection. Reaction kinetics of acetylperoxy radicals with nitric oxide and nitrogen dioxide were studied by Maricq and Szente⁹, where the peroxy radicals were generated via reaction of acetyl radical with O_2 . Acetyl radicals were generated by reaction of acetaldehyde with Cl atoms and Cl atoms were produced by 351 nm eximer laser pulses ca 300 mJ/pulse. Maricq and Szente provide data on nitric oxide plus acetyl and methyl peroxy radical decay and NO_2 formation versus time for modeling comparisons. Formyl methyl radicals, the other possible radical that may be formed by abstraction of H atoms from acetaldehyde, were generated by photodissociations of methyl-vinyl

ether by Zhu and Johnston¹⁰. $\text{CH}_3\text{-O-C}_2\text{H}_3 + h\nu \rightleftharpoons \text{CH}_3 + \text{C}_2\text{H}_3\text{O}$. Here the vinoxy radical undergoes rapid electron rearrangement to the lower energy form (ca 18 kcal/mole lower in energy) formyl methyl radical. Kinetic studies on this formyl methyl radical with O_2 show slower reaction, $k_2 = 1.2 \times 10^{11} \text{ cm}^3/\text{mole-sec}$, than rate constants reported for acetyl radical $k_1 = 1 \times 10^{12} \text{ cm}^3/\text{mole-sec}$. They suggest that if formyl methyl radicals are produced in reactions of Cl atoms or OH with acetaldehyde, they will react about one tenth as fast with O_2 , probably leading to small or no corrections to the faster acetyl + O_2 reactions.

Photo dissociation of PAN, (PeroxyAcetylNitrate) was used by Villalta and Howard¹¹ to generate acetylperoxy radicals for study of reaction kinetics with nitric oxide. Rate constants determined by this method agreed well with other reported values. This agreement of kinetic data where acetylperoxy radicals are generated by a very different and positive mechanism supports the assumption of Maricq and Szenté⁷, Sehested et al.⁴, Tyndall et al.³, Michael et al.⁷, and Slagle and Gutman⁸, that primarily acetyl radicals are generated by reaction with OH, or Cl atoms.

This study focuses on reaction mechanism of formyl methyl radical association with O_2 . Thermodynamic properties are estimated for reactants, intermediate, products and transition states along the reaction pathway. The thermodynamic parameters are used to calculate high-pressure limit rate constants using canonical Transition State Theory. Rate constants as a function of temperature and pressure are estimated using a multi frequency Quantum RRK analysis with modified strong collision analysis of Gilbert et al.¹²⁻¹⁴ for fall off. The data at relevant pressures and temperatures should be useful to both atmospheric and combustion modelers.

CHAPTER 3

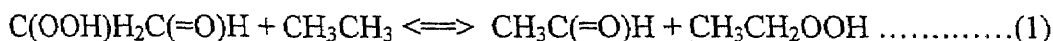
CALCULATION METHOD FOR PART FOUR

3.1 Determination of Enthalpies of Formation

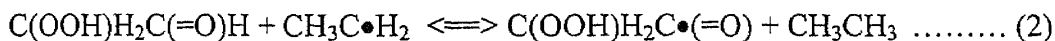
Enthalpies of formation ($\Delta H_f^{\circ}_{298}$) for reactants, intermediate radicals, transition states and products are calculated using CBS-Q composite method and density functionals. The initial structure of each compound or transition state is determined using ROHF or UHF/PM3 in MOPAC¹⁵, followed by optimization and vibrational frequency calculation at HF/6-31G(d') level of theory using GAUSSIAN 94¹⁶. Transition State (TS) geometries are identified by the existence of only one imaginary frequency, structure information and the TST reaction coordinate vibration information. Zero-point vibrational energies (ZPVE), vibrational frequencies and thermal contributions to enthalpy from harmonic frequencies are scaled by 0.91844 as recommended by Petersson et al.¹⁷. Single point energy calculation are carried out at the B3LYP/6-31G(d'). The complete basis set (CBS-Q) method of Petersson and coworkers for computing accurate energies¹⁸⁻²⁰ are chosen as our primary for determining enthalpies.

The CBS-Q calculation sequence is performed on the MP2/6-31G(d') geometry and followed by single point calculations at the theory level of QCISD(T)/6-31+G(d'), MP4(SDQ)/CbsB4 and MP2/CBSB3 CBSExtrap=(Nmin=10,Pop).

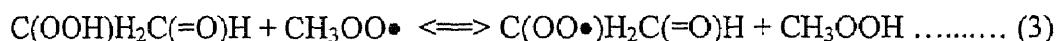
The isodesmic reactions are used to determine the heat of formation ($\Delta H_f^\circ_{298}$) for intermediate radicals. For estimation of $C(OOH)H_2C(=O)H$ [defined CQCHO, Q=OOH (hydroperoxy group)]



For estimation of $C(OOH)H_2C\bullet(=O)$ [defined CQCjO, j : radical site]



For estimation of $C(OO\bullet)H_2C(=O)H$ [defined CQjCHO, Qj : -OO•]



The method of isodesmic reactions relies upon the similarity of bonding environment in the reactants and products that leads to cancellation of systematic errors in the *ab initio* MO calculations.²¹ The basic requirement of the isodesmic reaction is that the number of bonds of each formal chemical bond type is conserved in the reaction. In reaction (1), *ab initio* calculations with ZPVE and thermal correction are performed for all of four compounds. Since $\Delta H_f^\circ_{298}$ of three compounds excepting CQCHO have been experimentally or theoretically calculated, the unknown $\Delta H_f^\circ_{298}$ of CQCHO is obtained. The remaining two radicals are calculated in the same manner.

The $\Delta H_f^\circ_{298}$ of transition state compounds are estimated by evaluation of $\Delta H_f^\circ_{298}$ of the stable radical adducts plus difference of total energies with ZPVE and thermal correction between these radical species and the transition state (TS).

TCQjCHOS : A peroxy radical CQjCHO isomerize to form a CQCjO isomer via hydrogen shift.

TCQjCHOE : A peroxy radical CQjCHO decompose to products, $CH_2CO + HO_2$ via HO_2 elimination.

TCXQCjO : A CQCjO isomer undergo β -scission to products, $\text{CH}_2\text{CO} + \text{HO}_2$

TCQXCjO : A CQCjO isomer undergo β -scission to products, $\text{CO} + \text{CH}_2\text{O} + \text{OH}$

3.2 Determination of Entropy and Heat Capacity

The contributions of external rotation and vibrations to entropies and heat capacities are calculated from scaled vibration frequencies and moments of inertia for the optimized HF/6-31G(d') structures. Contributions from frequencies corresponding to hindered internal rotation are replaced with contributions calculated from the method of Pitzer and Gwinn²² for S and $C_p(T)$. Number of optical isomers and spin degeneracy of unpaired electrons are also incorporated.

3.3 High-Pressure Limit A Factors (A_∞) and Rate Constants (k_∞) Determination

For the reactions where thermodynamic properties of TS are calculated by *ab initio* or density functional methods, k_∞ s are fit by three parameters A_∞ , n , and E_a over temperature range from 298 to 2000K, $k_\infty = A_\infty(T)^n \exp(-E_a/RT)$. Entropy differences between reactant and TS are used to determine the pre-exponential factor, A , via conventional transition state theory (TST) for unimolecular and bimolecular reactions $A = (k_b T/h_p) \exp(\Delta S^\ddagger/R)$ and $A = (ek_b T/h_p) \exp(\Delta S^\ddagger/R)$, respectively. h_p is Plank's constant and k_b is the Boltzman constant.

3.4 Kinetic Analysis

Once the potential energy surface and thermochemical properties are evaluated, forward or reverse rate for each, elementary reaction step are determined, Multi-frequency Quantum Rice-Ramsperger-Kassel (QRRK) analysis is then used for $k(E)$ and modified strong collision analysis of Gilbert et. al¹²⁻¹⁴ used for fall-off; to obtain rate constants as a function of temperature and pressure. Reactions which incur a change in number of moles, such as unimolecular dissociation, have energy of activation calculated as ΔU_{rxn} plus an E_a for the reverse addition, where U is internal energy.

A modified QRRK analysis we use in this study is described by Zhong and Bozzelli.²³ It is shown to yield reasonable results and provides a framework by which the effects of temperature and pressure can be evaluated in complex reaction systems. The current version of the QRRK computer code utilizes a reduced set of vibration frequencies which accurately reproduce the molecule (adduct) heat capacity data, with inclusion of one external rotation to calculate density of states $\rho(E)$.

Comparisons of ratios of these $\rho(E)/Q$ (partition function Q) with direct count $\rho(E)/Q$ are shown to be in good agreement.²³ Nonlinear Arrhenius effects resulting from changes in the thermodynamic properties of the respective TST's relative to the adduct with temperature are incorporated using a two parameter Arrhenius pre-exponential factor (A, n) in AT^n .

CHAPTER 4

RESULT AND DISCUSSION FOR PART FOUR

4.1 Geometries of Two Intermediate Radicals and Transition States

Figure 4.1 to 4.5 show MP2/6-31G(d') determined geometries of CQjCHO, CQCjO, TCQjCHOS, TCQjCHOE and TCQXCjO respectively. [names are defined in section 3.1] Figure 4.1 and Figure 4.2 show the optimized geometries of two intermediate radicals, CQjCHO and CQCjO, respectively. Figure 4.3 shows TCQjCHOS structure for isomerization (H shift) reaction. The H₄ atom is in a bridge structure shifting from C₂ to radical site O₅. The leaving bond length H₄-C₂ is calculated as 1.29Å with MP2/6-31G(d') determined geometry; where the H-C bond length in CQjCHO is calculated as 1.11Å. The forming bond length H₄-O₅ is calculated as 1.36Å. All bond lengths are from MP2/6-31G(d') determined geometries. The normal bond length H-O in CQCjO is calculated as 0.97Å. Figure 4.4 shows TCQjCHOE structure, HO₂ elimination of CQjCHO --> CH₂CO + HO₂. The leaving bond length of C₂-H₆ is calculated as 1.31Å and the C-H bond length in CQjCHO is calculated as 1.11Å. The leaving bond length of C₁-O₇ is calculated as 2.31Å and the C-O bond length in CQjCHO is calculated as 1.45Å. The leaving O₇-O₈ bond length is calculated as 1.26Å and the O-O bond length in CQCjO is calculated as 1.45Å. Again all bond lengths are from MP2/6-31G(d') determined geometries.

CQ_jCHO [Q_j = OO. (peroxy), j : radical site]

C(OO.)H₂C(=O)H

Geometry optimization at the MP2/6-31G(d') level of theory.

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C2-O1	1.21				
C3-C2	1.52	C3-C2-O1	121.7		
O4-C3	1.45	O4-C3-C2	111.1	O4-C3-C2-O1	179.5
O5-O4	1.30	O5-O4-C3	110.0	O5-O4-C3-C2	-65.1
H6-C2	1.11	H6-C2-O5	122.9	H6-C2-O5-C3	-179.6
H7-C3	1.10	H7-C3-C2	110.6	H7-C3-C2-O1	58.3
H8-C3	1.10	H8-C3-C2	110.7	H8-C3-C2-O1	-63.8

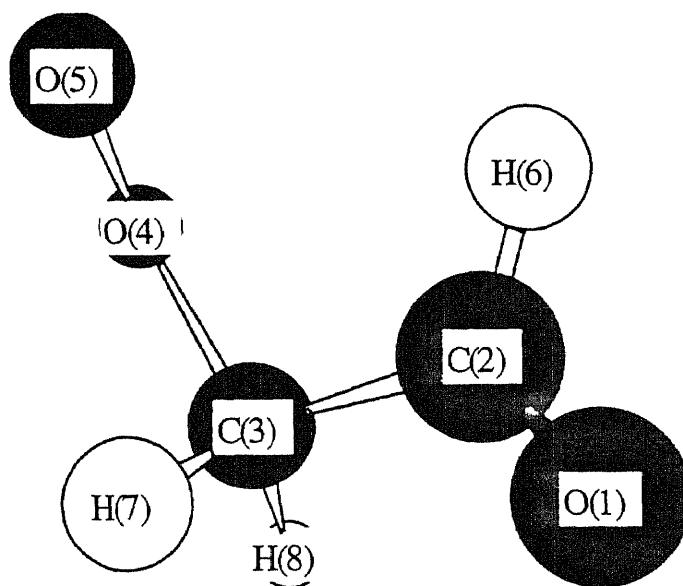


Figure 4.1 Structure for CQ_jCHO

CQCjO [Q = OOH (hydroperoxy group), j : radical site]

C(OOH)H₂C.(=O)

Geometry optimization at the MP2/6-31G(d') level of theory.

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C2-C1	1.54				
O3-C2	1.41	O3-C2-C1	112.3		
O4-O3	1.45	O4-O3-C2	105.1	O4-O3-C2-C1	66.8
O5-C1	1.19	O5-C1-C2	125.9	O5-C1-C2-O3	178.4
H6-C2	1.10	H6-C2-C1	109.1	H6-C2-C1-O3	-116.4
H7-C2	1.10	H7-C2-C1	108.7	H7-C2-C1-O3	123.7
H8-O4	0.97	H8-O4-O3	100.3	H8-O4-O3-C2	-105.2

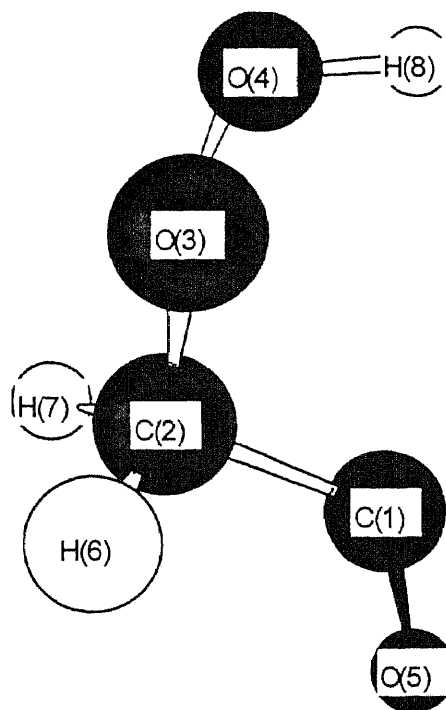
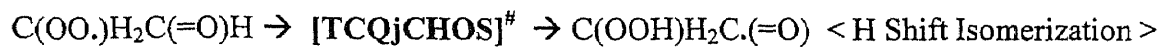


Figure 4.2 Structure for CQCjO

TCQjCHOS

Geometry optimization at the MP2/6-31G(d') level of theory.

