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## Thermochemical properties of methyl and chloro-methyl hypochlorites and ethers and reaction of methyl radical with CLO

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## ABSTRACT

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

Hypochlorites are formed from reactions of chlorine monoxide (ClO) addition to unsaturates and association with radicals. ClO is a prevalent and an important species in chemistry of the atmosphere and in combustion systems where chlorine is present. Thermochemical property data on these oxy-chlorocarbon species are important to understanding the reaction pathways and kinetics in these environments. Enthalpy,  $\Delta H_f^\circ_{298}$ , entropy,  $S^\circ_{298}$  and heat capacities,  $C_p(T)$  from 300 to 1500 K are determined for methyl hypochlorite and three chloro-methyl hypochlorites and formaldehyde-Cl atom complex radicals ( $\text{CH}_2\text{O}\text{--Cl}$ ,  $\text{CHClO}\text{--Cl}$ ,  $\text{CCl}_2\text{O}\text{--Cl}$ ) by density functional, and *ab initio* calculation methods. Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) density functional calculation level, with single point calculations for energy at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q levels of calculation. Enthalpies of formation are determined at each calculation level using the  $\Delta H^\circ_{\text{rxn}}$  and known enthalpies of other reactants in each of several working reactions (up to seven). Barriers for intramolecule rotation are calculated and contributions to entropy and heat capacity from internal rotation in the chloro-methyl hypochlorite, chloro-dimethyl ether, chloro-methoxy and formaldehyde-Cl atom coupling radicals are determined. Evaluation of enthalpy data from reaction (up to seven) schemes and the statistical distribution of rotation conformers, result in  $\Delta H_f^\circ_{298}$  values for  $\text{CH}_3\text{OCl}$  of  $-15.4 \pm 1.5$ ,  $\text{CH}_2\text{ClOCl}$  of  $-22.1 \pm 2$ ,  $\text{CHCl}_2\text{OCl}$  of  $-26.1 \pm 4$  and  $\text{CCl}_3\text{OCl}$  of  $-26.7 \pm 5$

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

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

**by  
Dawoon Jung**

**A Thesis  
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## APPROVAL PAGE

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Dawoon Jung, Chung-Ju Chen and Joseph W. Bozzelli, "Thermochemical Properties of Methyl and Chloro-methyl Oxychlorides and Reaction of Methyl radical with ClO"  
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Dawoon Jung, Sung Han Lee, "The Catalytic Reaction of CO and H<sub>2</sub>O over New Amorphous Ternary Metal Chalcogens" *Bulletin of the Korean chemical society*, 17, 1996, 5-7

To my beloved family

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Two roads diverged in a yellow wood, and sorry I could not travel both and be one traveler, long I stood and looked down one as far as I could to where it advanced in Computational Chemistry. Before, I don't know Gaussian function, density function, Ab initio methods, and composite calculations. Then took the other, as just as fair, and having perhaps the better claim, because it was higher basis set, Bozzelli Group. Though as for complex theory, had researched them really about nice work

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## CHAPTER 1

### INTRODUCTION

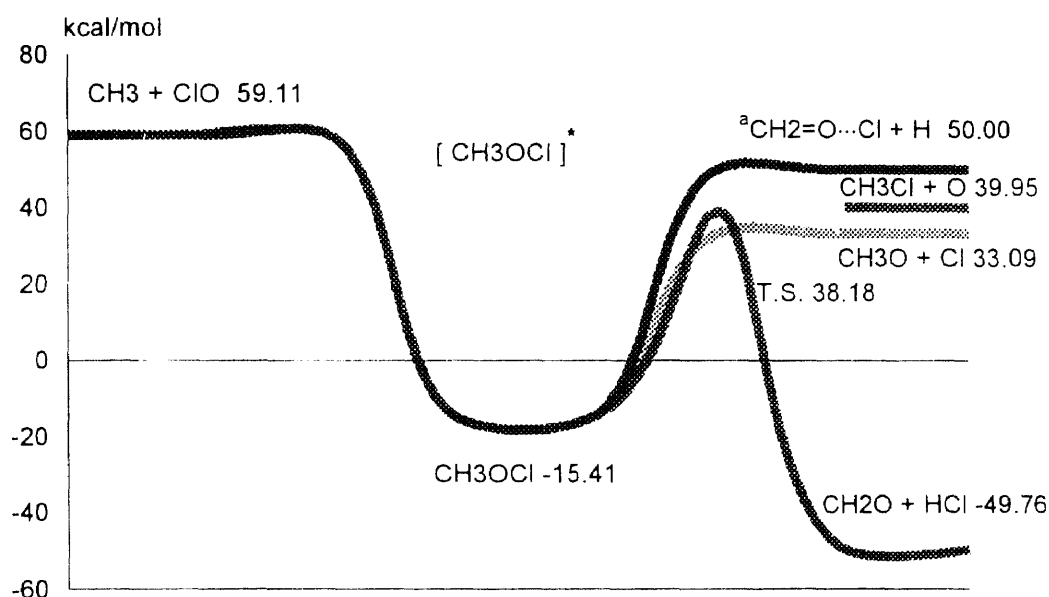
$\text{CH}_3\text{OCl}$  has been considered an important atmospheric species since the severe depletions in stratospheric ozone were first observed during the Antarctic spring in 1985.

<sup>1,2</sup> This ozone depletion is now believed to be the result from several reaction sequences involving the chlorine monoxide radical ( $\text{ClO}$ ).<sup>3,4</sup> At low temperature, methyl radical associates with chlorine monoxide radical ( $\text{ClO}$ ) and produces methyl hypochlorite ( $\text{CH}_3\text{OCl}$ ) but at higher temperature or low pressure, methoxy radical and Cl atom are dominant initial products from the association, with formaldehyde also observed.<sup>9</sup>

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

Chlorocarbon radicals are the initial intermediates from reaction of chlorocarbons in atmospheric and combustion systems. Chlorine substitution on methyl and alkyl radicals results in decreased stability (and lower reactivity to products) of peroxy adducts formed from reaction of these radicals with  $\text{O}_2$ . The slower reactions with  $\text{O}_2$  permit the chlorinated methyl radicals to build up to higher concentrations in combustion environments, relative to  $\text{CH}_3$ , where they are more likely to undergo reactions with the

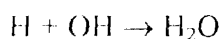
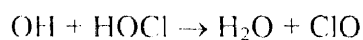
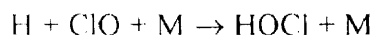
radical pool, of which HO<sub>2</sub>, OH and ClO are major species. These association reactions result in oxychlorides or chloro-methoxy species. Chlorine monoxide radicals are also active in combustion inhibition (termination reactions) via cycles similar to that for thermal catalytic ozone destruction in the stratosphere.<sup>6</sup>



**Figure 1.1** Overview schematic of CH<sub>3</sub>OCl Formation and Dissociation Paths

<sup>a</sup> Weakly bond (5kcal/mol), formaldehyde~Cl atom complete: this complete is lower in energy than C-H<sub>2</sub>OCl, hypochlorite-methyl radical.

Termination



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

bond. This often results in significant steady state levels of atomic and molecular chlorine as well as chlorine oxide in the combustion environment. Cl and ClO react rapidly with alkyl radicals, with ClO radicals undergoing association to form chemically activated oxychlorides that can be stabilized, or further react to new products. ClO also serves to convert CO to CO<sub>2</sub>.<sup>7</sup>

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



Thermodynamic property data on the oxygenated chlorocarbon species are needed for evaluation of reaction paths, kinetic processes, as well as stability of intermediate adducts and the oxy-chlorocarbon species formed as products.<sup>9,10</sup> These properties are also needed in kinetic modeling and in equilibrium computer codes (Examples: Chemkin, Nasa, Stanjan equilibrium codes, commercially available). There is very little or no thermodynamic data on these oxygenated chlorocarbons in the literature.<sup>15-17</sup> Francisco et al. report a theoretical study on the excited states<sup>14</sup> and  $\Delta H_f^\circ$  for methyl hypochlorite (CH<sub>3</sub>OCl) of  $-13.5 \pm 2$  kcal/mol with CCSD(T)/6-311G(2df,2p) level<sup>15</sup> of theory, which we convert to  $\Delta H_f^\circ_{298}$  of  $-15.9$  kcal/mol. Elrod et al. report Gaussian-2 *ab initio* study for  $\Delta H_f^\circ_{298}$  of CH<sub>3</sub>OCl as  $-17.7$  kcal/mol<sup>16</sup> and separately derive  $\Delta H_f^\circ_{298}$  of CH<sub>3</sub>OCl as  $-12.3$  kcal/mol by bond additivity based on methods developed by Colussi.<sup>17</sup> J. Espinosa-Garcia recently reported<sup>53</sup>  $\Delta H_f^\circ_{298}$  for CH<sub>3</sub>OCl of -



$13.2 \pm 2.3$  kcal/mol by the unweighted average of the results of MP4/6-31G(d,p)/MP2/6-31G(d), CCSD(T)/6-311G(3d,2p), CCSD/cc-pVTZ, and Truhlar's basis-set limit method. Melius includes unpublished BAC/MP4  $\Delta H_f^\circ_{298}$  for methyl hypochlorite on his web site -14.0 kcal/mol,<sup>18</sup> and Crowley et al.<sup>19</sup> used bond additivity values of Benson<sup>20</sup> to estimation of  $\Delta H_f^\circ_{298}$  of -14.6 kcal/mol for CH<sub>3</sub>OCl.