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C2-C1	1.60				
O3-C2	1.18	O3-C2-C1	131.6	H4-C2-C1-O3	-176.2
H4-C2	1.29	H4-C2-C1	90.9	O5-H4-C2-C1	3.3
O5-H4	1.36	O5-H4-C2	126.8	O6-O5-H4-C2	-31.1
O6-O5	1.37	O6-O5-H4	92.2	O7-C1-C2-O3	-39.8
H7-C1	1.09	O7-C1-C2	114.5	H8-C1-C2-O3	84.7
H8-C1	1.10	H8-C1-C2	104.9		

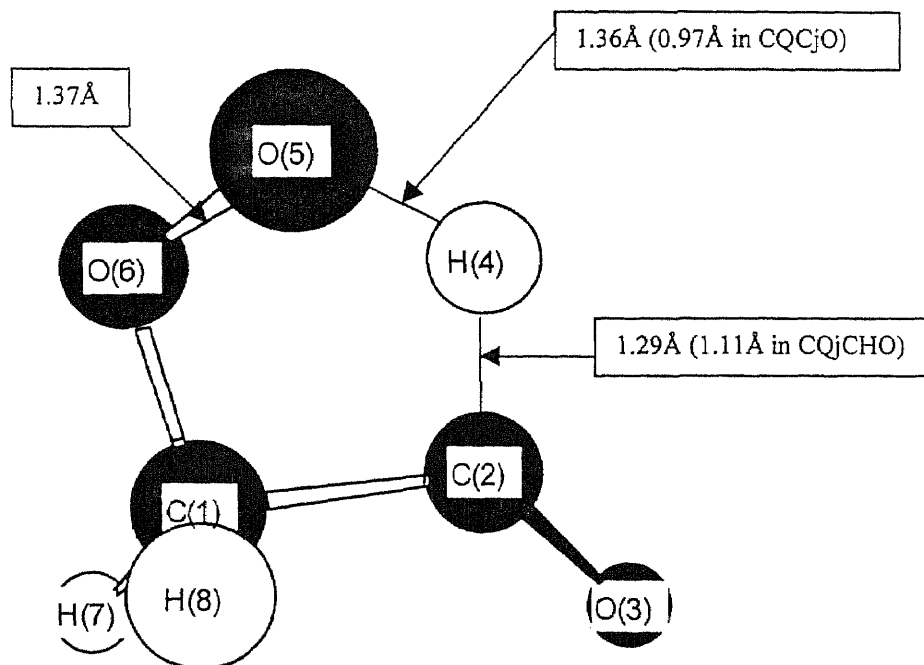
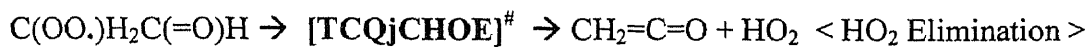


Figure 4.3 Structure for TCQjCHOS

TCQjCHOE



Geometry optimization at the MP2/6-31G(d') level of theory.

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C2-C1	1.39				
H3-C1	1.08	H3-C1-C2	120.8		
H4-C1	1.08	H4-C1-C2	120.8	H4-C1-C2-H3	-174.9
O5-C2	1.20	O5-C2-C1	146.9	O5-C2-C1-H3	-92.7
H6-O2	1.31	H6-C2-C1	97.6	H6-C2-C1-H3	87.4
O7-H6	1.97	O7-H6-C2	113.0	O7-H6-C2-C1	0.0
O8-O7	1.26	O8-O7-H6	42.9	O8-O7-C2-C2	180.0

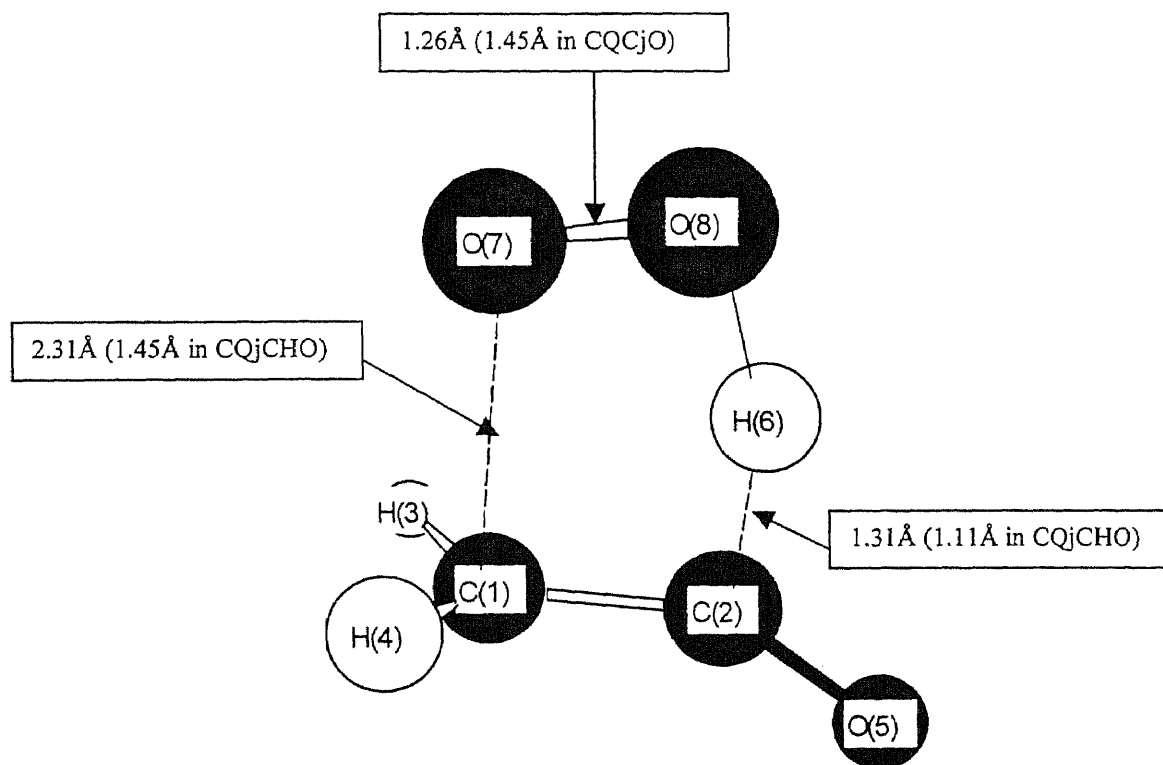


Figure 4.4 Structure for TCQjCHOE

TCQXCjO

Geometry optimization at the MP2/6-31G(d') level of theory.

Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)	
C2-C1	2.32				
O3-C2	1.36	O3-C2-C1	103.4		
O4-O3	1.45	O4-O3-C2	108.6	O4-O3-C2-C1	-73.8
O5-C1	1.16	O5-C1-C2	106.8	O5-C1-C2-O3	19.3
H6-C2	1.09	H6-C2-C1	99.5	H6-C2-C1-O3	-120.7
H7-C2	1.09	H7-O2-C1	103.1	H7-O2-C1-O3	114.9
H8-O4	0.98	H8-O4-O3	99.6	H8-O4-O3-C2	92.2

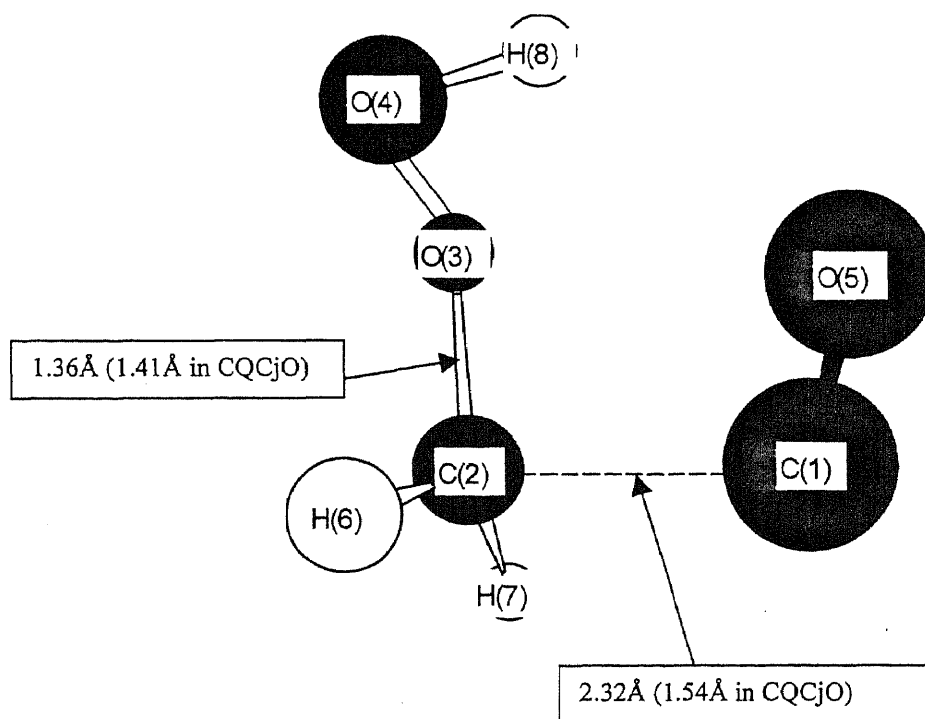


Figure 4.5 Structure for TCQXCjO

Figure 4.5 shows TCQXCjO structure, β -scission of CQCjO \rightarrow CO + CH₂OOH. The leaving bond length C₁-C₂ is calculated as 2.32Å and the C-C bond length in CQCjO is calculated as 1.54Å. The C₂-O₃ bond is calculated as 1.36Å and the C-O bond length in CQCjO is calculated as 1.41Å.

4.2 Estimation of Entropy ($S^{\circ}_{(298)}$) and Heat Capacity ($C_p(T)$'s, 300 - 1500K)

$S^{\circ}_{(298)}$ and $C_p(T)$'s are calculated based on vibration frequencies and moments of inertia of the optimized HF/6-31G(d') structures. (Table 4.1 and Table 4.2)

The calculation results using MP2/6-31G(d') determined geometries and HF/6-31G(d') determined frequencies are summarized in Table 4.3. TVR represents the sum of the contributions from translations, vibrations and external rotations for $S^{\circ}_{(298)}$ and $C_p(T)$'s. Symmetry, optical isomer and electronic spin are incorporated in estimation of $S^{\circ}_{(298)}$ as described in Table 4.3. Contributions of internal rotation for $S^{\circ}_{(298)}$ and $C_p(T)$'s are calculated based on rotational barrier heights, moments of inertia of the rotors using the method of Pitzer and Gwinn's²². (Table 4.4)

4.3 Estimation of Enthalpy of Formation ($\Delta H_f^{\circ}_{298}$) using Total Energies and Isodesmic Reactions

The overall energy diagram for the CjCHO + O₂ reaction system is illustrated in Figure 4.6.

CBSQ calculations are performed on the MP2/6-31G(d') determined geometries and HF/6-31G(d') determined frequencies. Density functionals are performed on the B3LYP/6-31G(d) determined geometries and frequencies.

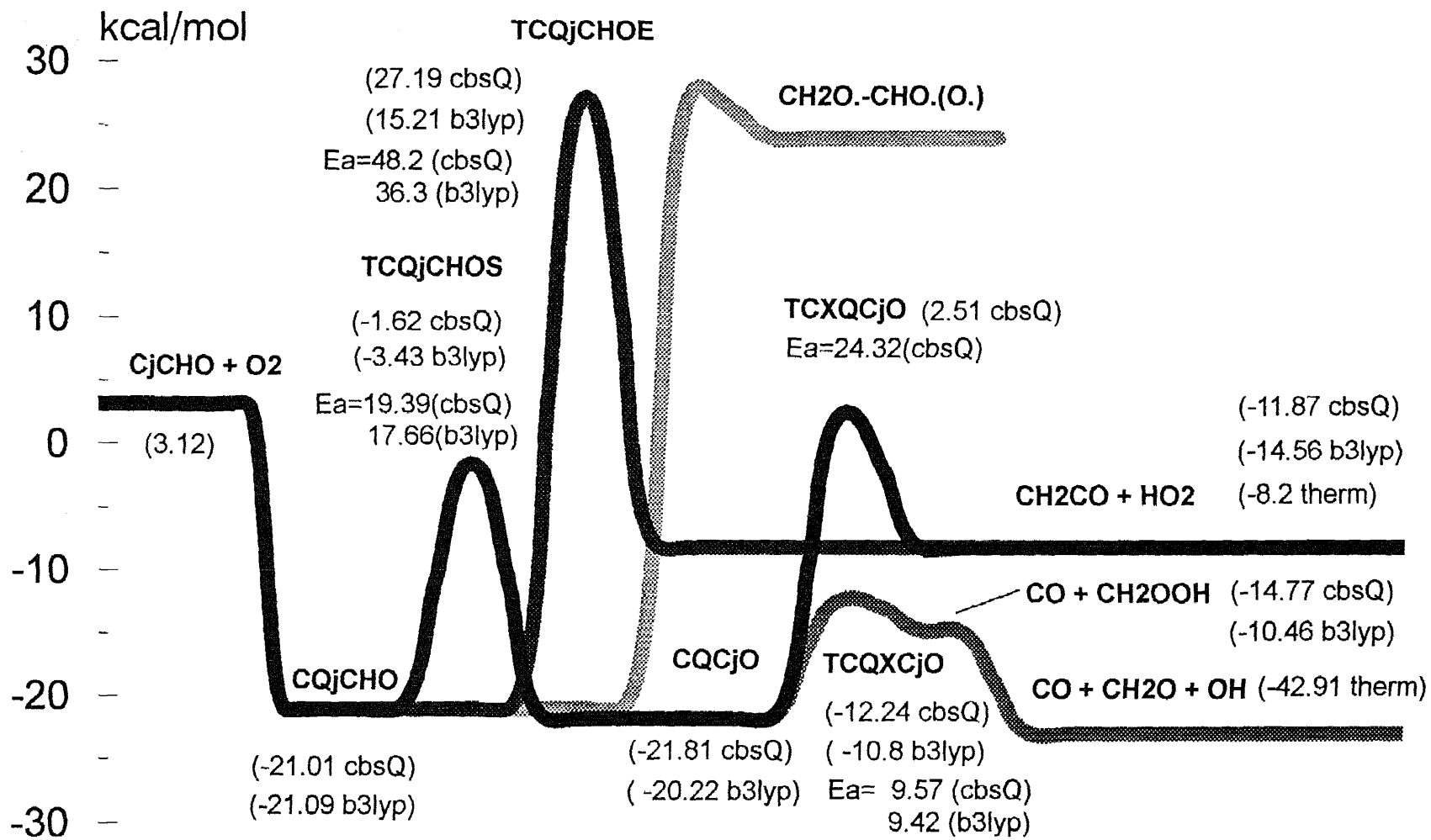


Figure 4.6 Potential Energy Diagram $C_jCHO + O_2$

[Q=OOH, Qj=OO., j=radical site]

Table 4.1 Vibrational Frequencies^a (ν cm^{-1}) HF/6-31G(d') level of calculation

Species	Vibrational Frequencies																	
CjCHO	522	536	769	1015	1051	1214	1424	1546	1599	3223	3325	3437						
CQCHO	74	86	181	336	459	620	810	1047	1134	1230	1246	1394	1468	1540	1588	1612	2035	3170
	3239	3298	4113															
CQjCHO	70	132	336	476	637	811	1088	1126	1240	1280	1400	1470	1542	1591	2038	3172	3258	3322
CQCjO	110	188	242	341	452	622	938	978	1067	1258	1388	1475	1576	1592	2156	3236	3305	4094
TCQjCHOS ^b	-3103.6 ^f	216	389	413	587	743	881	998	1062	1207	1215	1347	1427	1597	1826	2174	3226	3325
TCQjCHOE ^c	-3393.3 ^f	64	111	164	274	350	422	617	783	879	1023	1159	1412	1551	1623	2110	3313	3420
TCXQCjO ^d	-761.3 ^f	54	141	288	391	435	496	725	989	1085	1145	1188	1556	1602	2255	3316	3408	4060
TCQXCjO ^e	-858.9 ^f	19	30	40	87	101	252	362	439	899	1209	1243	1381	1566	2423	3296	3433	4097
CH2OOH	160.8 ^f	282	526	853	1045	1289	1314	1560	1620	3302	3440	4105						

^a non-scaled. ^{b,c,d,e} Transition State Structure described in results section.

^f Transition State, one imaginary frequency.

Table 4.2 Moments of Inertia ($\text{amu}\cdot\text{Bohr}^2$) HF/6-31G(d') level of calculation

Species	I_A	I_B	I_C	Species	I_A	I_B	I_C
CjCHO	26.75	155.67	182.43	TCQjCHOE	196.29	651.84	835.95
CQCHO	120.40	607.17	672.79	TCXQCjO	177.37	566.48	690.74
CQjCHO	103.48	609.46	665.24	TCQXCjO	158.53	945.93	1092.42
CQCjO	111.26	609.24	678.83	CH2OOH	31.28	154.47	181.22
TCQjCHOS	133.47	485.29	589.56				

Table 4.3 Ideal Gas Phase Thermodynamic Properties Obtained by CBSQ Calculation^a and by Therm*

Species (s, e, OI) ^g		$\Delta H_f^\circ_{298}$ ^b	S°_{298} ^c	C_{p300} ^c	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
CjCHO**	TVR ^d		61.25	11.77	14.21	16.32	18.07	20.76	22.71	25.71
(C.H2-C(=O)H)	Internal Rotor 1 ^f		4.69	1.64	1.42	1.30	1.21	1.12	1.08	1.03
(1,1/2,1)	Total		65.94	13.41	15.63	17.62	19.28	21.88	23.79	26.74
	THERM	3.12	61.79	12.93	15.35	17.44	19.24	22.10	24.17	27.14
CQCHO***	TVR		69.25	15.10	18.82	22.20	25.05	29.44	32.58	37.30
(C(OOH)H2-C(=O)H)	Internal Rotor 1,2,3		13.56	3.99	5.82	5.92	5.93	5.84	5.68	5.20
(1,0,2)	Total	-56.61	82.81	19.09	24.64	28.12	30.98	35.28	38.26	42.50
	THERM	-57.15	82.24	22.34	25.60	28.29	30.68	34.77	37.81	
CQjCHO***	TVR		68.79	14.86	18.37	21.49	24.10	28.06	30.81	34.77
(C(OO.)H2-C(=O)H)	Internal Rotor 1,2		11.34	1.99	1.94	1.80	1.66	1.44	1.32	1.15
(1,1/2,1)	Total	-21.01	80.13	16.85	20.31	23.29	25.76	29.50	32.13	35.92
	THERM	-21.05	82.46	20.29	22.76	24.74	26.59	30.05	32.84	
CQCjO	TVR		70.40	14.64	17.81	20.58	22.89	26.39	28.88	32.62
(C(OOH)H2-C(=O))	Internal Rotor 1,2,3		11.38	5.90	6.35	6.49	6.45	6.09	5.59	4.59
(1,1/2,2)	Total	-21.81	81.78	20.54	24.16	27.07	29.34	32.48	34.47	37.21
	THERM	-20.25	80.85	22.15	24.75	26.70	28.47	31.56	33.92	
TCQjCHOS	TVR		70.09	17.85	21.71	24.96	27.58	31.41	33.98	37.51
(1,1/2,2)	Total	-1.62	70.09	17.85	21.71	24.96	27.58	31.41	33.98	37.51
TCQjCHOE	TVR		81.23	22.66	25.70	28.18	30.17	33.12	35.15	38.05
(1,1/2,2)	Total	27.19	81.23	22.66	25.70	28.18	30.17	33.12	35.15	38.05
TCXQCjO	TVR		70.81	16.98	19.98	22.41	24.37	27.35	29.52	32.89
(1,1/2,2)	Internal Rotor 1,2		5.34	3.60	4.06	4.33	4.46	4.37	4.07	3.33
	Total	2.51	76.15	20.58	24.04	26.74	28.83	31.72	33.59	36.22
TCQXCjO	TVR		85.82	20.33	22.39	24.17	25.69	28.12	30.01	33.10
(1,1/2,2)	Internal Rotor 1,2,3		11.38	5.90	6.35	6.49	6.45	6.09	5.59	4.59
	Total	-12.24	97.20	26.23	28.74	30.66	32.14	34.21	35.60	37.69
CH2OOH	TVR		61.46	11.15	13.22	15.05	16.57	18.93	20.68	23.52
(1,1/2,2)	Internal Rotor 1,2		4.77	3.61	4.05	4.33	4.48	4.45	4.19	3.44
	Total		66.23	14.76	17.27	19.38	21.05	23.38	24.87	26.96
	THERM	15.20	65.41	15.60	18.12	20.15	21.79	24.14	25.65	27.65

* : therm values for stable species are included for comparison

** j : radical site, *** Q = OOH (hydroperoxy group), Qj = OO.(peroxy)

a : Thermodynamic properties are referred to a standard state of an ideal gas of pure enantiomer at 1 atm.

b : Units in kcal/mol c : Units in cal/mol-K

d : Sum of contributions from translations, vibrations, and external rotations.

f : Contribution from internal rotation

g : Symmetry number, optical isomer and electronic spin are taken into account, -Rln(s), Rln2, Rln2, respectively.

s = number of symmetry, e = electronic spin, OI = number of optical isomer

Table 4.4 Moments of Inertia ($\text{amu}\cdot\text{A}^2$) and Rotational Barriers (kcal/mole)
for Internal Rotors

Species	Rotor	I_A	I_B	V	n^a
CjCHO ^b	C.H2--C(=O)H	1.75	18.90	1.20	2
CQCHO ^c	CHO--C(OOH)H2	18.90	114.36	13.00	6
	CHOC(H2)--OOH	114.63	1.56	2.50	3
	CHOC(H2)O--OH	120.00	0.86	6.38	1
CQjCHO ^d	CHO--C(OO.)H2	18.90	108.88	13.00	6
	CHOC(H2)--OO.	114.63	1.47	2.50	3
CQCjO	C.O--C(OOH)H2	23.81	114.36	3.26	3
	C(C.O)H2--OOH	116.71	1.56	5.40	3
	C(C.O)H2O--OH	100.00	0.86	6.38	1
TCXQCjO	C(C.O)H2--OOH	116.71	1.56	5.40	3
	C(C.O)H2O--OH	100.00	0.86	6.38	1
TCQXCjO	C.O--C(OOH)H2	23.81	114.36	3.26	3
	C(C.O)H2--OOH	116.71	1.56	5.40	3
	C(C.O)H2O--OH	100.00	0.86	6.38	1
CH2OOH	C.H2--OOH	1.75	1.56	6.46	2
	C.H2O--OH	27.44	1.10	5.98	1

^a n : foldness

^b "j" stands for radical site.

^c "Q" stands for hydroperoxy group(OOH).

^d "Qj" stands for peroxy (OO.).

Table 4.5 List of Total Energy, ZPVE, and Thermal Correction of CBSQ Calculation^a

Species	Total Energy at 0K ^b	ZPVE ^c	Thermal Correction ^d	Total Energy at 298K ^b
CjCHO ^e	-152.9289585	0.0447890	0.0043670	-152.9245915
CQCHO ^f	-303.7676261	0.0698900	0.0068810	-303.7607451
CQjCHO ^g	-303.1306731	0.0569290	0.0061780	-303.1244951
CQCjO	-303.1274466	0.0569890	0.0065010	-303.1209456
TCQjCHOS	-303.0965504	0.0515610	0.0053710	-303.0911794
TCQjCHOE	-303.0514196	0.0439090	0.0073810	-303.0440386
TCXQCjO	-303.0889178	0.0526960	0.0067360	-303.0821818
TCQXCjO	-303.1128718	0.0483070	0.0071840	-303.1056878
CH2OOH	-189.9367183	0.0444130	0.0051750	-189.9315433

^a Unit in Hartree 1 HF=627.51 kcal/mol.

^b Scaled ZPVE are included. Scaling factor is recommended as 0.91844 by Petersson et.al [22]

^c Non-scaled.

^d Non-scaled.

^e "j" stands for radical site.

^f "Q" stands for hydroperoxy group(OOH).

^g "Qj" stands for peroxy(OO.).

Isodesmic reactions are applied to accurately estimate $\Delta H_f^{\circ}_{298}$ of CQCHO and two intermediate radicals, CQCjO and CQjCHO. Zero point Vibration energies (ZPVE's) and thermal corrections to 298.15 K are taken into account. The total energies at 0 K including scaled ZPVE's, nonscaled ZPVE's, thermal corrections to 298.15 K, and total energies at 298 K including scaled ZPVE's are shown in Table 4.5 for CBSQ calculations. Frequencies are scaled by 0.91844 for HF/6-31G(d') determined frequencies as recommended by Petersson et al.¹⁷

Table 4.6 Molecule Considered to Have Known $\Delta H_f^{\circ}_{298}$ for Use in Isodesmic Reactions.

Compounds	$\Delta H_f^{\circ}_{298}$ (kcal/mole) [reference]
CH ₃ CH ₃	-20.03 [24]
CH ₃ C(=O)H	-39.72 [24]
CH ₃ CH ₂ OOH	-39.9 [25]

The evaluated enthalpies of formation for the molecules considered to have known $\Delta H_f^{\circ}_{298}$ values, for use in the isodesmic reaction, are: -20.03[24], -39.72[24], and -39.9[25] for CH₃CH₃, CH₃C(=O)H, and CH₃CH₂OOH, respectively. A low or zero $\Delta H^{\circ}_{\text{rxn},298}$ supports the hypothesis of group additivity and increases credibility of the calculations.

The CBSQ and density functionals determined enthalpy of reaction (1) is -2.98 and -3.16 kcal/mole, respectively. $\Delta H_f^{\circ}_{298}$ [CQCHO] is evaluated from

$$\begin{aligned} \Delta H^{\circ}_{\text{rxn},298} &= \Delta H_f^{\circ}_{298} [\text{CH}_3\text{C}(=\text{O})\text{H}] + \Delta H_f^{\circ}_{298} [\text{CH}_3\text{CH}_2\text{OOH}] \\ &\quad - \Delta H_f^{\circ}_{298} [\text{CQCHO}] - \Delta H_f^{\circ}_{298} [\text{CH}_3\text{CH}_3] = -2.98 \text{ or } -3.16 \\ &= -39.72 + (-39.9) - X - (-20.03) \text{ kcal/mole} \dots\dots\dots(4) \end{aligned}$$

The enthalpy of formation of CCOQ obtained is -56.61 and -56.43 kcal/mole in CBSQ and density functionals calculations, respectively.

The enthalpy of formation of two intermediate radicals, CQCjO and CQjCHO by CBSQ and density functionals are obtained from use of isodesmic reactions (2) and (3) and bond dissociation energy of $\text{C}_2\text{H}_5\text{—H}$ (101.6 kcal/mole) and $\text{CH}_3\text{OO—H}$ (86.3 kcal/mole) The data results in enthalpy values are -21.81 and -20.22 for CQCjO, -21.01 and -21.09 for CQjCHO, in CBSQ and density functionals calculations, respectively.

Formation of CQjCHO adduct has a well depth of 24.13 kcal/mole.

The activation energy for isomerization, TCQjCHOS, is estimated from both the reactant CQjCHO and the product CQCjO. The averaged result is 19.39 and 17.66 kcal/mole in CBSQ and density functionals, respectively. The activation energy for direct HO_2 elimination, TCQjCHOE, is estimated by taking the difference of total energy with ZPVE and thermal correction between transition state(TS) and peroxy reactant, resulting in 27.19 and 15.21 kcal/mole in CBSQ and density functionals, respectively. The activation energy for HO_2 elimination from the hydroperoxide isomer, TCXQCjO, is estimated by taking the difference of total energy with ZPVE and thermal correction between transition state(TS) and reactant, resulting in 24.32 kcal/mole via CBSQ. The activation energy for β -scission to $\text{CO} + \text{CH}_2\text{OOH}$, TCQXCjO, is estimated by taking the difference of total energy with ZPVE and thermal correction between transition state(TS) and hydroperoxide isomer, resulting in 9.57 and 9.42 kcal/mole in CBSQ and density functionals, respectively.

4.4 QRRK Calculation Results

QRRK calculations for $k(E)$ and modified strong collision analysis of Gilbert et. al¹²⁻¹⁴ for fall-off are performed on the $C_2HCHO + O_2$ reaction to obtain rate constants as a function of temperature and pressure and results are listed in Table 4.7. ΔE down of 400 cal/mole is used for bath gas N_2 .

Plots of rate constants at 1 atm pressure versus $1000/T$ are illustrated in Figure 4.7. Stabilization (C_2HCHO), reverse dissociation, and $CO + CH_2O + OH$ products via H shift are important at lower temperatures, 1 atm pressure, with reverse dissociation, $CO + CH_2O + OH$ products via H shift and ketene + HO_2 products via H shift important at higher temperatures.

Plots of rate constants at 298 K versus pressure are illustrated in Figure 4.8.

The figure illustrates that stabilization is the dominant path at high pressures, while stabilization (C_2HCHO), reverse dissociation, and $CO + CH_2O + OH$ products via H shift are important at low pressures.

Plots of rate constants at 1000 K versus pressure are illustrated in Figure 4.9.

The figure illustrates that stabilization decreases as pressure is decreased. Reverse dissociation and $CO + CH_2O + OH$ products via H shift are most important at both high and low pressures.

Table 4.7 Input Parameters^a and High-Pressure Limit Rate Constants (K_{∞})^b for QRRK Calculations^c and the Resulting Rate Constants (Temp=298K) : CBSQ Result (adjusted)

Input parameters for QRRK calculations			
High-pressure Limit Rate Constants			
Reaction	A[S ⁻¹ or cm ³ /(mole s)]	k_{∞}	
		n	Ea (kcal/mole)
1 CjCHO + O ₂ => CQjCHO ^d	1.57E+11	0.0	0.0
-1 CQjCHO => CjCHO + O ₂ ^e	1.96E+13	0.0	23.03
2 CQjCHO => CQCjO ^f	5.00E+5	2.14	18.57
3 CQjCHO => CH ₂ CO + HO ₂ ^f	4.99E+5	2.74	47.48
4 CQCjO => CO +CH ₂ O + OH ^f	8.47E+10	2.04	9.40
5 CQCjO => CH ₂ CO + HO ₂ ^f	1.47E+10	0.65	24.61

Calculated Reaction Parameters at P = 1atm, $k=A(T/K)^n \exp(-E_a/RT)$ (T=298-2000K)

Reaction	A	n	Ea (kcal/mole)	$k_{298}(s^{-1}$ or cm ³ /(mole s))
1 CjCHO + O ₂ => CQjCHO	2.87E+37	-8.73	6.42	1.41E+11
6 CjCHO + O ₂ => CH ₂ CO + HO ₂	2.68E-06	5.46	21.76	9.00E-09
7 CjCHO + O ₂ => CO +CH ₂ O + OH	1.25E+14	-1.05	4.99	6.90E+07
8 CjCHO + O ₂ => CQCjO	2.07E+14	-3.74	2.71	1.19E+03
2 CQjCHO => CQCjO	3.11E+29	-8.48	22.88	5.00E-09
3 CQjCHO => CH ₂ CO + HO ₂	1.02E+16	-1.64	48.33	3.19E-24
4 CQCjO => CO +CH ₂ O + OH	3.44E+18	-2.90	6.93	1.90E+06
5 CQCjO => CH ₂ CO + HO ₂	5.57E+09	-1.92	21.86	9.17E-12

^aGeometric mean frequency (from CPFIT, Ref.[34]: 529.0 cm⁻¹(6.962); 1518.5 cm⁻¹ (8.074); 3999.8 cm⁻¹ (1.964). Lennard-Jones parameters: $\sigma_{ij}=5.19\text{\AA}$, $\epsilon/k=533.08$

^bThe units of A factors and rate constants k are s⁻¹ for unimolecular reactions and cm³/(mole s) for bimolecular reactions.