These estimates exhibit the wide range in enthalpy values at 298 K from -12.3 to -17.7 kcal/mol. There is, in addition, no literature data on thermodynamic properties of chloro-methyl hypochlorites (CH<sub>2</sub>ClOCl, CHCl<sub>2</sub>OCl, and CCl<sub>3</sub>OCl). There is no published values for heat capacity or entropy on CH<sub>3</sub>OCl or any of the chloro methyl hypochlorites, too.

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

## CHAPTER 2

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

#### 2.1 Calculation Methods

##### 2.1.1 Selection of Calculation Methods and Basic Sets

B3LYP/6-31G(d,p) is chosen because it is computationally economical and thus, possibly applicable to larger molecules, if it is accurate. It is also commonly used and is reported to yield accurate geometry and reasonable energies<sup>21,22</sup> Comparison of calculation results from this level against data from higher calculation levels for  $\Delta H_f^\circ$  values, will provide some calibration of the B3LYP/6-31G(d,p) values (with similar working reactions) for larger molecules, where this may be one of the few calculation methods available. B3LYP/6-311+G(3df,2p) is chosen to see if this larger basic set results in an improvement to the above commonly used density functional calculation method.<sup>22</sup> QCISD(T)/6-31G(d,p) is a configuration interaction method; but with a small, economical base set.<sup>23,24</sup> CBS-Q//B3LYP/6-31G(d,p) calculation is a high level composite method with empirical corrections; it is reported to be comparable with QCISD(T)/6-311+G(3df,2p).<sup>29,30</sup> This CBS-Q//B3LYP/6-31G(d,p) method similar to the Radom research group's CBS/RAD<sup>25</sup> method; it has B3LYP/6-31g(d,p) geometry, which they indicate is very close to QCISD(T) values and a QCISD(T) calculation in place of CCSD(T). These calculations are referred to as CBSQ//B3\*\* in the present study for brevity.

### 2.1.2 Thermodynamic Properties Using *ab initio* Calculations

Enthalpy,  $\Delta H_f^\circ_{298}$ , entropy,  $S^\circ_{298}$  and heat capacities  $C_p(T)$ , from 300 to 1500 K are determined for four chloro-methyl hypochlorites,  $\text{CH}_3\text{OCl}$ ,  $\text{CH}_2\text{ClOCl}$ ,  $\text{CHCl}_2\text{OCl}$  and  $\text{CCl}_3\text{OCl}$  using density functional B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p) and *ab initio* QCISD(T)/6-31G(d,p) and CBS-Q calculation methods.<sup>25-30</sup>

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

### 2.1.3 Calculation of Hindered Rotation Contribution to Thermodynamic Parameters

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

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

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

## 2.2 Results and Discussion

### 2.2.1 Vibrational Frequencies and geometries

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

**TABLE 2.1-a.** Vibrational Frequencies<sup>a</sup> (cm<sup>-1</sup>) for Methyl Hypochlorite

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

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

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

**TABLE 2.1-c.** Vibrational Frequencies<sup>a</sup> (cm<sup>-1</sup>), Rotation Constants (Ghz) and Moment of Inertia (amu-Bohr) for Chloro-methyl hypochlorite

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

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

TABLE 2.2. Optimized Geometry of Chloro-methyl Hypochlorites<sup>a</sup>

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

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

<sup>a</sup> Geometry is optimized in B3LYP/6-31g(d,p) density functional calculation level, <sup>b</sup> B3LYP/6-311++G(3df,3pd) level in reference 15, <sup>c</sup> CCSD(T)/6-311(2df,2p) level in reference 15, and <sup>d</sup> BAC/MP4 level in reference 18. <sup>e</sup> Experimental value in reference 47. <sup>f</sup> Bond length or the distance between two atoms of number in Å. <sup>g</sup> Bond angle or the angle among three atoms of number in degree. <sup>h</sup> Dihedral angle among the four number atoms.

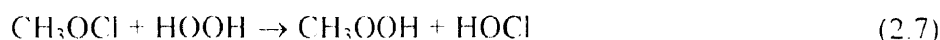
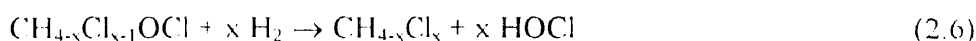
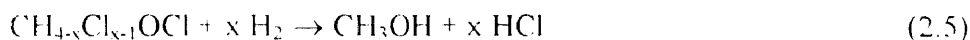
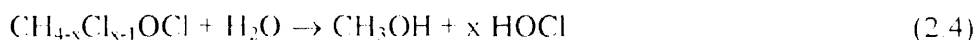
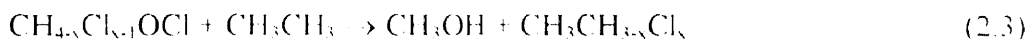
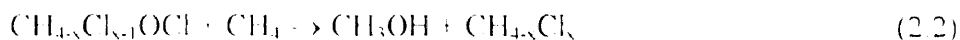
B3LYP/6-311++G(3df,3pd),<sup>15</sup> 3040 cm<sup>-1</sup> in CCSD(T)/6-311G(2df,2p),<sup>15</sup> 2880 cm<sup>-1</sup> in BAC/MP4,<sup>18</sup> and 2998 cm<sup>-1</sup> in the spectra of Crowley et al.<sup>10</sup> and 2820 cm<sup>-1</sup> by Jungkamp et al.<sup>46</sup> The vibrational frequencies and rotational constants for multiple chloro-methyl hypochlorites are given in Table 2.1.

The optimized B3LYP/6-31G(d, p) geometries for the methyl and three chlorinated methyl hypochlorites are illustrated in Table 2.2. Numerical values of the structural parameters including carbon-hydrogen, carbon-chlorine, carbon-oxygen, oxygen-hydrogen bond distances along with applicable bond angles are also listed in Table 2.2. Effects of chlorine  $\alpha$ -substitution on molecular geometry can be seen from Table 2.2. The C-H and O-Cl bond lengths in the equilibrium conformations of four title molecules: CH<sub>3</sub>OCl, CH<sub>2</sub>ClOCl, CHCl<sub>2</sub>OCl, and CCl<sub>3</sub>OCl optimized at the B3LYP/6-31G(d, p) are similar, while the C-O bond lengths (R4) decrease in order; 1.425 Å in CH<sub>3</sub>OCl, 1.390 Å in CH<sub>2</sub>ClOCl, 1.375 Å in CHCl<sub>2</sub>OCl, 1.383 Å in CCl<sub>3</sub>OCl. The Cl-C bond lengths (R1) in the chloro-methyl hypochlorites also decrease with increase in number of chlorines; it is 1.818, 1.807, and 1.801 Å in CH<sub>2</sub>ClOCl, CHCl<sub>2</sub>OCl, and CCl<sub>3</sub>OCl. The Cl-O bond length (R5) increases in this series at 1.736, 1.739, 1.738 and 1.742 Å in CH<sub>3</sub>OCl, CH<sub>2</sub>ClOCl, CHCl<sub>2</sub>OCl, and CCl<sub>3</sub>OCl. The geometry parameters of Melius were obtained by conversion of his cartesian coordinates. The geometry of CH<sub>3</sub>OCl in this work is similar with values reported by Francisco,<sup>15</sup> Melius,<sup>18</sup> and experimental values of Rigden et al.<sup>47</sup> in Table 2.2. The C-O bond distance (R4) of CH<sub>3</sub>OCl is 1.425 Å in this work and in Francisco's calculation, 1.411 Å in BAC/MP4, and 1.389 Å in the study of Rigden et al.. The O-Cl bond length (R4) of CH<sub>3</sub>OCl is 1.736 Å in B3LYP/6-31G(d,p) level, 1.702 Å in B3LYP/6-311++G(3df,3pd) calculation,

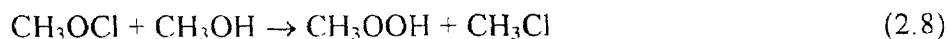
1.709 Å in CCSD(T)/6-31G(2df, 2p) method, and 1.674 Å in the experiment.<sup>47</sup> We conclude that the geometry and frequencies of methyl hypochlorite optimized B3LYP/6-31G(d,p) is reliable, because higher level calculations with larger basis sets<sup>15</sup> and experiments<sup>10,46,47</sup> demonstrate consistent results with these. Distance between the hypochlorite chloride and hydrogen on the methyl group in the low energy conformers are 3.531, 3.523, 3.538 Å for CH<sub>3</sub>OCl, CH<sub>2</sub>ClOCl, and CHCl<sub>2</sub>OCl, probably too long for significant hydrogen bonding.