^c ΔE down of 400 cal/mole is used.

^d $k_{\infty,1}$: Baulch et al. [26]

^e $k_{\infty,-1}$: thermodynamics and microscopic reversibility <MR>

^f A is calculated using TST and entropy of transition state, $\Delta S_{298}^{\ddagger}$ from HF/6-31G(d') (see Table 4.3); Ea is from CBSQ calculation (see Table 4.3 and description for determination of Ea in Results section). All parameters A, n, Ea, are fit over the temperature range of 298-2000K.

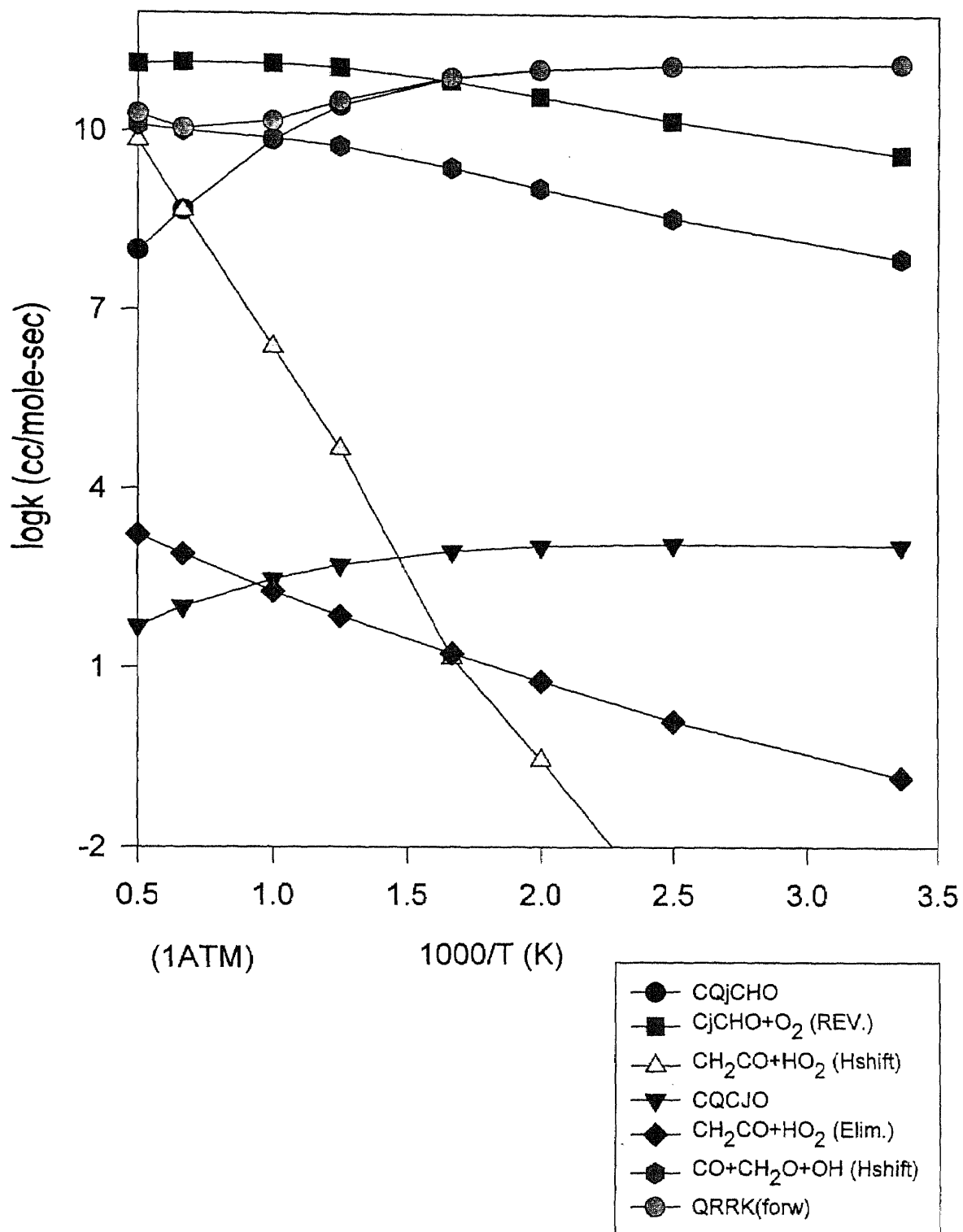


Figure 4.7 k vs. Temperature at 1atm CjCHO + O₂

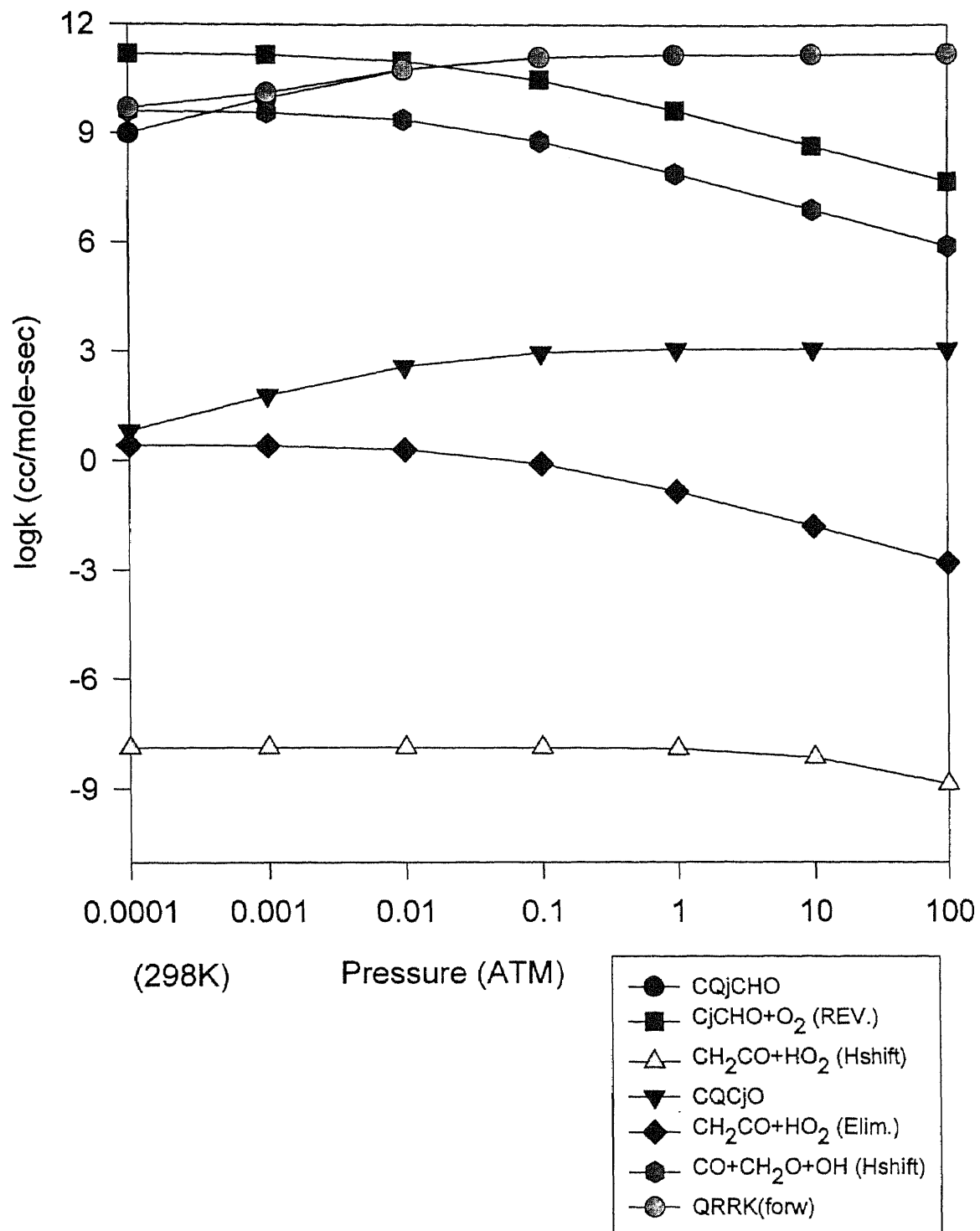


Figure 4.8 k vs. Pressure at 298K CjCHO + O₂

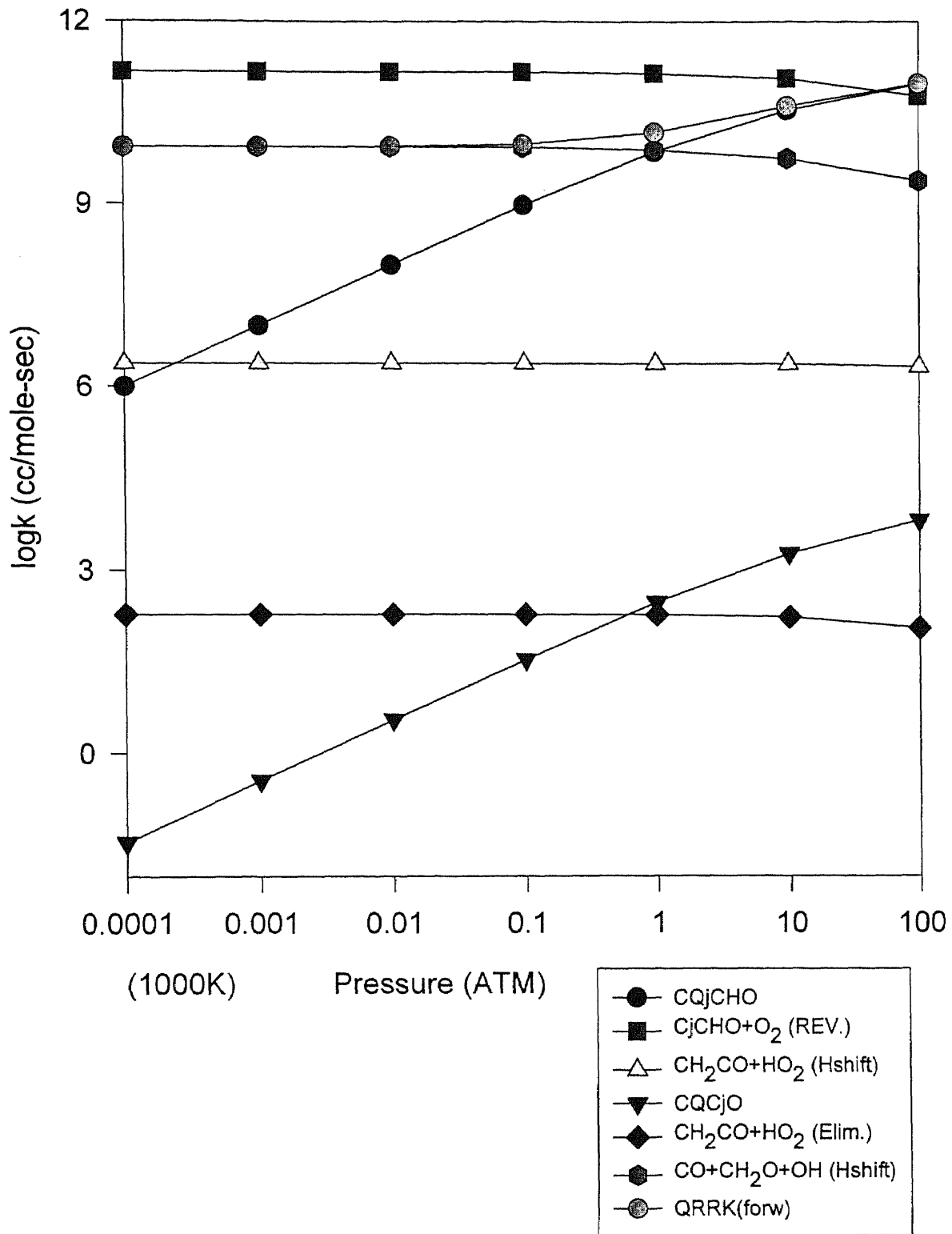


Figure 4.9 k vs. Pressure at 1000K CjCHO + O₂

CHAPTER 5

SUMMARY FOR PART FOUR

Thermodynamic properties of stable radicals and transition states on $C_jCHO + O_2$ reaction system are calculated using density functional and *ab initio* methods.

Enthalpies of formation ($\Delta H_f^\circ_{298}$) are determined using the CBSQ composite method and density functional calculations with isodesmic reactions. Entropies (S°_{298}) and heat capacities ($C_p(T)$ 300 –1500 K) are determined using geometric parameters and vibrational frequencies obtained at the HF/6-31G(d') level of theory.

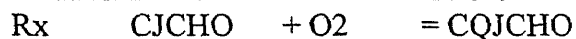
Reaction pathways and kinetics are analyzed on $C_jCHO + O_2$ reaction system using QRRK for $k(E)$ and modified strong collision analysis of Gilbert et. al¹²⁻¹⁴ for fall-off.

Major reaction paths at 1atm pressure are stabilization of CQ_jCHO peroxy adduct at low temperature and $CO + CH_2O + OH$ products via H shift and ketene + HO_2 products via H shift at high temperature.