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

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







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

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

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

Density functional and ab initio calculations with ZPVE and thermal correction are performed for all four compounds in each reaction, and enthalpy of reaction  $\Delta H_{\text{rxn}}^{\circ}{}_{298}$  is calculated. Since enthalpies of formation of three compounds have been experimentally determined or theoretically calculated, the unknown enthalpies of formation of CH<sub>3</sub>OCl, CH<sub>2</sub>ClOCl, CHCl<sub>2</sub>OCl, and CCl<sub>3</sub>OH are obtained. As example,  $\Delta H_{\text{f}}^{\circ}{}_{298}$  (CH<sub>3</sub>OCl) is calculated from

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

and the listed known enthalpies of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{Cl}$  and  $\text{CH}_4$ .

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

2.4. The  $\Delta H_f^\circ_{298}$  on the standard compounds in reaction sets are from literature in Table

2.5 and are used to determine  $\Delta H_f^\circ_{298}$  values in Table 2.6.

**TABLE 2.4.** Reaction Enthalpies (in kcal/mol) at 298 K<sup>a</sup>

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

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

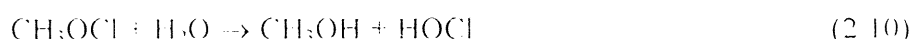
**TABLE 2.5.** Enthalpy Data Used in Reactions to Determine  $\Delta H_f^\circ_{298}$  of Target  
Oxychlorides

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

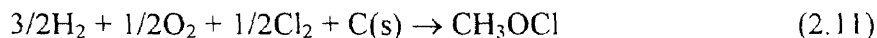
<sup>a</sup> Units in kcal/mol. <sup>b</sup> The uncertainty comes from 1,1,2,2-tetrachloroethane (CHCl<sub>2</sub>CHCl<sub>2</sub>).

<sup>c</sup> The standard deviation of Table 2.5 in reference 35.

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



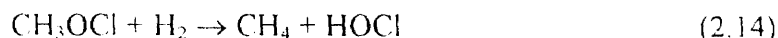
which we calculate as -15.9 kcal/mol at 298 K using the reaction below and data in this study.



Elord et al.<sup>16</sup> report  $\Delta H_f^\circ_{298}$  of  $\text{CH}_3\text{OCl}$  at -17.69 kcal/mol from G2 analysis on the isodesmic reaction:



They also calculated  $\Delta H_f^\circ_{298}$  of  $\text{CH}_3\text{OCl}$  at -12.3 kcal/mol from bond additivity by Colussi's values.<sup>17</sup> Espinosa-Garcia recently reported<sup>53</sup>  $\Delta H_f^\circ_{298}$  for  $\text{CH}_3\text{OCl}$  of  $-13.2 \pm 2.3$  kcal/mol by the unweighted average of the results of MP4/6-31G(d,p)/MP2/6-31G(d), CCSD(T)/6-311G(3d,2p), CCSD/cc-pVTZ, and Truhlar's basis-set limit method using hydrogenation reactions.



Melius reports  $\Delta H_f^\circ_{298}$  of -14.0 kcal/mol based on BAC/MP4<sup>18</sup> calculation. The available literature data on  $\text{CH}_3\text{OCl}$  show a variation in standard enthalpies of formation, -12.3 to -17.7 kcal/mol at 298 K.

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

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

**TABLE 2.6:** Comparison of Enthalpies of Formation<sup>a</sup> at 298 K (in kcal/mol)

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

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

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

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

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

### 2.2.3 Test of Calculation Method: Enthalpy of HOCl

Methyl hypochlorite and hypochlorous acid both have the oxy-chloride bond and an electron donor group, methyl and H atom respectively. We analyze  $\Delta H_f^\circ_{298}$  of  $HOCl$  by similar reaction sets to try and evaluate the accuracy of our calculation methods; data are illustrated in Table 2.7. The evaluated  $\Delta H_f^\circ_{298}$  of  $HOCl$  is  $-17.8$  kcal/mol<sup>52</sup>, with a more recent value of  $-18.5 \pm 0.5$  recommended by Espinosa-Garcia<sup>53</sup>. Our calculated  $\Delta H_f^\circ_{298}$  for hypochlorous acid are  $-19.2$ ,  $-17.6$ ,  $-17.6$ ,  $-17.6$ ,  $-17.5$ ,  $-17.9$  kcal/mol using CBS-Q//B3\*\* and reaction schemes 1 to 6 as shown in Table 2.7. Data from the reaction schemes in Table 2.7 obtained at the other calculation levels do not show this good agreement with the experimental value of  $HOCl$ . The next most reasonable values for  $\Delta H_f^\circ_{298}$  of  $HOCl$  are not the QCISD(T) but the density function values with the large basis set, in table 2.7.

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

**TABLE 2.7.** Enthalpies of formation at 298 K (in kcal/mol)<sup>a</sup>

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

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

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

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

<sup>a</sup> The average values from the selected reaction in Table 2.6. <sup>b</sup> value from working reaction (6) in Table 2.7.

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

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

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

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

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

## 2.2.4 Enthalpies of Rotational Conformers

There are two staggered structures, which show different enthalpies in CH<sub>2</sub>ClOCl, and CHCl<sub>2</sub>OCl as shown in Figures 2.2 and 2.3. We calculate the correction to enthalpy of formation using statistical analysis of the conformer values listed in Table 2.11. The  $\Delta H_f^\circ_{298}$  of CH<sub>3</sub>OCl, CH<sub>2</sub>ClOCl, CHCl<sub>2</sub>OCl, and CCl<sub>3</sub>OCl are  $-15.4 \pm 1.5$  kcal/mol,  $-22.1 \pm 2.4$  kcal/mol,  $-26.1 \pm 3.6$  kcal/mol, and  $-26.7 \pm 4.7$  kcal/mol respectively. These are the average data using all reactions except reaction series 4 based on CBS-Q calculation level results and considering statistical distribution of rotation conformers in Table 2.11.



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

There still exists a significant discrepancy in the  $\Delta H_f^\circ_{298}$  for  $\text{CH}_3\text{OCl}$ . We did not intend to resolve this issue in this study. Our primary object is to obtain more complete ( $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$ , and  $C_p(T)$ ) thermodynamic properties and groups for group additivity of oxygenated chloro carbon species, i.e. for estimation of thermodynamic properties of higher molecular weight hypochlorites. The very high level *ab initio* calculation values of Espinosa-Garcia<sup>54</sup> with one working reaction are 2.2 kcal/mol above our value; but our values are close to other reported data.

### 2.2.5 Comparison to Semiempirical (MOPAC) Data

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

### 2.2.6 Rotational Barriers

Potential barriers for internal rotations of  $\text{CH}_3\text{OCl}$ ,  $\text{CH}_2\text{ClOCl}$ ,  $\text{CHCl}_2\text{OCl}$ , and  $\text{CCl}_3\text{OCl}$  are calculated at the B3LYP/6-31G(d, p) level. Potential energy as function of torsion

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

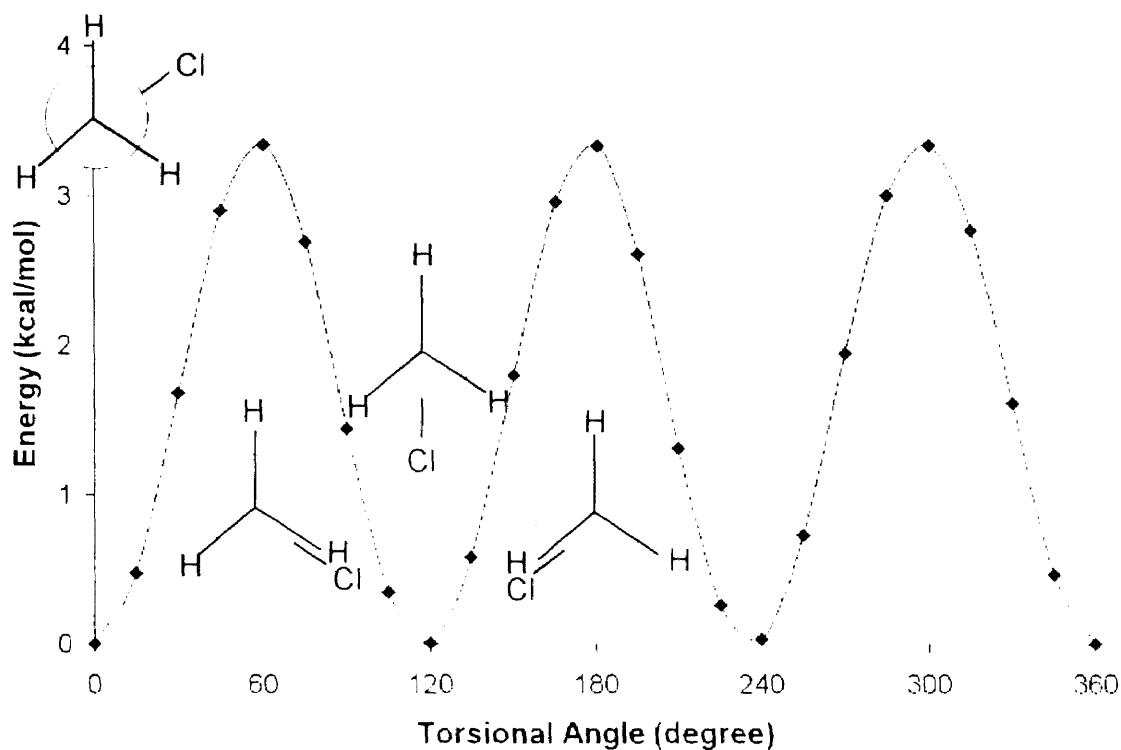
**Table 2.10.** Total Energy<sup>a</sup> (Hartree) of Molecules by Torsion angle

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

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

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

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

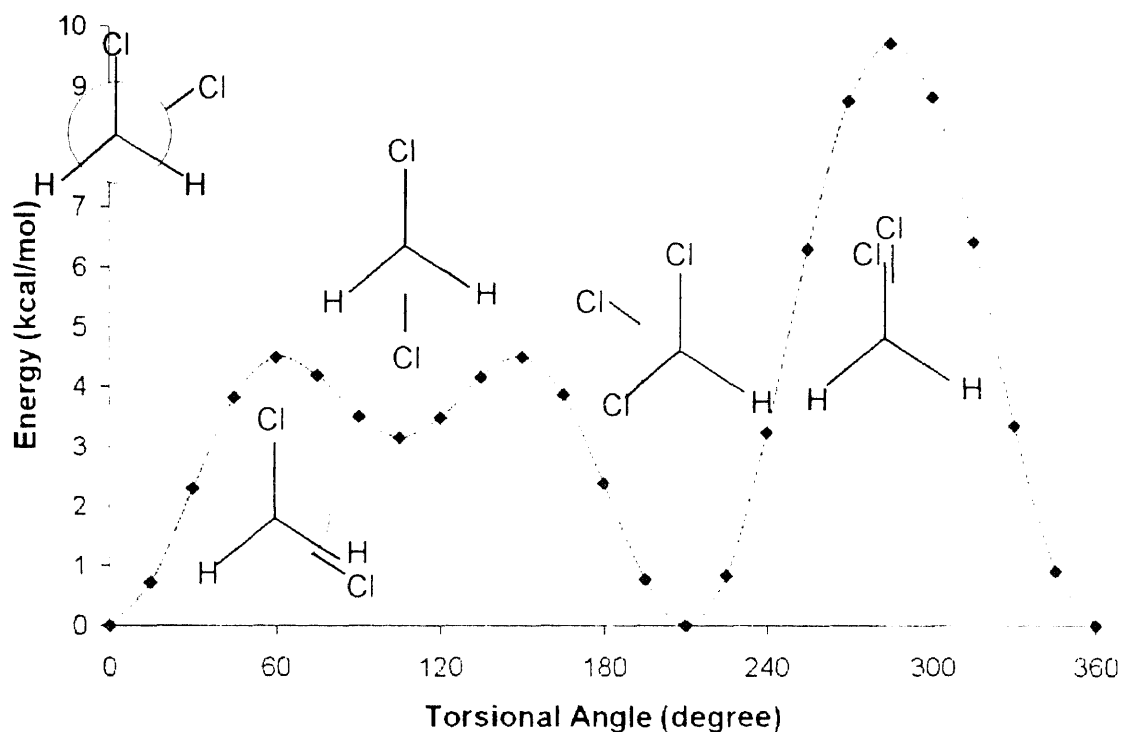


**Figure 2.1.** Potential energy for internal rotation about C-O bond of  $\text{CH}_3\text{OCl}$  versus torsion angle.

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

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

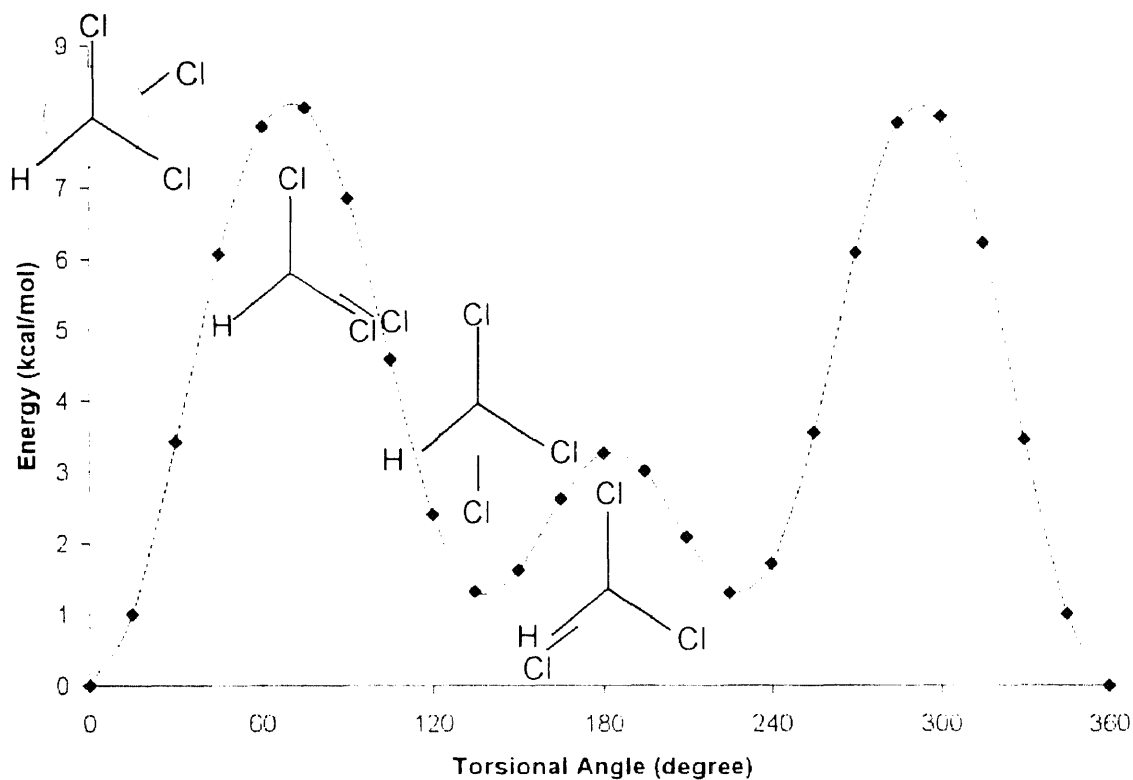
bonding electrons. The H-Cl eclipsed rotational barrier is 4.5 kcal/mol and the Cl-Cl eclipsed rotational barrier is 9.7 kcal/mol. The Cl/Cl interaction is stronger than H/Cl interaction across the oxygen link on 1-chloro-methyl hypochlorite.



**Figure 2.2.** Potential energy for internal rotation about C-O bond of  $\text{CH}_2\text{ClOCl}$  versus torsion angle.

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

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



**Figure 2.3.** Potential energy for internal rotation about C-O bond of  $\text{CHCl}_2\text{OCl}$  versus torsion angle.