APPENDIX 4.1

THERMODYNAMIC ANALYSIS FOR C_jCHO + O₂ REACTION

THERMODYNAMIC ANALYSIS for REACTION



Hf {Kcal/mol} 3.120 .000 -21.010

S {cal/mol K} 65.940 46.630 80.130

dHr {kcal/mol} (298K) = -24.13 dHr avg (298., 1500. K) = -24.82

dU (dE) {kcal/mol} (") = -23.54 dUr avg (298., 1500. K) = -23.03

dSr {cal/mol K} (") = -32.44 dSr avg (298., 1500. K) = -33.85

dGr {kcal/mol} (") = -14.46 dGr avg (298., 1500. K) = 5.61

Af/Ar (") = 5.401E-03 Af/Ar avg (298., 1500. K) = 8.024E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.414E+01	-2.354E+01	-3.247E+01	5.359E-03	-1.440E+01
400.00	-2.453E+01	-2.374E+01	-3.360E+01	4.032E-03	-1.109E+01
500.00	-2.483E+01	-2.383E+01	-3.427E+01	3.613E-03	-7.693E+00
600.00	-2.504E+01	-2.385E+01	-3.466E+01	3.550E-03	-4.245E+00
800.00	-2.531E+01	-2.372E+01	-3.505E+01	3.895E-03	2.733E+00
1000.00	-2.543E+01	-2.344E+01	-3.519E+01	4.539E-03	9.760E+00
1200.00	-2.548E+01	-2.310E+01	-3.524E+01	5.319E-03	1.680E+01
1500.00	-2.550E+01	-2.252E+01	-3.525E+01	6.595E-03	2.738E+01
2000.00	-2.545E+01	-2.148E+01	-3.522E+01	8.920E-03	4.500E+01

APPENDIX 4.2

KINETIC ANALYSIS FOR C_jCHO + O₂ REACTION

THERMODYNAMIC ANALYSIS for REACTION

Rx CQJCHO = TCQJCHOS

Hf {Kcal/mol} -21.010 -1.620

S {cal/mol K} 80.130 70.090

dHr {kcal/mol} (298K) = 19.39 dHr avg (298., 1500. K) = 20.79

dU (dE) {kcal/mol} (") = 19.39 dUr avg (298., 1500. K) = 20.79

dSr {cal/mol K} (") = -10.04 dSr avg (298., 1500. K) = -8.36

dGr {kcal/mol} (") = 22.38 dGr avg (298., 1500. K) = 28.31

Af/Ar (") = 6.391E-03 Af/Ar avg (298., 1500. K) = 1.488E-02

Fit Af/Ar : A = 1.380E-04 n = .63 alpha = -5.650E-04 avg error 3.62 %

Fit Af/Ar w/ddU: A = 2.963E-06 n = 1.31 alpha = -4.459E-04 avg error 5.51 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	1.939E+01	1.939E+01	-1.003E+01	6.411E-03	2.240E+01
400.00	1.951E+01	1.951E+01	-9.694E+00	7.608E-03	2.339E+01
500.00	1.966E+01	1.966E+01	-9.352E+00	9.035E-03	2.434E+01
600.00	1.985E+01	1.985E+01	-9.015E+00	1.071E-02	2.526E+01
800.00	2.030E+01	2.030E+01	-8.373E+00	1.479E-02	2.700E+01
1000.00	2.082E+01	2.082E+01	-7.795E+00	1.978E-02	2.861E+01
1200.00	2.137E+01	2.137E+01	-7.293E+00	2.547E-02	3.012E+01
1500.00	2.219E+01	2.219E+01	-6.681E+00	3.466E-02	3.221E+01
2000.00	2.350E+01	2.350E+01	-5.926E+00	5.067E-02	3.535E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{prime} * T^n * \exp(-E_a/RT)$

$A_{prime} = 5.0008E+04$ $n = 2.14395$ $E_a = 1.8566E+04$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	4.008E+10	2.046E+05	2.984E-04	3.041E-04
400.00	6.341E+10	3.790E+05	1.384E+00	1.357E+00
500.00	9.413E+10	6.116E+05	2.386E+02	2.341E+02
600.00	1.338E+11	9.041E+05	7.864E+03	7.796E+03
800.00	2.465E+11	1.675E+06	7.016E+05	7.089E+05
1000.00	4.122E+11	2.703E+06	1.162E+07	1.183E+07
1200.00	6.369E+11	3.996E+06	8.165E+07	8.297E+07
1500.00	1.083E+12	6.447E+06	6.327E+08	6.354E+08
2000.00	2.112E+12	1.195E+07	5.706E+09	5.588E+09

THERMODYNAMIC ANALYSIS for REACTION

Rx CQCJO = TCQJCHOS

Hf {Kcal/mol} -21.810 -1.620

S {cal/mol K} 81.780 70.090

dHr {kcal/mol} (298K) = 20.19 dHr avg (298., 1500. K) = 20.14

dU (dE) {kcal/mol} (") = 20.19 dUr avg (298., 1500. K) = 20.14

dSr {cal/mol K} (") = -11.69 dSr avg (298., 1500. K) = -12.31

dGr {kcal/mol} (") = 23.68 dGr avg (298., 1500. K) = 31.21

Af/Ar (") = 2.786E-03 Af/Ar avg (298., 1500. K) = 2.038E-03

Fit Af/Ar : A = 3.897E+01 n = -1.78 alpha = -1.860E-03 avg error 4.41 %

Fit Af/Ar w/ddU: A = 1.595E+04 n = -2.94 alpha = -3.409E-03 avg error 12.67 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.018E+01	2.018E+01	-1.171E+01	2.762E-03	2.370E+01
400.00	1.992E+01	1.992E+01	-1.246E+01	1.891E-03	2.491E+01
500.00	1.970E+01	1.970E+01	-1.295E+01	1.475E-03	2.618E+01
600.00	1.953E+01	1.953E+01	-1.326E+01	1.262E-03	2.749E+01
800.00	1.937E+01	1.937E+01	-1.351E+01	1.116E-03	3.018E+01
1000.00	1.942E+01	1.942E+01	-1.346E+01	1.144E-03	3.288E+01
1200.00	1.962E+01	1.962E+01	-1.327E+01	1.256E-03	3.555E+01
1500.00	2.008E+01	2.008E+01	-1.293E+01	1.491E-03	3.948E+01
2000.00	2.108E+01	2.108E+01	-1.236E+01	1.987E-03	4.580E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$ A_{prime} = 1.1349E+08 n = .82014 E_a = 1.9946E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.726E+10	1.075E+02	3.398E-05	3.586E-05
400.00	1.576E+10	1.362E+02	2.045E-01	1.950E-01
500.00	1.536E+10	1.635E+02	3.745E+01	3.543E+01
600.00	1.578E+10	1.899E+02	1.208E+03	1.168E+03
800.00	1.860E+10	2.404E+02	9.493E+04	9.692E+04
1000.00	2.384E+10	2.887E+02	1.359E+06	1.431E+06
1200.00	3.141E+10	3.352E+02	8.371E+06	8.858E+06
1500.00	4.660E+10	4.026E+02	5.520E+07	5.667E+07
2000.00	8.279E+10	5.097E+02	4.113E+08	3.823E+08

THERMODYNAMIC ANALYSIS for REACTION

Rx CQJCHO = TCQJCHOE

Hf {Kcal/mol} -21.010 27.190

S {cal/mol K} 80.130 81.230

dHr {kcal/mol} (298K) = 48.20. dHr avg (298., 1500. K) = 50.17

dU (dE) {kcal/mol} (") = 48.20 dUr avg (298., 1500. K) = 50.17

dSr {cal/mol K} (") = 1.10 dSr avg (298., 1500. K) = 4.21

dGr {kcal/mol} (") = 47.87 dGr avg (298., 1500. K) = 46.39

Af/Ar (") = 1.740E+00 Af/Ar avg (298., 1500. K) = 8.327E+00

Fit Af/Ar : A = 7.022E-08 n = 3.08 alpha = 1.545E-03 avg error 4.29 %

Fit Af/Ar w/ddU: A = 3.717E-13 n = 5.35 alpha = 3.562E-03 avg error 15.55 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	4.821E+01	4.821E+01	1.136E+00	1.772E+00	4.787E+01
400.00	4.877E+01	4.877E+01	2.746E+00	3.983E+00	4.767E+01
500.00	4.927E+01	4.927E+01	3.866E+00	6.999E+00	4.734E+01
600.00	4.972E+01	4.972E+01	4.682E+00	1.055E+01	4.691E+01
800.00	5.047E+01	5.047E+01	5.766E+00	1.821E+01	4.585E+01
1000.00	5.106E+01	5.106E+01	6.432E+00	2.546E+01	4.463E+01
1200.00	5.155E+01	5.155E+01	6.875E+00	3.182E+01	4.329E+01
1500.00	5.214E+01	5.214E+01	7.323E+00	3.986E+01	4.116E+01
2000.00	5.289E+01	5.289E+01	7.753E+00	4.950E+01	3.738E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$ A_{prime} = 4.9884E+05 n = 2.74176 E_a = 4.7476E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.107E+13	6.190E+06	8.314E-23	7.955E-23
400.00	3.320E+13	1.362E+07	7.460E-14	7.770E-14
500.00	7.291E+13	2.511E+07	2.114E-08	2.210E-08
600.00	1.319E+14	4.140E+07	1.022E-04	1.048E-04
800.00	3.035E+14	9.111E+07	4.948E+00	4.860E+00
1000.00	5.305E+14	1.680E+08	3.669E+03	3.520E+03
1200.00	7.957E+14	2.769E+08	3.253E+05	3.112E+05
1500.00	1.246E+15	5.106E+08	3.143E+07	3.078E+07
2000.00	2.063E+15	1.124E+09	3.427E+09	3.633E+09

THERMODYNAMIC ANALYSIS for REACTION

Rx CQCJO = TCXQCJO

Hf {Kcal/mol} -21.810 2.510

S {cal/mol K} 81.780 76.150

dHr {kcal/mol} (298K) = 24.32 dHr avg (298., 1500. K) = 23.89

dU (dE) {kcal/mol} (") = 24.32 dUr avg (298., 1500. K) = 23.89

dSr {cal/mol K} (") = -5.63 dSr avg (298., 1500. K) = -6.09

dGr {kcal/mol} (") = 26.00 dGr avg (298., 1500. K) = 29.37

Af/Ar (") = 5.881E-02 Af/Ar avg (298., 1500. K) = 4.656E-02

Fit Af/Ar : A = 8.471E-02 n = -.04 alpha = 3.522E-04 avg error 1.56 %

Fit Af/Ar w/ddU: A = 1.711E-01 n = -.15 alpha = 4.561E-04 avg error 2.80 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.432E+01	2.432E+01	-5.629E+00	5.884E-02	2.601E+01
400.00	2.432E+01	2.432E+01	-5.637E+00	5.860E-02	2.657E+01
500.00	2.428E+01	2.428E+01	-5.708E+00	5.654E-02	2.714E+01
600.00	2.423E+01	2.423E+01	-5.804E+00	5.389E-02	2.771E+01
800.00	2.409E+01	2.409E+01	-6.005E+00	4.869E-02	2.889E+01
1000.00	2.393E+01	2.393E+01	-6.188E+00	4.441E-02	3.011E+01
1200.00	2.375E+01	2.375E+01	-6.347E+00	4.099E-02	3.137E+01
1500.00	2.347E+01	2.347E+01	-6.558E+00	3.687E-02	3.330E+01
2000.00	2.289E+01	2.289E+01	-6.887E+00	3.125E-02	3.667E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$

$A_{\text{prime}} = 1.4687E+10$ $n = .64845$ $E_a = 2.4611E+04$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	3.678E+11	4.039E+01	7.028E-07	6.958E-07
400.00	4.884E+11	4.867E+01	2.522E-02	2.548E-02
500.00	5.890E+11	5.625E+01	1.428E+01	1.441E+01
600.00	6.737E+11	6.331E+01	1.003E+03	1.007E+03
800.00	8.116E+11	7.629E+01	2.126E+05	2.116E+05
1000.00	9.253E+11	8.817E+01	5.454E+06	5.408E+06
1200.00	1.025E+12	9.924E+01	4.836E+07	4.797E+07
1500.00	1.152E+12	1.147E+02	4.385E+08	4.368E+08
2000.00	1.302E+12	1.382E+02	4.101E+09	4.148E+09

THERMODYNAMIC ANALYSIS for REACTION

Rx CQCJO = TCQXCJO

Hf {Kcal/mol} -21.810 -12.240

S {cal/mol K} 81.780 97.200

dHr {kcal/mol} (298K) = 9.57 dHr avg (298., 1500. K) = 10.72

dU (dE) {kcal/mol} (") = 9.57 dUr avg (298., 1500. K) = 10.72

dSr {cal/mol K} (") = 15.42 dSr avg (298., 1500. K) = 17.53

dGr {kcal/mol} (") = 4.97 dGr avg (298., 1500. K) = -5.04

Af/Ar (") = 2.346E+03 Af/Ar avg (298., 1500. K) = 6.790E+03

Fit Af/Ar : A = 2.001E-03 n = 2.57 alpha = 1.720E-03 avg error 8.13 %

Fit Af/Ar w/ddU: A = 2.173E-07 n = 4.30 alpha = 3.502E-03 avg error 22.46 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	9.581E+00	9.581E+00	1.546E+01	2.388E+03	4.944E+00
400.00	1.009E+01	1.009E+01	1.692E+01	4.991E+03	3.319E+00
500.00	1.049E+01	1.049E+01	1.782E+01	7.842E+03	1.579E+00
600.00	1.080E+01	1.080E+01	1.840E+01	1.049E+04	-2.341E-01
800.00	1.124E+01	1.124E+01	1.904E+01	1.449E+04	-3.986E+00
1000.00	1.152E+01	1.152E+01	1.935E+01	1.693E+04	-7.828E+00
1200.00	1.170E+01	1.170E+01	1.951E+01	1.839E+04	-1.171E+01
1500.00	1.188E+01	1.188E+01	1.964E+01	1.966E+04	-1.759E+01
2000.00	1.205E+01	1.205E+01	1.974E+01	2.067E+04	-2.744E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$

$A_{\text{prime}} = 8.4672E+10$ $n = 2.04186$ $E_a = 9.3533E+03$

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.493E+16	1.143E+05	1.563E+09	1.483E+09
400.00	4.159E+16	2.056E+05	1.280E+11	1.349E+11
500.00	8.170E+16	3.243E+05	2.127E+12	2.239E+12
600.00	1.311E+17	4.705E+05	1.521E+13	1.560E+13
800.00	2.415E+17	8.466E+05	2.046E+14	1.995E+14
1000.00	3.527E+17	1.335E+06	1.071E+15	1.021E+15
1200.00	4.597E+17	1.938E+06	3.402E+15	3.246E+15
1500.00	6.143E+17	3.056E+06	1.143E+16	1.122E+16
2000.00	8.615E+17	5.498E+06	4.157E+16	4.424E+16

APPENDIX 4.3

KINETIC DATA FOR C_jCHO + O₂ REACTIONS ARRHENIUS FORM

Chemical Activation CjCHO + O₂

CJCHO+O2	<=>	CQJCHO	1.08E+32	-8.43	2907.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	18% err,	1.00 x N2
CJCHO+O2	<=>	CQJCHO	1.63E+33	-8.48	3021.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	18% err,	1.00 x N2
CJCHO+O2	<=>	CQJCHO	2.06E+35	-8.79	3762.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	19% err,	1.00 x N2
CJCHO+O2	<=>	CQJCHO	9.57E+37	-9.24	5435.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	18% err,	1.00 x N2
CJCHO+O2	<=>	CQJCHO	2.87E+37	-8.73	6423.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	14% err,	1.00 x N2
CJCHO+O2	<=>	CQJCHO	3.54E+32	-6.94	5815.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	19% err,	1.00 x N2
CJCHO+O2	<=>	CQJCHO	8.79E+24	-4.41	3987.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	20% err,	1.00 x N2
CJCHO+O2	<=>	CJCHO+O2	2.95E+11	-.10	74.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	1% err,	1.00 x N2
CJCHO+O2	<=>	CJCHO+O2	4.22E+11	-.14	165.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	1% err,	1.00 x N2
CJCHO+O2	<=>	CJCHO+O2	4.55E+12	-.44	784.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	2% err,	1.00 x N2
CJCHO+O2	<=>	CJCHO+O2	2.02E+15	-1.18	2569.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	3% err,	1.00 x N2
CJCHO+O2	<=>	CJCHO+O2	2.55E+17	-1.74	4762.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	7% err,	1.00 x N2
CJCHO+O2	<=>	CJCHO+O2	4.13E+15	-1.14	5804.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	27% err,	1.00 x N2
CJCHO+O2	<=>	CJCHO+O2	8.80E+08	.88	4968.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	51% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	1.81E-06	5.50	21640.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	79% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	1.81E-06	5.50	21640.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	79% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	1.82E-06	5.50	21641.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	79% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	1.89E-06	5.50	21653.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	79% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	2.68E-06	5.46	21760.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	79% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	2.16E-05	5.20	22475.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	80% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	2.97E-05	5.22	23754.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	99% err,	1.00 x N2
CJCHO+O2	<=>	CQCJO	1.21E+07	-2.91	-1374.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	16% err,	1.00 x N2
CJCHO+O2	<=>	CQCJO	1.82E+08	-2.96	-1265.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	17% err,	1.00 x N2
CJCHO+O2	<=>	CQCJO	2.34E+10	-3.28	-545.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	18% err,	1.00 x N2
CJCHO+O2	<=>	CQCJO	2.95E+13	-3.85	1228.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	16% err,	1.00 x N2
CJCHO+O2	<=>	CQCJO	2.07E+14	-3.74	2711.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	3% err,	1.00 x N2
CJCHO+O2	<=>	CQCJO	6.03E+10	-2.34	2695.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	17% err,	1.00 x N2
CJCHO+O2	<=>	CQCJO	3.56E+03	.11	1146.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	30% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	1.40E-09	3.67	-180.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	12% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	1.77E-09	3.64	-123.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	11% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	9.74E-09	3.43	297.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	9% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	2.72E-06	2.73	1777.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	5% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	5.40E-03	1.81	4208.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	6% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	1.77E-02	1.73	6059.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	24% err,	1.00 x N2
CJCHO+O2	<=>	CH2CO+HO2	2.92E-07	3.21	6000.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	55% err,	1.00 x N2
CJCHO+O2	<=>	CO+CH2O+OH	5.19E+09	.13	558.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	5% err,	1.00 x N2
CJCHO+O2	<=>	CO+CH2O+OH	7.76E+09	.08	664.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	6% err,	1.00 x N2
CJCHO+O2	<=>	CO+CH2O+OH	1.02E+11	-.24	1372.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	7% err,	1.00 x N2
CJCHO+O2	<=>	CO+CH2O+OH	2.33E+13	-.90	3200.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	6% err,	1.00 x N2
CJCHO+O2	<=>	CO+CH2O+OH	1.25E+14	-1.05	4991.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	10% err,	1.00 x N2
CJCHO+O2	<=>	CO+CH2O+OH	4.62E+10	.04	5421.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	30% err,	1.00 x N2
CJCHO+O2	<=>	CO+CH2O+OH	1.11E+03	2.33	4177.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	50% err,	1.00 x N2