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

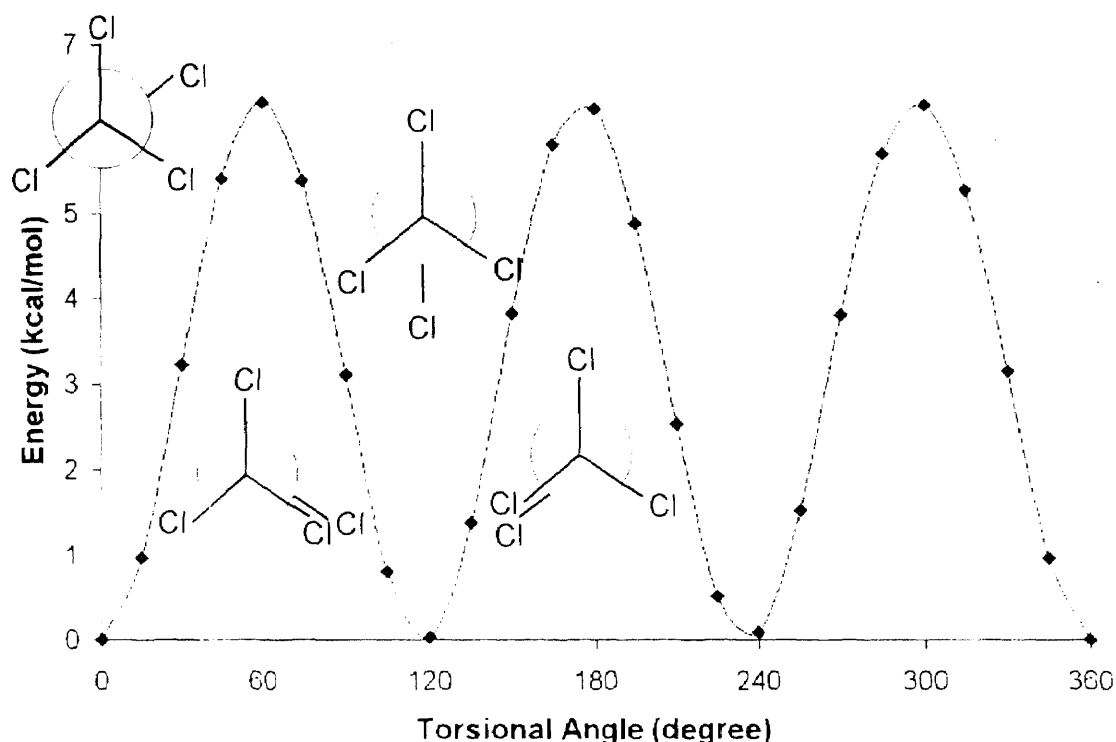
Compound	energy(kcal/mol) <sup>c</sup>	relative (%) <sup>d</sup>	final value(kcal/mol) <sup>e</sup>
CH <sub>3</sub> OCl	-15.41	100.00	-15.41±1.52
CH <sub>2</sub> ClOCl <sup>a</sup>	-22.06	99.76	
CH <sub>2</sub> ClOCl <sup>b</sup>	-18.91	0.24	-22.05±2.41
CHCl <sub>2</sub> OCl <sup>a</sup>	-26.27	90.14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

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

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

Entropy correction	
CH <sub>2</sub> ClOCl <sup>a</sup>	$-R\{0.9976 \times \ln(0.9976) + 0.0024 \times \ln(0.0024)\} = 0.03$
CHCl <sub>2</sub> OCl <sup>b</sup>	$-R\{0.9014 \times \ln(0.9014) + 0.0986 \times \ln(0.0986)\} = 0.64$

<sup>a</sup> Entropy for CH<sub>2</sub>ClOCl at 298K. Entropy (CH<sub>2</sub>ClOCl) = Entropy (C/Cl/H<sub>2</sub>/O) + Entropy (O/C/Cl) + Entropy correction (CH<sub>2</sub>ClOCl). <sup>b</sup> Entropy for CHCl<sub>2</sub>OCl at 298K. Entropy (CHCl<sub>2</sub>OCl) = Entropy (C/Cl<sub>2</sub>/H/O) + Entropy (O/C/Cl) + Entropy correction (CHCl<sub>2</sub>OCl)



**Figure 2.4.** Potential energy for internal rotation about C-O bond of  $\text{CHCl}_2\text{OCl}$  versus torsion angle.

### 2.2.7 Entropy, $S_{298}^\circ$ and Heat Capacity, $C_p(T)$ from 300 to 1500 K

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

**TABLE 2.12.** Coefficients<sup>a</sup> (kcal/mol) of Truncated Fourier Series Representation

Expansion for Internal Rotation Potentials

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

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

**TABLE 2.13.** Ideal Gas Phase Thermodynamic Properties<sup>a</sup> at 298 K

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

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



There is no published data on entropy and heat capacity values for  $\text{CH}_3\text{OCl}$ ,  $\text{CH}_2\text{ClOCl}$ ,  $\text{CHCl}_2\text{OCl}$  or  $\text{CCl}_3\text{OCl}$ . There is one data set, *ab initio* calculation, in the web site of C. Melius for methyl hypochlorite.<sup>18</sup> Our calculation results show a good agreement for the entropy and heat capacity with the BAC/MP4 values of Melius<sup>18</sup> for  $\text{CH}_3\text{OCl}$ ; the BAC/MP4 method uses HF/6-31G\* structures and frequencies. Table 2.1 shows a comparison of frequencies among B3LYP/6-31G(d,p), BAC/MP4<sup>18</sup> theory along with experimental data,<sup>10,46</sup> and calculated rotation constants.

### 2.2.8 Group Values and Group Additivity Correction Terms

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

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

The group value for thermodynamic properties of C/H3/O are from existing literature.<sup>20,59</sup> Values for C/Cl/H2/O, C/Cl2/H/O and C/Cl3/O are taken from recent work in this research group on chlorinated methanols<sup>38</sup> and ethers.<sup>60</sup> The properties of the C/Cl/H2/O, C/Cl2/H/O and C/Cl3/O groups for example, are derived from chloro-

methanol ( $\text{CH}_2\text{ClOH}$ ), 1,1-dichloro-methanol ( $\text{CHCl}_2\text{OH}$ ), and 1,1,1-trichloro-methanol ( $\text{CCl}_3\text{OH}$ ), respectively and from chloro-dimethyl ether ( $\text{CH}_2\text{ClOCH}_3$ ), 1,1-dichloro-dimethyl ether ( $\text{CHCl}_2\text{OCH}_3$ ), and 1,1,1-trichloro-dimethyl ether ( $\text{CCl}_3\text{OCH}_3$ ), respectively. In the present work, we estimate group values for O/C/Cl and chlorine interaction terms across the oxygen link on methyl oxychlorides of OCl/Cl, OCl/Cl<sub>2</sub>, and OCl/Cl<sub>3</sub>. There are no chlorines, other halogens, or bulky groups/fragments on the carbon atom adjacent to the oxygen atom containing the chlorine in the defining O/C/Cl group for methyl hypochlorite ( $\text{CH}_3\text{OCl}$ ). Enthalpy of formation ( $\Delta H_f^{\circ 298}$ ) and heat capacities,  $C_p(T)$  of the O/C/Cl group are calculated on the basis of the equation 2.15

$$(\text{CH}_3\text{OCl}) = (\text{C/H3/O}) + (\text{O/C/Cl}) \quad (2.15)$$

$S^{\circ}_{298}$  of O/C/Cl is calculated on the basis of the equation 2.16

$$(\text{CH}_3\text{OCl}) = (\text{C/H3/O}) + (\text{O/C/Cl}) - R \ln(\sigma) \quad (2.16)$$

$R = 1.987$  (cal/mol K), and  $\sigma$  is symmetry number, which is 3 for  $\text{CH}_3\text{OCl}$ .

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

The interaction values between chlorine(s) on the methyl and the chlorine attached to the oxygen (OCl/Cl, OCl/Cl<sub>2</sub>, and OCl/Cl<sub>3</sub>) are calculated from differences

between the sum of defined chlorinated oxyhydrocarbon group values and the determined thermodynamic properties of the parent compounds. For example,  $\Delta H_f^{\circ}_{298}$  and  $C_p$ 's for the OCl/Cl2 interaction term are estimated by the equation 2.17 and  $\Delta H_f^{\circ}_{298}$  for  $\text{CHCl}_2\text{OCl}$ .

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

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

$S^{\circ}_{298}$  for the OCl/Cl2 interaction term is calculated from equation 2.18 using the S for the parent molecule. Equation 4 and 5 both use the CCl2/H/O group from dichloromethanol and 1,1 dichloro methylether and the O/C/Cl group from  $\text{CH}_3\text{OCl}$ .  $R = 1.987$  (cal/mol K), and  $\sigma$  is symmetry number, which is 1 for  $\text{CHCl}_2\text{OCl}$ . Entropy of mixing =  $-R \sum \{ (n_i) \times \ln(n_i) \}$ ; where  $n_i$  is fraction of conformer i. Mixing entropy is included in the (C/Cl2/H/O) group, as it is in hydrocarbon and other molecular groups. For  $\text{CHCl}_2\text{OCl}$ , the mixing term is:  $-R \{ 0.9014 \times \ln(0.9014) + 0.0986 \times \ln(0.0986) \} = 0.64$  cal/mol K in Table 2.11-b. The other interaction values are also estimated in the same manner

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

methyl hypochlorite ( $\text{CH}_3\text{OCl}$ ) in this work by equations 2.15 and equation 2.16; The enthalpy, entropy at 298 K, and heat capacity at 300 K values are -5.41 kcal/mol, 37.0 and 7.4 cal/mol·K.

Interaction term values are also listed in Table 2.14 and are significant; they indicate a several kcal/mol increase in enthalpy due to destabilizing interaction of chlorine(s) on the methyl group with the hypochlorite group. The group additivity corrections for enthalpy of formation at 298 K are 4.2, 6.5, and 6.7 kcal/mol for  $\text{OCl/Cl}$ ,  $\text{OCl/Cl}_2$ , and  $\text{OCl/Cl}_3$ , respectively. Interaction terms for entropies at 298 K and heat capacities are relatively small. Entropy terms are 0.8, 1.7, and -0.5 cal/mol·K for  $\text{OCl/Cl}$ ,  $\text{OCl/Cl}_2$ , and  $\text{OCl/Cl}_3$ , respectively at 298 K. The interaction values for heat capacity at 300 K are 0.1, 1.0, and -0.1 cal/mol·K for  $\text{OCl/Cl}$ ,  $\text{OCl/Cl}_2$ , and  $\text{OCl/Cl}_3$ , respectively. These low values for entropy and heat capacity interaction terms are encouraging. They suggest reasonable accuracy and consistency throughout our calculations and that the interaction terms are primarily needed for enthalpies.

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

**TABLE 2.14-a: Thermodynamic Properties of Chlorine Groups**

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

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

**TABLE 2.14-b: Thermodynamic Properties of OCl-Cl<sub>x</sub> interactions**

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

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

**TABLE 2.15. Groups and Interaction Terms for Four Oxychlorides**

Compounds	CH <sub>3</sub> OCl	CH <sub>2</sub> ClOC1	CHCl <sub>2</sub> OCl	CCl <sub>3</sub> OCl
	C/H3/O	C/Cl/H2/O	C/Cl2/H/O	C/Cl3/O
	O/C/Cl	O/C/Cl	O/C/Cl	O/C/Cl
interaction	OCl/Cl	OCl/Cl2	OCl/Cl3	

### 2.3 Summary

Thermochemical Properties of  $\text{CH}_3\text{OCl}$  and three chlorinated methyl hypochlorites are calculated using density functional *ab initio* calculations. Enthalpies,  $\Delta H_f^\circ_{298}$  are presented as average data from the selected reaction schemes (up to seven) based on CBS-Q calculation level results considering statistical distribution of rotational conformers. CBS-Q calculation values of  $\Delta H_f^\circ_{298}$  show consistency for all reaction schemes, which is not observed in the B3LYP/6-31G(d, p), B3LYP/6-311+G (3df, 2p), QCISD(T)/6-31G(d, p) calculations. Entropies,  $S^\circ_{298}$  and heat capacities,  $C_p(T)$  from 300 K to 1500 K are reported along with groups and oxychloride-chloride interaction group values for use in group additivity. Torsion potentials are presented for intramolecular rotations. Semiempirical methods do not seem satisfactory for estimation of oxy – chlorocarbon thermochemical properties.

## CHAPTER 3

### GEOMETRIES, VIBRATIONAL FREQUENCIES AND THERMODYNAMIC PROPERTIES OF CHLORO-ETHERS

#### 3.1 Overview

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

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

properties of chlorinated oxygenated hydrocarbons with the exception of acid chlorides and methyl hypochlorites. The thermodynamic values for dimethyl ether are well known<sup>63</sup> but surprisingly there is no literature data, to our knowledge, for any chlorinated ether.

This research estimates fundamental thermodynamic property data on these species using *ab initio* and density functional calculations. These thermodynamic properties on chloro-dimethyl ethers allow estimation of C/Cl/H<sub>2</sub>/O, C/Cl<sub>2</sub>/H/O, C/Cl<sub>3</sub>/O groups for use in group additivity on larger hydrocarbons.

## 3.2 Method

### 3.2.1 Computational Methods

All *ab initio* calculations are performed using the Gaussian 94 program suite.<sup>64</sup> The structural parameters are fully optimized at B3LYP/6-31G(d,p) level of theory. Harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. The optimized geometry parameters are used to obtain total electronic energies in B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) single point calculations.<sup>30,65,66</sup>

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



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

B3LYP/6-311+G(3df,2p) is chosen to evaluate if this large basic set results in an improvement to the above commonly used density functional calculation method. QCISD(T)/6-31G(d,p) is a configuration interaction method; but with a small, economical basis set.<sup>23,53</sup> CBS-Q calculation is a high level composite method with empirical correction; it is reported to be nearly equivalent to QCISD(T)/6-311+G(3df,2p).<sup>23,30</sup> The CBS-Q method<sup>70</sup> attempts to approximate the energy of a species at the infinite basis set limit by an extrapolation of the energies of pair natural orbital at the MP2 level. The effects of going from MP2 to QCISD(T) are accounted for with an additivity scheme. The geometry is obtained at the MP2 /6-31G level of theory, while the ZPE used is the scaled (by 0.9135) HF/6-31G value. For the open-shell systems, there is also a correction for spin contamination in the unrestricted Hartree-

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

The CBS-Q//B3LYP/6-31G(d,p) method used here, differs from CBS-Q in that it employs an improved geometry and ZPVE. The CBS-Q//B3LYP/6-31G(d,p) employs geometry optimized at B3LYP/6-31G(d,p) and a ZPVE calculation from B3LYP/6-31G(d,p) harmonic vibrational frequencies scaled (by 0.9806)<sup>31</sup>. This is very similar to the Radom research group's CBS/RAD<sup>23</sup> method; it has B3LYP/6-31g(d,p) geometry, which they indicate is very close to QCISD(T) values and a QCISD(T) calculation in place of CCSD(T). These calculations are referred to as CBSQ//B3\*\* in the present study.

### 3.2.2 Thermodynamic Properties Using *ab initio* Calculations

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

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

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

### 3.2.3 Calculation of Hindered Rotation Contribution to Thermodynamic

#### Parameters

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

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

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

**Table 3.1** Vibrational Frequencies<sup>a</sup> (cm<sup>-1</sup>), and moments of inertia (amu·Bohr<sup>2</sup>)<sup>b</sup>

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

<sup>a</sup> Nonscaled frequencies are calculated at the B3LYP/6-31G(D,P) level of theory. <sup>b</sup> The moment of inertia units are amu·Bohr<sup>2</sup>.

### 3.3 Results and Discussion

#### 3.3.1 Vibrational frequencies and geometry

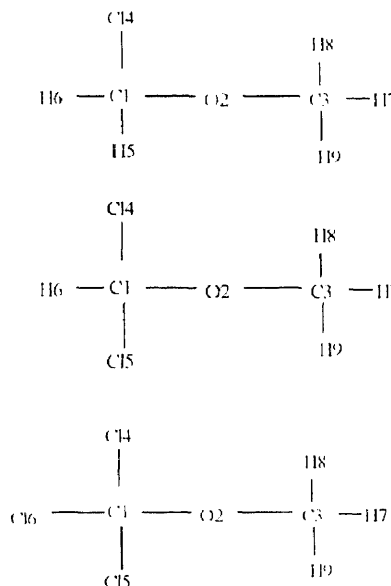
Harmonic vibrational frequencies are calculated for three chloro-dimethyl ethers at the B3LYP/6-31G(d, p) level of theory on the basis of optimized geometry at the same level of theory. The vibrational frequencies and the moment of inertia (amu·Bohr<sup>2</sup>) for the multiple chlo-dimethyl ethers are given in Table 3.1.

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

Table 3.2. Optimized geometry of chlorinated ethers.<sup>a</sup>

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

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



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

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

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

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

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

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

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

<sup>a,b,c</sup> Total energies are in Hartree at 0K: <sup>a</sup> B3LYP/6-31G(d,p), <sup>b</sup> B3LYP/6-311+G(3df,2p), <sup>c</sup> QCISD(T)/6-31G(d,p).

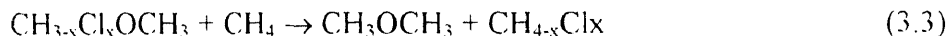
<sup>d</sup> CBS-Q enthalpies are in Hartree, which include thermal correction and zero-point energy at 298.15 K. <sup>e</sup> ZPE is in Hartree and scaled by 0.9806. <sup>f</sup> Thermal corrections are in Hartree.