Dissociation

CQJCHO	<=>	CJCHO+O2	1.49E+34	-8.46	25999.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	21% err,	1.00 x N2
CQJCHO	<=>	CJCHO+O2	2.21E+35	-8.51	26108.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=>	CJCHO+O2	2.61E+37	-8.82	26829.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	23% err,	1.00 x N2
CQJCHO	<=>	CJCHO+O2	1.25E+40	-9.27	28497.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	20% err,	1.00 x N2
CQJCHO	<=>	CJCHO+O2	3.97E+39	-8.76	29493.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	14% err,	1.00 x N2
CQJCHO	<=>	CJCHO+O2	5.00E+34	-6.98	28888.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	16% err,	1.00 x N2
CQJCHO	<=>	CJCHO+O2	1.25E+27	-4.45	27061.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	17% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	6.84E+11	-1.59	48214.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	6.84E+12	-1.59	48214.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	6.87E+13	-1.59	48215.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	7.14E+14	-1.60	48226.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	1.02E+16	-1.64	48330.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	1.03E+18	-1.92	49047.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	23% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	8.48E+19	-2.15	50550.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	16% err,	1.00 x N2
CQJCHO	<=>	CQCJO	9.81E+35	-12.88	22341.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	33% err,	1.00 x N2
CQJCHO	<=>	CQCJO	3.41E+40	-13.57	24714.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	26% err,	1.00 x N2
CQJCHO	<=>	CQCJO	9.53E+39	-12.75	25462.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	9% err,	1.00 x N2
CQJCHO	<=>	CQCJO	1.05E+35	-10.67	24395.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	8% err,	1.00 x N2
CQJCHO	<=>	CQCJO	3.11E+29	-8.48	22875.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	9% err,	1.00 x N2
CQJCHO	<=>	CQCJO	6.81E+23	-6.29	21177.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	8% err,	1.00 x N2
CQJCHO	<=>	CQCJO	1.27E+18	-4.11	19297.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	7% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	1.81E+08	-3.21	23315.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	24% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	2.57E+09	-3.25	23406.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	24% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	2.71E+11	-3.55	24038.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	26% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	7.91E+14	-4.24	25820.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	27% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	1.53E+17	-4.55	27767.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	19% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	1.83E+15	-3.62	28378.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	16% err,	1.00 x N2
CQJCHO	<=>	CH2CO+HO2	7.67E+08	-1.40	27215.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	23% err,	1.00 x N2
CQJCHO	<=>	CO+CH2O+OH	6.98E+40	-10.72	24722.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	28% err,	1.00 x N2
CQJCHO	<=>	CO+CH2O+OH	4.21E+44	-11.48	27150.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	25% err,	1.00 x N2
CQJCHO	<=>	CO+CH2O+OH	4.45E+43	-10.82	28115.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	20% err,	1.00 x N2
CQJCHO	<=>	CO+CH2O+OH	1.73E+38	-8.89	27311.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	19% err,	1.00 x N2
CQJCHO	<=>	CO+CH2O+OH	6.07E+31	-6.68	25971.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	21% err,	1.00 x N2
CQJCHO	<=>	CO+CH2O+OH	3.46E+24	-4.27	24253.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	23% err,	1.00 x N2
CQJCHO	<=>	CO+CH2O+OH	5.13E+16	-1.72	22146.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	18% err,	1.00 x N2
CQCJO	<=>	CQJCHO	2.87E+27	-9.98	10836.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=>	CQJCHO	2.87E+29	-9.98	10836.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=>	CQJCHO	2.87E+31	-9.98	10836.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=>	CQJCHO	2.87E+33	-9.98	10836.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=>	CQJCHO	2.87E+35	-9.98	10836.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=>	CQJCHO	2.87E+37	-9.98	10836.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=>	CQJCHO	2.87E+39	-9.98	10836.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=>	CJCHO+O2	7.01E+11	-4.09	22120.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	24% err,	1.00 x N2
CQCJO	<=>	CJCHO+O2	1.05E+13	-4.14	22225.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	24% err,	1.00 x N2
CQCJO	<=>	CJCHO+O2	1.36E+15	-4.45	22929.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	26% err,	1.00 x N2

CQCJO	<=>	CJCHO+O2	3.08E+18	-5.11	24751.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	25% err,	1.00 x N2
CQCJO	<=>	CJCHO+O2	1.61E+20	-5.25	26533.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	11% err,	1.00 x N2
CQCJO	<=>	CJCHO+O2	5.06E+17	-4.15	26929.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	9% err,	1.00 x N2
CQCJO	<=>	CJCHO+O2	1.03E+11	-1.84	25636.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	25% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	3.52E-01	-.01	46342.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	19% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	3.53E+00	-.01	46342.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	19% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	3.54E+01	-.01	46343.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	19% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	3.68E+02	-.01	46354.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	19% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	5.31E+03	-.06	46459.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	19% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	5.68E+05	-.35	47184.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	20% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	6.69E+07	-.62	48744.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	12% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	5.57E+05	-1.92	21863.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	5.57E+06	-1.92	21863.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	5.57E+07	-1.92	21863.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	5.57E+08	-1.92	21863.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	5.57E+09	-1.92	21863.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	5.58E+10	-1.92	21863.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=>	CH2CO+HO2	5.63E+11	-1.92	21865.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=>	CO+CH2O+OH	3.39E+14	-2.90	6929.	!	1.00E-04	(1.00E-04)	atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=>	CO+CH2O+OH	3.39E+15	-2.90	6929.	!	1.00E-03	(1.00E-03)	atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=>	CO+CH2O+OH	3.39E+16	-2.90	6929.	!	1.00E-02	(1.00E-02)	atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=>	CO+CH2O+OH	3.40E+17	-2.90	6929.	!	1.00E-01	(1.00E-01)	atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=>	CO+CH2O+OH	3.44E+18	-2.90	6932.	!	1.00E+00	(1.00E+00)	atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=>	CO+CH2O+OH	3.91E+19	-2.91	6963.	!	1.00E+01	(1.00E+01)	atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=>	CO+CH2O+OH	1.20E+21	-3.05	7233.	!	1.00E+02	(1.00E+02)	atm,	298-2000 K,	31% err,	1.00 x N2

APPENDIX 4.4

**LOG RATE CONSTANTS VS PRESSURE AND TEMPERATURE
FOR C_jCHO + O₂ REACTION**

Chemical Activation Reaction (CjCHO + O₂) Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	8.990	11.182	-7.875	.808	.414	9.596	9.692
1.00E-04	400.	2.50E+00	8.515	11.179	-3.201	.340	.768	9.752	9.777
1.00E-04	500.	2.00E+00	8.063	11.176	-.539	-.094	1.092	9.834	9.842
1.00E-04	600.	1.67E+00	7.618	11.174	1.166	-.480	1.385	9.878	9.881
1.00E-04	800.	1.25E+00	6.760	11.173	4.662	-1.067	1.885	9.915	9.915
1.00E-04	1000.	1.00E+00	5.998	11.171	6.373	-1.448	2.276	9.936	9.936
1.00E-04	1500.	6.67E-01	4.698	11.165	8.663	-1.984	2.897	10.012	10.031
1.00E-04	2000.	5.00E-01	4.004	11.139	9.836	-2.314	3.224	10.099	10.288

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	9.958	11.159	-7.875	1.778	.399	9.568	10.107
1.00E-03	400.	2.50E+00	9.501	11.171	-3.201	1.328	.765	9.741	9.938
1.00E-03	500.	2.00E+00	9.056	11.173	-.539	.900	1.091	9.830	9.897
1.00E-03	600.	1.67E+00	8.615	11.173	1.166	.517	1.385	9.876	9.899
1.00E-03	800.	1.25E+00	7.759	11.172	4.662	-.068	1.885	9.915	9.918
1.00E-03	1000.	1.00E+00	6.998	11.171	6.373	-.448	2.276	9.936	9.936
1.00E-03	1500.	6.67E-01	5.698	11.165	8.663	-.984	2.897	10.012	10.031
1.00E-03	2000.	5.00E-01	5.004	11.139	9.836	-1.314	3.224	10.099	10.288

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	10.741	10.998	-7.875	2.576	.295	9.374	10.760
1.00E-02	400.	2.50E+00	10.390	11.107	-3.201	2.229	.734	9.651	10.463
1.00E-02	500.	2.00E+00	9.999	11.149	-.539	1.853	1.082	9.789	10.208
1.00E-02	600.	1.67E+00	9.586	11.164	1.166	1.495	1.382	9.858	10.044
1.00E-02	800.	1.25E+00	8.751	11.171	4.662	.928	1.884	9.911	9.940
1.00E-02	1000.	1.00E+00	7.996	11.171	6.373	.551	2.276	9.935	9.940
1.00E-02	1500.	6.67E-01	6.698	11.165	8.663	.015	2.897	10.012	10.031
1.00E-02	2000.	5.00E-01	6.004	11.139	9.836	-.314	3.224	10.099	10.288

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	11.100	10.483	-7.879	2.966	-.091	8.784	11.102
1.00E-01	400.	2.50E+00	10.945	10.826	-3.203	2.830	.569	9.280	10.954
1.00E-01	500.	2.00E+00	10.708	11.009	-.540	2.609	1.019	9.574	10.739
1.00E-01	600.	1.67E+00	10.405	11.100	1.166	2.355	1.360	9.743	10.491
1.00E-01	800.	1.25E+00	9.690	11.160	4.662	1.888	1.882	9.884	10.099
1.00E-01	1000.	1.00E+00	8.975	11.169	6.373	1.540	2.276	9.929	9.975
1.00E-01	1500.	6.67E-01	7.695	11.165	8.663	1.015	2.897	10.011	10.032
1.00E-01	2000.	5.00E-01	7.004	11.139	9.836	.686	3.224	10.099	10.289

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	11.183	9.645	-7.911	3.067	-.838	7.898	11.184
1.00E+00	400.	2.50E+00	11.148	10.207	-3.220	3.080	.100	8.565	11.149
1.00E+00	500.	2.00E+00	11.063	10.605	-.550	3.038	.766	9.055	11.067
1.00E+00	600.	1.67E+00	10.913	10.862	1.160	2.950	1.238	9.396	10.926
1.00E+00	800.	1.25E+00	10.439	11.093	4.660	2.716	1.859	9.758	10.521
1.00E+00	1000.	1.00E+00	9.859	11.152	6.372	2.476	2.271	9.890	10.176
1.00E+00	1500.	6.67E-01	8.675	11.164	8.663	2.008	2.897	10.009	10.047
1.00E+00	2000.	5.00E-01	7.999	11.138	9.836	1.685	3.224	10.099	10.290

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	11.195	8.673	-8.149	3.081	-1.786	6.915	11.195
1.00E+01	400.	2.50E+00	11.190	9.321	-3.362	3.140	-.705	7.639	11.190
1.00E+01	500.	2.00E+00	11.174	9.876	-.637	3.194	.171	8.248	11.175
1.00E+01	600.	1.67E+00	11.132	10.318	1.106	3.247	.850	8.753	11.134
1.00E+01	800.	1.25E+00	10.917	10.855	4.648	3.308	1.734	9.427	10.931
1.00E+01	1000.	1.00E+00	10.545	11.066	6.368	3.270	2.236	9.748	10.609
1.00E+01	1500.	6.67E-01	9.588	11.155	8.662	2.973	2.893	9.991	10.150
1.00E+01	2000.	5.00E-01	8.971	11.136	9.836	2.677	3.223	10.095	10.306

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	11.196	7.676	-8.866	3.082	-2.780	5.917	11.196
1.00E+02	400.	2.50E+00	11.195	8.339	-3.940	3.148	-1.669	6.650	11.195
1.00E+02	500.	2.00E+00	11.193	8.940	-1.085	3.225	-.712	7.290	11.193
1.00E+02	600.	1.67E+00	11.187	9.479	.771	3.333	.105	7.868	11.187
1.00E+02	800.	1.25E+00	11.133	10.313	4.544	3.613	1.336	8.803	11.135
1.00E+02	1000.	1.00E+00	10.974	10.780	6.333	3.823	2.065	9.386	10.985
1.00E+02	1500.	6.67E-01	10.357	11.099	8.655	3.843	2.866	9.908	10.495
1.00E+02	2000.	5.00E-01	9.871	11.118	9.832	3.631	3.213	10.068	10.413