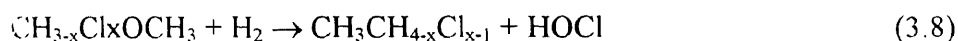
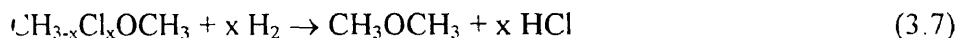
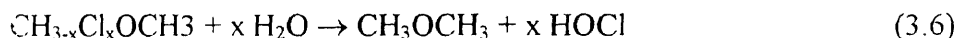
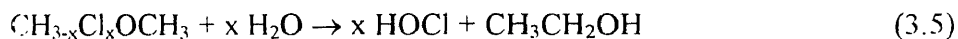
thermal corrections to 298 K from the B3LYP/6-31G(d, p), and the total energies at 298 K from B3LYP/6-311+G(3df+2p), QCISD(T)/6-31G(d, p) and CBS-Q/B3\*\* calculation levels are listed in Table 3.33.

As example;  $\Delta H_f^\circ_{298}$  (CH<sub>2</sub>ClOCH<sub>3</sub>) is calculated from reaction scheme (1),

$$\Delta H_{rxn(298)} = \Delta H_f^\circ_{298} \{(\text{CH}_3\text{OCH}_3) + (\text{CH}_3\text{Cl}) - (\text{CH}_2\text{ClOCH}_3) - (\text{CH}_4)\} \quad (3.2)$$

and the listed known enthalpies of CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>Cl and CH<sub>4</sub>.





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

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

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

### 3.3.3 Test of Calculation Method: Enthalpy of HOCl

In earlier chapter, we compared the reaction schemes for the enthalpy of formation at 298 K on methyl hypochlorite and observed that working reaction with the reactant of hydrogen and product of hydrochloric acid did not result in accurate  $\Delta H_f^\circ_{298}$  of target molecule in CE S-Q//B3\*\* method. A similar trend is observed in the calculation analysis of HOCl as shown in Table 3.7. The recommended  $\Delta H_f^\circ_{298}$  for HOCl is -17.8 kcal/mol<sup>20</sup>



**TABLE 3.4.** Reaction Enthalpies (in kcal/mol) at 298.15 K<sup>a</sup>

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

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

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

reaction sets that are more consistent and thus it is deemed more accurate. B3LYP/6-31G(d, p), B3LYP/6-311+G(3df, 2p), and QCISD(T)/6-31G(d, p) calculate slightly lower values for HOCl than CBS-Q//B3\*\* values. This same phenomenon is shown in the study of  $\Delta H_f^\circ_{298}$  of chloro-dimethyl ethers.

**TABLE 3.5:** Enthalpy Data Used in Reactions to Determine  $\Delta H_f^\circ_{298}$  of Target

Ethers

Compound	$\Delta H_f^\circ_{298}$ <sup>a</sup>	source	uncertainty	source
CH <sub>4</sub>	-17.89	Ref.32	±0.1	Ref.32 (74)
CH <sub>3</sub> Cl	-19.60	Ref.33	±0.2	Ref.33 (75)
CH <sub>2</sub> Cl <sub>2</sub>	-22.83	Ref.32	±0.3	Ref.32
CHCl <sub>3</sub>	-24.20	Ref.33	±0.3	Ref.33 (77)
C <sub>2</sub> H <sub>6</sub>	-20.24	Ref.32	±0.1	Ref.32 (74)
CH <sub>3</sub> CH <sub>2</sub> Cl	-26.84	Ref.33	±0.2	Ref.33 (74)
CH <sub>3</sub> CHCl <sub>2</sub>	-31.09	Ref.33	±0.3	Ref.33 (73)
CH <sub>3</sub> CCl <sub>3</sub>	-34.01	Ref.33	±0.3	Ref.33 (76)
CH <sub>3</sub> OH	-48.08	Ref.34	±0.1	Ref.33 (77)
CH <sub>2</sub> ClOH	-58.00	Ref.34	±0.5	Ref.34
CHCl <sub>2</sub> OH	-64.42	Ref.34	±2.3	Ref.34
CCl <sub>3</sub> OH	-65.01	Ref.34	±2.3	Ref.34
CH <sub>3</sub> CH <sub>2</sub> OH	-56.12	Ref.33	±0.4	Ref.33 (77)
HCl	-22.06	Ref.32	±0.1	Ref.32
HOCl	-17.80	Ref.33	±0.5	Ref.33
HOOH	-32.53			Ref.32
H <sub>2</sub> O	-57.80	Ref.34	±0.01	Ref.34

<sup>a</sup> Units in kcal/mol

TABLE 3.6. Comparison of Enthalpies of Formation<sup>a</sup> (in kcal/mol)

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

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

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

**TABLE 3.7.** Enthalpies of formation<sup>a</sup> (in kcal/mol) at 298.15 K for HOCl

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

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

### 3.3.4 Analysis of Data Trends by Isodesmic versus Non isodesmic Reaction

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

reactions 1 and 7 also show good consistency among the non – composite calculations methods. Non isodesmic reactions 3 and 4, which use H<sub>2</sub>O and HOCl are completely unacceptable for the non composite calculation methods for the di and tri chloro ethers.

### 3.3.5 Recommended values

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

The  $\Delta H_f^\circ_{298}$  considering statistical distribution of rotational conformers of CH<sub>2</sub>ClOCH<sub>3</sub>, CHCl<sub>2</sub>OCH<sub>3</sub>, and CCl<sub>3</sub>OCH<sub>3</sub> are -55.4±1 kcal/mol, -61.8 ± 2 kcal/mol, -62.8 ± 3.0 kcal/mol, respectively. The uncertainty in Table 3.6 is the standard deviation of the reaction sets plus the average of maximum error from standard compounds in the reaction schemes.

### 3.3.6 Comparison to Semiempirical (MOPAC) data

The AM1<sup>56,57</sup> and PM3<sup>58</sup> methods in the MOPAC 6.0 package<sup>55</sup> are used to perform the semiempirical MO calculations. The enthalpy of formation of three title molecules are calculated with AM1 and PM3 parameters and compared to those obtained from the density functional and *ab initio* studies. Direct results from the MOPAC calculations, as well as results from reaction analysis with MOPAC data are presented. The results, listed

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

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

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

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

**Table 3.9.** Total Energy<sup>a</sup> (Hartrees) of Molecules by Torsion angle.<sup>b</sup>

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

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

### 3.3.7 Rotational Barriers

Potential barriers for the two internal rotations of CH<sub>2</sub>ClOCH<sub>3</sub>, CHCl<sub>2</sub>OCH<sub>3</sub>, and CCl<sub>3</sub>OCH<sub>3</sub> are calculated at the B3LYP/6-31G(d, p) level. Potential energy as function of dihedral angle is determined by varying the torsion angle at 15° intervals and allowing the remaining molecular structural parameters to be optimized. The geometry and harmonic vibrational frequencies are calculated for all rotational conformers at

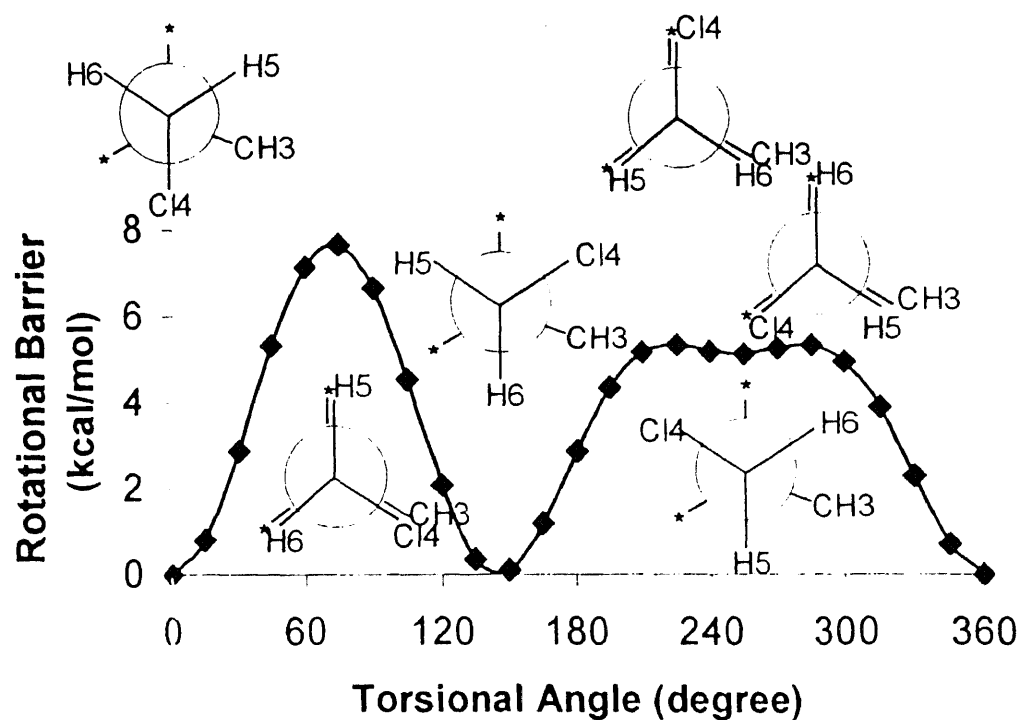


Figure 3.1. Potential energy for internal rotation about  $\text{CH}_2\text{Cl}-\text{OCH}_3$  bond by torsional angle.