Chemical Activation Reaction (CjCHO + O₂) Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	8.990	11.182	-7.875	.808	.414	9.596	9.692
298.	3.36E+00	1.00E-03	9.958	11.159	-7.875	1.778	.399	9.568	10.107
298.	3.36E+00	1.00E-02	10.741	10.998	-7.875	2.576	.295	9.374	10.760
298.	3.36E+00	1.00E-01	11.100	10.483	-7.879	2.966	-.091	8.784	11.102
298.	3.36E+00	1.00E+00	11.183	9.645	-7.911	3.067	-.838	7.898	11.184
298.	3.36E+00	1.00E+01	11.195	8.673	-8.149	3.081	-1.786	6.915	11.195
298.	3.36E+00	1.00E+02	11.196	7.676	-8.866	3.082	-2.780	5.917	11.196
T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	8.515	11.179	-3.201	.340	.768	9.752	9.777
400.	2.50E+00	1.00E-03	9.501	11.171	-3.201	1.328	.765	9.741	9.938
400.	2.50E+00	1.00E-02	10.390	11.107	-3.201	2.229	.734	9.651	10.463
400.	2.50E+00	1.00E-01	10.945	10.826	-3.203	2.830	.569	9.280	10.954
400.	2.50E+00	1.00E+00	11.148	10.207	-3.220	3.080	.100	8.565	11.149
400.	2.50E+00	1.00E+01	11.190	9.321	-3.362	3.140	-.705	7.639	11.190
400.	2.50E+00	1.00E+02	11.195	8.339	-3.940	3.148	-1.669	6.650	11.195
T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	8.063	11.176	-.539	-.094	1.092	9.834	9.842
500.	2.00E+00	1.00E-03	9.056	11.173	-.539	.900	1.091	9.830	9.897
500.	2.00E+00	1.00E-02	9.999	11.149	-.539	1.853	1.082	9.789	10.208
500.	2.00E+00	1.00E-01	10.708	11.009	-.540	2.609	1.019	9.574	10.739
500.	2.00E+00	1.00E+00	11.063	10.605	-.550	3.038	.766	9.055	11.067
500.	2.00E+00	1.00E+01	11.174	9.876	-.637	3.194	.171	8.248	11.175
500.	2.00E+00	1.00E+02	11.193	8.940	-1.085	3.225	-.712	7.290	11.193
T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	7.618	11.174	1.166	-.480	1.385	9.878	9.881
600.	1.67E+00	1.00E-03	8.615	11.173	1.166	.517	1.385	9.876	9.899
600.	1.67E+00	1.00E-02	9.586	11.164	1.166	1.495	1.382	9.858	10.044
600.	1.67E+00	1.00E-01	10.405	11.100	1.166	2.355	1.360	9.743	10.491
600.	1.67E+00	1.00E+00	10.913	10.862	1.160	2.950	1.238	9.396	10.926
600.	1.67E+00	1.00E+01	11.132	10.318	1.106	3.247	.850	8.753	11.134
600.	1.67E+00	1.00E+02	11.187	9.479	.771	3.333	.105	7.868	11.187
T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	6.760	11.173	4.662	-1.067	1.885	9.915	9.915
800.	1.25E+00	1.00E-03	7.759	11.172	4.662	-.068	1.885	9.915	9.918
800.	1.25E+00	1.00E-02	8.751	11.171	4.662	.928	1.884	9.911	9.940

800.	1.25E+00	1.00E-01	9.690	11.160	4.662	1.888	1.882	9.884	10.099
800.	1.25E+00	1.00E+00	10.439	11.093	4.660	2.716	1.859	9.758	10.521
800.	1.25E+00	1.00E+01	10.917	10.855	4.648	3.308	1.734	9.427	10.931
800.	1.25E+00	1.00E+02	11.133	10.313	4.544	3.613	1.336	8.803	11.135

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	5.998	11.171	6.373	-1.448	2.276	9.936	9.936
1000.	1.00E+00	1.00E-03	6.998	11.171	6.373	-.448	2.276	9.936	9.936
1000.	1.00E+00	1.00E-02	7.996	11.171	6.373	.551	2.276	9.935	9.940
1000.	1.00E+00	1.00E-01	8.975	11.169	6.373	1.540	2.276	9.929	9.975
1000.	1.00E+00	1.00E+00	9.859	11.152	6.372	2.476	2.271	9.890	10.176
1000.	1.00E+00	1.00E+01	10.545	11.066	6.368	3.270	2.236	9.748	10.609
1000.	1.00E+00	1.00E+02	10.974	10.780	6.333	3.823	2.065	9.386	10.985

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	4.698	11.165	8.663	-1.984	2.897	10.012	10.031
1500.	6.67E-01	1.00E-03	5.698	11.165	8.663	-.984	2.897	10.012	10.031
1500.	6.67E-01	1.00E-02	6.698	11.165	8.663	.015	2.897	10.012	10.031
1500.	6.67E-01	1.00E-01	7.695	11.165	8.663	1.015	2.897	10.011	10.032
1500.	6.67E-01	1.00E+00	8.675	11.164	8.663	2.008	2.897	10.009	10.047
1500.	6.67E-01	1.00E+01	9.588	11.155	8.662	2.973	2.893	9.991	10.150
1500.	6.67E-01	1.00E+02	10.357	11.099	8.655	3.843	2.866	9.908	10.495

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	4.004	11.139	9.836	-2.314	3.224	10.099	10.288
2000.	5.00E-01	1.00E-03	5.004	11.139	9.836	-1.314	3.224	10.099	10.288
2000.	5.00E-01	1.00E-02	6.004	11.139	9.836	-.314	3.224	10.099	10.288
2000.	5.00E-01	1.00E-01	7.004	11.139	9.836	.686	3.224	10.099	10.289
2000.	5.00E-01	1.00E+00	7.999	11.138	9.836	1.685	3.224	10.099	10.290
2000.	5.00E-01	1.00E+01	8.971	11.136	9.836	2.677	3.223	10.095	10.306
2000.	5.00E-01	1.00E+02	9.871	11.118	9.832	3.631	3.213	10.068	10.413

Adduct (CQjCHO) Dissociation Reaction Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	-5.900	-27.540	-12.398	-16.867	-3.895	-3.891
1.00E-04	400.	2.50E+00	-2.030	-18.608	-9.626	-12.778	-.513	-.500
1.00E-04	500.	2.00E+00	.040	-13.455	-8.402	-10.504	1.204	1.233
1.00E-04	600.	1.67E+00	1.267	-10.080	-7.859	-9.078	2.148	2.201
1.00E-04	800.	1.25E+00	2.488	-5.991	-7.606	-7.469	2.946	3.076
1.00E-04	1000.	1.00E+00	2.974	-3.616	-7.730	-6.612	3.131	3.361
1.00E-04	1500.	6.67E-01	3.369	-.349	-8.274	-5.444	3.028	3.533
1.00E-04	2000.	5.00E-01	3.532	1.434	-8.822	-4.750	2.931	3.631

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	-4.930	-26.540	-11.252	-15.891	-3.736	-3.709
1.00E-03	400.	2.50E+00	-1.044	-17.608	-8.244	-11.787	-.103	-.056
1.00E-03	500.	2.00E+00	1.034	-12.455	-6.787	-9.507	1.848	1.910
1.00E-03	600.	1.67E+00	2.264	-9.080	-6.074	-8.079	2.954	3.035
1.00E-03	800.	1.25E+00	3.487	-4.991	-5.663	-6.469	3.897	4.040
1.00E-03	1000.	1.00E+00	3.974	-2.616	-5.746	-5.612	4.118	4.353
1.00E-03	1500.	6.67E-01	4.369	.651	-6.276	-4.444	4.027	4.532
1.00E-03	2000.	5.00E-01	4.532	2.434	-6.822	-3.750	3.931	4.631

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	-4.141	-25.540	-10.229	-15.060	-3.708	-3.572
1.00E-02	400.	2.50E+00	-.152	-16.609	-7.147	-10.860	.011	.238
1.00E-02	500.	2.00E+00	1.978	-11.455	-5.553	-8.539	2.113	2.352
1.00E-02	600.	1.67E+00	3.236	-8.080	-4.667	-7.092	3.400	3.626
1.00E-02	800.	1.25E+00	4.479	-3.991	-3.948	-5.471	4.647	4.872
1.00E-02	1000.	1.00E+00	4.972	-1.616	-3.865	-4.612	5.021	5.298
1.00E-02	1500.	6.67E-01	5.369	1.651	-4.298	-3.444	5.013	5.528
1.00E-02	2000.	5.00E-01	5.531	3.434	-4.830	-2.750	4.928	5.631

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	-3.777	-24.544	-9.224	-14.606	-3.701	-3.436
1.00E-01	400.	2.50E+00	.409	-15.610	-6.117	-10.183	.055	.568
1.00E-01	500.	2.00E+00	2.692	-10.455	-4.473	-7.714	2.223	2.819
1.00E-01	600.	1.67E+00	4.059	-7.080	-3.512	-6.181	3.600	4.188
1.00E-01	800.	1.25E+00	5.419	-2.991	-2.573	-4.490	5.083	5.584
1.00E-01	1000.	1.00E+00	5.952	-.616	-2.263	-3.616	5.685	6.139
1.00E-01	1500.	6.67E-01	6.367	2.651	-2.425	-2.444	5.932	6.503
1.00E-01	2000.	5.00E-01	6.531	4.434	-2.882	-1.750	5.908	6.627

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	-3.692	-23.574	-8.223	-14.469	-3.699	-3.394
1.00E+00	400.	2.50E+00	.613	-14.624	-5.107	-9.856	.073	.723
1.00E+00	500.	2.00E+00	3.048	-9.463	-3.432	-7.184	2.291	3.118
1.00E+00	600.	1.67E+00	4.568	-6.084	-2.418	-5.482	3.745	4.629
1.00E+00	800.	1.25E+00	6.170	-1.992	-1.342	-3.592	5.402	6.238
1.00E+00	1000.	1.00E+00	6.837	.384	-.886	-2.647	6.168	6.921
1.00E+00	1500.	6.67E-01	7.347	3.651	-.745	-1.447	6.728	7.441
1.00E+00	2000.	5.00E-01	7.526	5.434	-1.041	-.750	6.844	7.611

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	-3.681	-22.796	-7.223	-14.447	-3.699	-3.389
1.00E+01	400.	2.50E+00	.656	-13.747	-4.105	-9.767	.077	.757
1.00E+01	500.	2.00E+00	3.160	-8.530	-2.421	-6.964	2.312	3.218
1.00E+01	600.	1.67E+00	4.788	-5.121	-1.380	-5.094	3.812	4.832
1.00E+01	800.	1.25E+00	6.649	-1.004	-.191	-2.898	5.635	6.689
1.00E+01	1000.	1.00E+00	7.523	1.379	.408	-1.778	6.582	7.570
1.00E+01	1500.	6.67E-01	8.259	4.650	.829	-.466	7.454	8.323
1.00E+01	2000.	5.00E-01	8.498	6.433	.717	.245	7.733	8.570

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	-3.680	-22.492	-6.224	-14.445	-3.700	-3.388
1.00E+02	400.	2.50E+00	.661	-13.279	-3.105	-9.754	.077	.762
1.00E+02	500.	2.00E+00	3.179	-7.910	-1.419	-6.916	2.315	3.235
1.00E+02	600.	1.67E+00	4.843	-4.374	-.372	-4.968	3.827	4.883
1.00E+02	800.	1.25E+00	6.865	-.103	.868	-2.512	5.738	6.896
1.00E+02	1000.	1.00E+00	7.953	2.340	1.579	-1.139	6.847	7.985
1.00E+02	1500.	6.67E-01	9.028	5.640	2.298	.441	8.072	9.074
1.00E+02	2000.	5.00E-01	9.398	7.428	2.391	1.211	8.544	9.459

Adduct (CQjCHO) Dissociation Reaction Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	-5.900	-27.540	-12.398	-16.867	-3.895	-3.891
298.	3.36E+00	1.00E-03	-4.930	-26.540	-11.252	-15.891	-3.736	-3.709
298.	3.36E+00	1.00E-02	-4.141	-25.540	-10.229	-15.060	-3.708	-3.572
298.	3.36E+00	1.00E-01	-3.777	-24.544	-9.224	-14.606	-3.701	-3.436
298.	3.36E+00	1.00E+00	-3.692	-23.574	-8.223	-14.469	-3.699	-3.394
298.	3.36E+00	1.00E+01	-3.681	-22.796	-7.223	-14.447	-3.699	-3.389
298.	3.36E+00	1.00E+02	-3.680	-22.492	-6.224	-14.445	-3.700	-3.388

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	-2.030	-18.608	-9.626	-12.778	-.513	-.500
400.	2.50E+00	1.00E-03	-1.044	-17.608	-8.244	-11.787	-.103	-.056
400.	2.50E+00	1.00E-02	-.152	-16.609	-7.147	-10.860	.011	.238
400.	2.50E+00	1.00E-01	.409	-15.610	-6.117	-10.183	.055	.568
400.	2.50E+00	1.00E+00	.613	-14.624	-5.107	-9.856	.073	.723
400.	2.50E+00	1.00E+01	.656	-13.747	-4.105	-9.767	.077	.757
400.	2.50E+00	1.00E+02	.661	-13.279	-3.105	-9.754	.077	.762

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	.040	-13.455	-8.402	-10.504	1.204	1.233
500.	2.00E+00	1.00E-03	1.034	-12.455	-6.787	-9.507	1.848	1.910
500.	2.00E+00	1.00E-02	1.978	-11.455	-5.553	-8.539	2.113	2.352
500.	2.00E+00	1.00E-01	2.692	-10.455	-4.473	-7.714	2.223	2.819
500.	2.00E+00	1.00E+00	3.048	-9.463	-3.432	-7.184	2.291	3.118
500.	2.00E+00	1.00E+01	3.160	-8.530	-2.421	-6.964	2.312	3.218
500.	2.00E+00	1.00E+02	3.179	-7.910	-1.419	-6.916	2.315	3.235

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	1.267	-10.080	-7.859	-9.078	2.148	2.201
600.	1.67E+00	1.00E-03	2.264	-9.080	-6.074	-8.079	2.954	3.035
600.	1.67E+00	1.00E-02	3.236	-8.080	-4.667	-7.092	3.400	3.626
600.	1.67E+00	1.00E-01	4.059	-7.080	-3.512	-6.181	3.600	4.188
600.	1.67E+00	1.00E+00	4.568	-6.084	-2.418	-5.482	3.745	4.629
600.	1.67E+00	1.00E+01	4.788	-5.121	-1.380	-5.094	3.812	4.832
600.	1.67E+00	1.00E+02	4.843	-4.374	-.372	-4.968	3.827	4.883

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	2.488	-5.991	-7.606	-7.469	2.946	3.076
800.	1.25E+00	1.00E-03	3.487	-4.991	-5.663	-6.469	3.897	4.040
800.	1.25E+00	1.00E-02	4.479	-3.991	-3.948	-5.471	4.647	4.872

800.	1.25E+00	1.00E-01	5.419	-2.991	-2.573	-4.490	5.083	5.584
800.	1.25E+00	1.00E+00	6.170	-1.992	-1.342	-3.592	5.402	6.238
800.	1.25E+00	1.00E+01	6.649	-1.004	-.191	-2.898	5.635	6.689
800.	1.25E+00	1.00E+02	6.865	-.103	.868	-2.512	5.738	6.896

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	2.974	-3.616	-7.730	-6.612	3.131	3.361
1000.	1.00E+00	1.00E-03	3.974	-2.616	-5.746	-5.612	4.118	4.353
1000.	1.00E+00	1.00E-02	4.972	-1.616	-3.865	-4.612	5.021	5.298
1000.	1.00E+00	1.00E-01	5.952	-.616	-2.263	-3.616	5.685	6.139
1000.	1.00E+00	1.00E+00	6.837	.384	-.886	-2.647	6.168	6.921
1000.	1.00E+00	1.00E+01	7.523	1.379	.408	-1.778	6.582	7.570
1000.	1.00E+00	1.00E+02	7.953	2.340	1.579	-1.139	6.847	7.985

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	3.369	-.349	-8.274	-5.444	3.028	3.533
1500.	6.67E-01	1.00E-03	4.369	.651	-6.276	-4.444	4.027	4.532
1500.	6.67E-01	1.00E-02	5.369	1.651	-4.298	-3.444	5.013	5.528
1500.	6.67E-01	1.00E-01	6.367	2.651	-2.425	-2.444	5.932	6.503
1500.	6.67E-01	1.00E+00	7.347	3.651	-.745	-1.447	6.728	7.441
1500.	6.67E-01	1.00E+01	8.259	4.650	.829	-.466	7.454	8.323
1500.	6.67E-01	1.00E+02	9.028	5.640	2.298	.441	8.072	9.074

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	3.532	1.434	-8.822	-4.750	2.931	3.631
2000.	5.00E-01	1.00E-03	4.532	2.434	-6.822	-3.750	3.931	4.631
2000.	5.00E-01	1.00E-02	5.531	3.434	-4.830	-2.750	4.928	5.631
2000.	5.00E-01	1.00E-01	6.531	4.434	-2.882	-1.750	5.908	6.627
2000.	5.00E-01	1.00E+00	7.526	5.434	-1.041	-.750	6.844	7.611
2000.	5.00E-01	1.00E+01	8.498	6.433	.717	.245	7.733	8.570
2000.	5.00E-01	1.00E+02	9.398	7.428	2.391	1.211	8.544	9.459

Adduct (CQCjO) Dissociation Reaction Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	-5.241	-14.595	-34.554	-15.114	2.160	2.160
1.00E-04	400.	2.50E+00	-4.354	-10.751	-25.690	-11.095	3.339	3.339
1.00E-04	500.	2.00E+00	-4.126	-8.734	-20.638	-8.905	3.817	3.817
1.00E-04	600.	1.67E+00	-4.167	-7.525	-17.335	-7.530	4.012	4.012
1.00E-04	800.	1.25E+00	-4.523	-6.159	-13.233	-5.876	4.125	4.125
1.00E-04	1000.	1.00E+00	-4.941	-5.380	-10.716	-4.875	4.170	4.170
1.00E-04	1500.	6.67E-01	-5.822	-4.373	-7.216	-3.524	4.279	4.279
1.00E-04	2000.	5.00E-01	-6.593	-3.967	-5.491	-2.924	4.331	4.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	-3.241	-13.623	-33.554	-14.114	3.160	3.160
1.00E-03	400.	2.50E+00	-2.354	-9.762	-24.690	-10.095	4.339	4.339
1.00E-03	500.	2.00E+00	-2.126	-7.739	-19.638	-7.905	4.817	4.817
1.00E-03	600.	1.67E+00	-2.167	-6.527	-16.335	-6.530	5.012	5.012
1.00E-03	800.	1.25E+00	-2.523	-5.159	-12.233	-4.876	5.125	5.125
1.00E-03	1000.	1.00E+00	-2.941	-4.380	-9.716	-3.875	5.170	5.170
1.00E-03	1500.	6.67E-01	-3.822	-3.373	-6.216	-2.524	5.279	5.279
1.00E-03	2000.	5.00E-01	-4.593	-2.967	-4.491	-1.924	5.331	5.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	-1.241	-12.816	-32.555	-13.114	4.160	4.160
1.00E-02	400.	2.50E+00	-.354	-8.851	-23.690	-9.095	5.339	5.339
1.00E-02	500.	2.00E+00	-.126	-6.780	-18.638	-6.905	5.817	5.817
1.00E-02	600.	1.67E+00	-.167	-5.545	-15.335	-5.530	6.012	6.012
1.00E-02	800.	1.25E+00	-.523	-4.162	-11.233	-3.876	6.125	6.125
1.00E-02	1000.	1.00E+00	-.941	-3.381	-8.716	-2.875	6.170	6.170
1.00E-02	1500.	6.67E-01	-1.822	-2.373	-5.216	-1.524	6.279	6.279
1.00E-02	2000.	5.00E-01	-2.593	-1.967	-3.491	-.924	6.331	6.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	.759	-12.404	-31.558	-12.114	5.160	5.160
1.00E-01	400.	2.50E+00	1.646	-8.219	-22.691	-8.095	6.339	6.339
1.00E-01	500.	2.00E+00	1.874	-5.992	-17.639	-5.905	6.817	6.817
1.00E-01	600.	1.67E+00	1.833	-4.658	-14.336	-4.530	7.012	7.012
1.00E-01	800.	1.25E+00	1.477	-3.190	-10.233	-2.876	7.125	7.125
1.00E-01	1000.	1.00E+00	1.059	-2.387	-7.716	-1.875	7.170	7.170
1.00E-01	1500.	6.67E-01	.178	-1.373	-4.216	-.524	7.279	7.279
1.00E-01	2000.	5.00E-01	-.593	-.967	-2.491	.076	7.331	7.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	2.759	-12.289	-30.588	-11.114	6.160	6.160
1.00E+00	400.	2.50E+00	3.646	-7.933	-21.706	-7.095	7.339	7.339
1.00E+00	500.	2.00E+00	3.874	-5.510	-16.646	-4.905	7.817	7.817
1.00E+00	600.	1.67E+00	3.833	-4.005	-13.340	-3.530	8.012	8.012
1.00E+00	800.	1.25E+00	3.477	-2.317	-9.234	-1.876	8.125	8.125
1.00E+00	1000.	1.00E+00	3.059	-1.427	-6.717	-.875	8.170	8.170
1.00E+00	1500.	6.67E-01	2.178	-.377	-3.216	.476	8.279	8.279
1.00E+00	2000.	5.00E-01	1.407	.032	-1.491	1.076	8.331	8.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	4.759	-12.271	-29.809	-10.114	7.152	7.154
1.00E+01	400.	2.50E+00	5.646	-7.858	-20.826	-6.095	8.337	8.338
1.00E+01	500.	2.00E+00	5.874	-5.317	-15.711	-3.905	8.817	8.817
1.00E+01	600.	1.67E+00	5.833	-3.651	-12.375	-2.530	9.012	9.012
1.00E+01	800.	1.25E+00	5.477	-1.656	-8.244	-.876	9.125	9.125
1.00E+01	1000.	1.00E+00	5.059	-.579	-5.721	.125	9.170	9.170
1.00E+01	1500.	6.67E-01	4.178	.602	-2.217	1.476	9.279	9.279
1.00E+01	2000.	5.00E-01	3.407	1.027	-.491	2.076	9.331	9.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	6.759	-12.270	-29.504	-9.115	8.086	8.106
1.00E+02	400.	2.50E+00	7.646	-7.847	-20.353	-5.095	9.322	9.331
1.00E+02	500.	2.00E+00	7.874	-5.276	-15.082	-2.905	9.813	9.818
1.00E+02	600.	1.67E+00	7.833	-3.539	-11.617	-1.530	10.010	10.013
1.00E+02	800.	1.25E+00	7.477	-1.293	-7.334	.124	10.125	10.126
1.00E+02	1000.	1.00E+00	7.059	.038	-4.755	1.125	10.170	10.171
1.00E+02	1500.	6.67E-01	6.178	1.504	-1.224	2.476	10.279	10.279
1.00E+02	2000.	5.00E-01	5.407	1.994	.505	3.076	10.331	10.331

Adduct (CQCjO) Dissociation Reaction Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	-5.241	-14.595	-34.554	-15.114	2.160	2.160
298.	3.36E+00	1.00E-03	-3.241	-13.623	-33.554	-14.114	3.160	3.160
298.	3.36E+00	1.00E-02	-1.241	-12.816	-32.555	-13.114	4.160	4.160
298.	3.36E+00	1.00E-01	.759	-12.404	-31.558	-12.114	5.160	5.160
298.	3.36E+00	1.00E+00	2.759	-12.289	-30.588	-11.114	6.160	6.160
298.	3.36E+00	1.00E+01	4.759	-12.271	-29.809	-10.114	7.152	7.154
298.	3.36E+00	1.00E+02	6.759	-12.270	-29.504	-9.115	8.086	8.106
T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	-4.354	-10.751	-25.690	-11.095	3.339	3.339
400.	2.50E+00	1.00E-03	-2.354	-9.762	-24.690	-10.095	4.339	4.339
400.	2.50E+00	1.00E-02	-.354	-8.851	-23.690	-9.095	5.339	5.339
400.	2.50E+00	1.00E-01	1.646	-8.219	-22.691	-8.095	6.339	6.339
400.	2.50E+00	1.00E+00	3.646	-7.933	-21.706	-7.095	7.339	7.339
400.	2.50E+00	1.00E+01	5.646	-7.858	-20.826	-6.095	8.337	8.338
400.	2.50E+00	1.00E+02	7.646	-7.847	-20.353	-5.095	9.322	9.331
T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	-4.126	-8.734	-20.638	-8.905	3.817	3.817
500.	2.00E+00	1.00E-03	-2.126	-7.739	-19.638	-7.905	4.817	4.817
500.	2.00E+00	1.00E-02	-.126	-6.780	-18.638	-6.905	5.817	5.817
500.	2.00E+00	1.00E-01	1.874	-5.992	-17.639	-5.905	6.817	6.817
500.	2.00E+00	1.00E+00	3.874	-5.510	-16.646	-4.905	7.817	7.817
500.	2.00E+00	1.00E+01	5.874	-5.317	-15.711	-3.905	8.817	8.817
500.	2.00E+00	1.00E+02	7.874	-5.276	-15.082	-2.905	9.813	9.818
T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	-4.167	-7.525	-17.335	-7.530	4.012	4.012
600.	1.67E+00	1.00E-03	-2.167	-6.527	-16.335	-6.530	5.012	5.012
600.	1.67E+00	1.00E-02	-.167	-5.545	-15.335	-5.530	6.012	6.012
600.	1.67E+00	1.00E-01	1.833	-4.658	-14.336	-4.530	7.012	7.012
600.	1.67E+00	1.00E+00	3.833	-4.005	-13.340	-3.530	8.012	8.012
600.	1.67E+00	1.00E+01	5.833	-3.651	-12.375	-2.530	9.012	9.012
600.	1.67E+00	1.00E+02	7.833	-3.539	-11.617	-1.530	10.010	10.013
T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	-4.523	-6.159	-13.233	-5.876	4.125	4.125
800.	1.25E+00	1.00E-03	-2.523	-5.159	-12.233	-4.876	5.125	5.125
800.	1.25E+00	1.00E-02	-.523	-4.162	-11.233	-3.876	6.125	6.125

800.	1.25E+00	1.00E-01	1.477	-3.190	-10.233	-2.876	7.125	7.125
800.	1.25E+00	1.00E+00	3.477	-2.317	-9.234	-1.876	8.125	8.125
800.	1.25E+00	1.00E+01	5.477	-1.656	-8.244	-.876	9.125	9.125
800.	1.25E+00	1.00E+02	7.477	-1.293	-7.334	.124	10.125	10.126

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	-4.941	-5.380	-10.716	-4.875	4.170	4.170
1000.	1.00E+00	1.00E-03	-2.941	-4.380	-9.716	-3.875	5.170	5.170
1000.	1.00E+00	1.00E-02	-.941	-3.381	-8.716	-2.875	6.170	6.170
1000.	1.00E+00	1.00E-01	1.059	-2.387	-7.716	-1.875	7.170	7.170
1000.	1.00E+00	1.00E+00	3.059	-1.427	-6.717	-.875	8.170	8.170
1000.	1.00E+00	1.00E+01	5.059	-.579	-5.721	.125	9.170	9.170
1000.	1.00E+00	1.00E+02	7.059	.038	-4.755	1.125	10.170	10.171

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	-5.822	-4.373	-7.216	-3.524	4.279	4.279
1500.	6.67E-01	1.00E-03	-3.822	-3.373	-6.216	-2.524	5.279	5.279
1500.	6.67E-01	1.00E-02	-1.822	-2.373	-5.216	-1.524	6.279	6.279
1500.	6.67E-01	1.00E-01	.178	-1.373	-4.216	-.524	7.279	7.279
1500.	6.67E-01	1.00E+00	2.178	-.377	-3.216	.476	8.279	8.279
1500.	6.67E-01	1.00E+01	4.178	.602	-2.217	1.476	9.279	9.279
1500.	6.67E-01	1.00E+02	6.178	1.504	-1.224	2.476	10.279	10.279

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	-6.593	-3.967	-5.491	-2.924	4.331	4.331
2000.	5.00E-01	1.00E-03	-4.593	-2.967	-4.491	-1.924	5.331	5.331
2000.	5.00E-01	1.00E-02	-2.593	-1.967	-3.491	-.924	6.331	6.331
2000.	5.00E-01	1.00E-01	-.593	-.967	-2.491	.076	7.331	7.331
2000.	5.00E-01	1.00E+00	1.407	.032	-1.491	1.076	8.331	8.331
2000.	5.00E-01	1.00E+01	3.407	1.027	-.491	2.076	9.331	9.331
2000.	5.00E-01	1.00E+02	5.407	1.994	.505	3.076	10.331	10.331

REFERENCES (PART FOUR)

1. Benson, S. W. *Thermochemical Kinetics* ; 2nd ed. John Wiley and Sons : New York, 1976.
2. Slagle, I. R.; Ratajczak, E.; Gutman, D. J. *J. Phys. Chem.*, 1986, 90, 402.
3. Tyndall, G. S.; Staffelbach, T. A.; Orlando, J. J.; Calvert, J. G. *Int. J. Chem. Kinet.* 1995, 27, 1009.
4. Sehested, I.; Christensen, L. K.; Nielsen, O. J.; Wallington, T.J. *Int. J. Chem. Kinet.* 1998, 30, 913.
5. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data* 1989, 18, 881.
6. Bartels, M.; Hoyermann, K. *An. Asoc. Quim. Argent.* 1985, 73, 253.
7. Michael, J. V.; Keil, D. G.; Klemm, R. B. *J. Chem. Phys.* 1985, 83, 1630.
8. Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.*, 1982, 104, 4741.
9. Maricq, M. M.; Szente, J. J. *J. Chem. Phys. Lett.* 1996, 100, 12380.
10. Zhu, L.; Johnston, G. *J. Phys. Chem.* 1995, 99, 15114.
11. Villalta, P. W.; Howard, C. J. *J. Phys. Chem.* 1996, 100, 13624.
12. Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions* ; Oxford Press : Boston, MA, 1990.
13. Gilbert, R. G.; Smith, S. C. UNIMOL, 1990.
14. Gilbert, R. G.; Luther, K.; Troe, J. *Ber. Bunsen-Gas. Phys. Chem.* 1983, 87, 169.
15. Stewart, J. J. P., *MOPAC 6.0*, Frank J. Seiler Research Lab., US Air Force Academy, Colorado, 1990.
16. Frisch, M.j.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Pople, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.;

17. Ochterski, J. W.; Petersson, G. A.; Montgomery, Jr., J. A. *J. Chem. Phys.* 1996, 104, 2598.
18. Nyden, M. R.; Petersson, G. A. *J. Chem. Phys.* 1991, 75, 1843.
19. Petersson, G. A. *J. Chem. Phys.* 1994, 94, 6081.
20. Montgomery, J. A.; Petersson, G. A. *J. Phys. Chem.* 1994, 101, 5900.
21. Hehre, W. J.; Random, L.; Schleyer, P. R.; Pople, J. A. *Ab-Initio Molecular Orbital Theory*; John Wiley & Sons: New York, NY, 1986.
22. Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* 1942, 10, 428.
23. (a) Zhong, X.; Bozzelli, J. W. *J. Phys. Chem. A* 1998, 102, 3537. (b) Bozzelli, J. W.; Chang, A. Y.; Dean, A. M. *Int. J. Chem. Kint.* 1997, 29, 161.
24. Rodgers, A. S. *Selected Values for Properties of Chemical Compounds*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1982.
25. Lay, T. H.; Bozzelli, J. W. *J. Phys. Chem. A* 1997, 101, 9505-9510.
26. Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, Th.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* 1992, 21, 411.