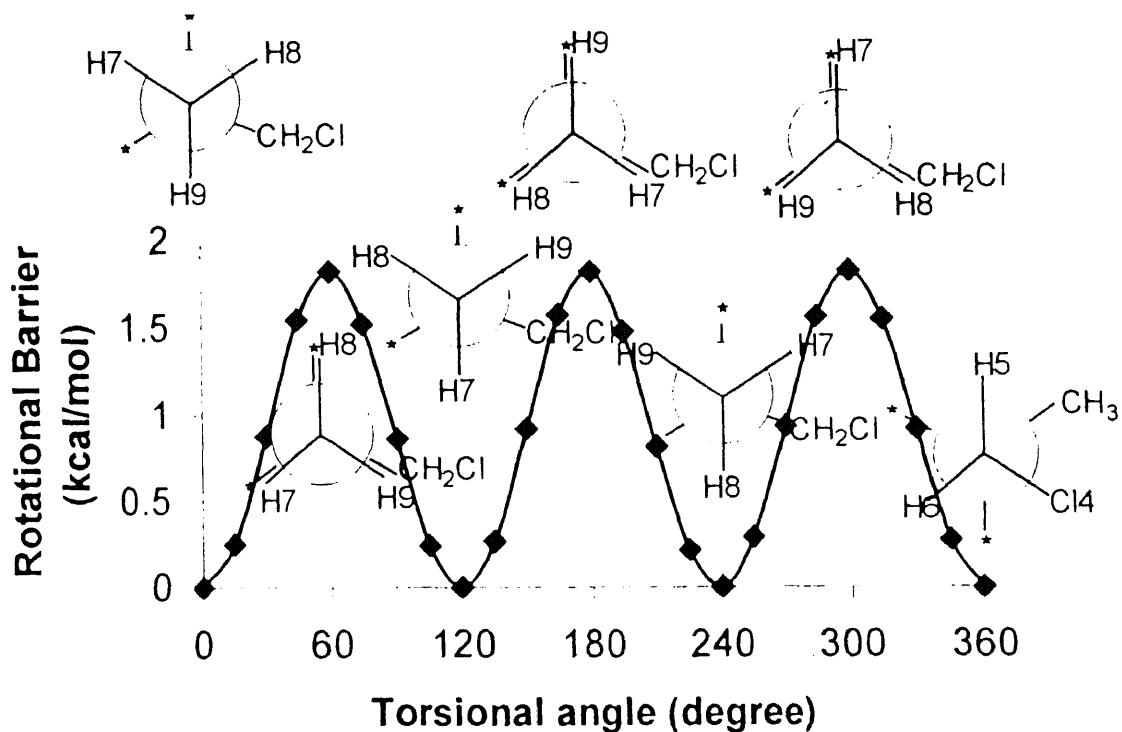


Figure 3.2. Potential energy for internal rotation about  $\text{CH}_2\text{ClO}-\text{CH}_3$  bond by torsional angle.



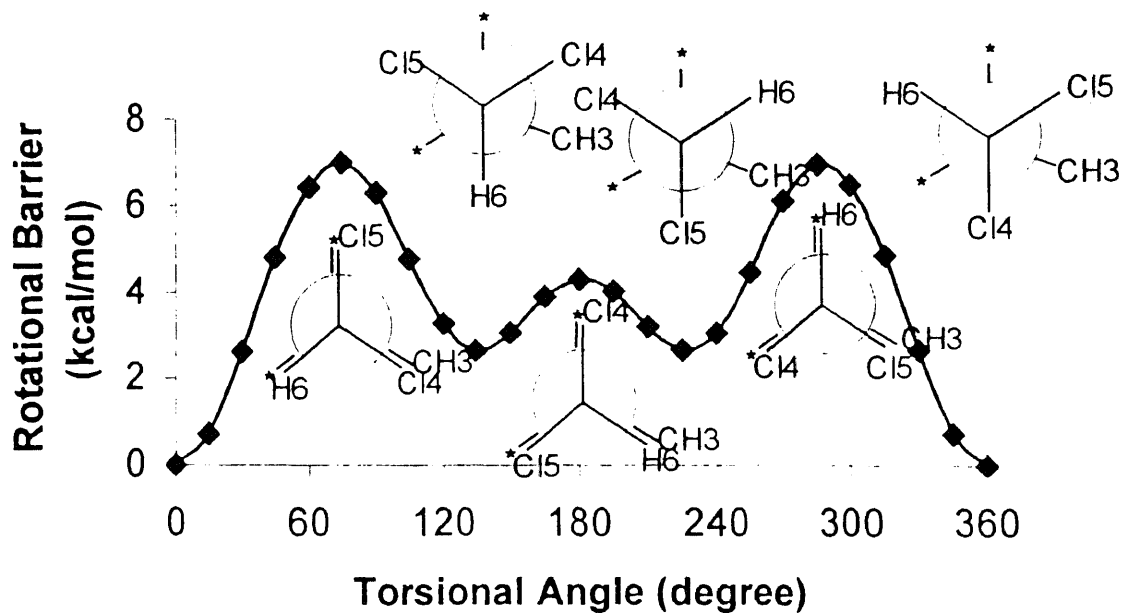


Figure 3.3 Potential energy for internal rotation about  $\text{CHCl}_2\text{-OCH}_3$  bond by torsional angle.

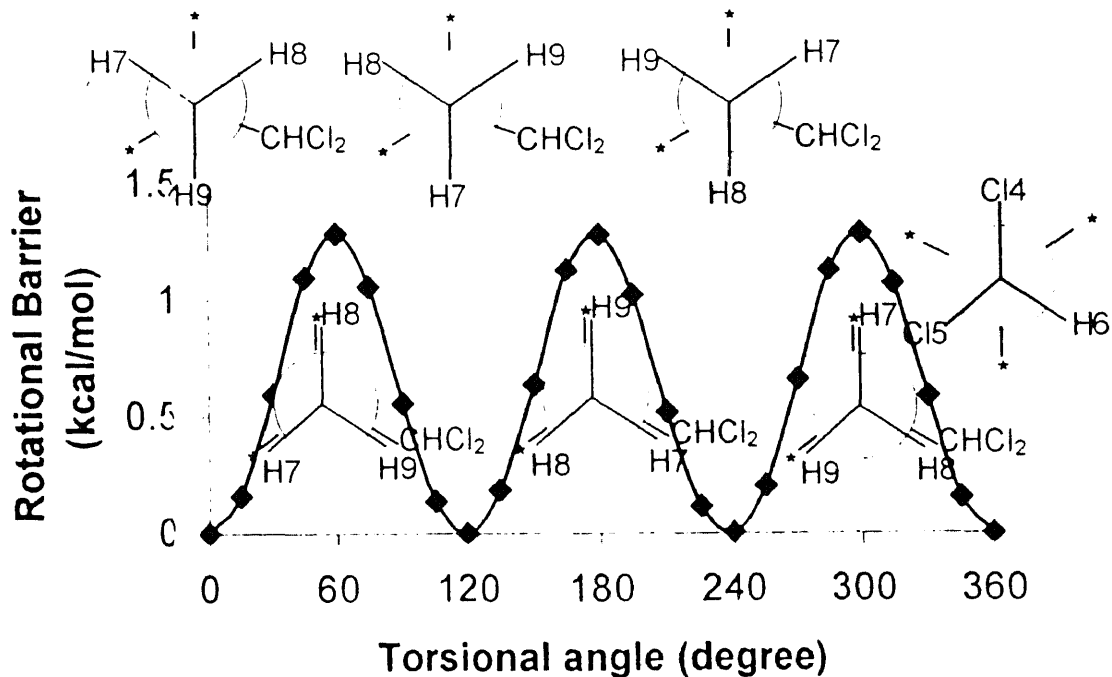


Figure 3.4 Potential energy for internal rotation about  $\text{CHCl}_2\text{-O-CH}_3$  bond by torsional angle.

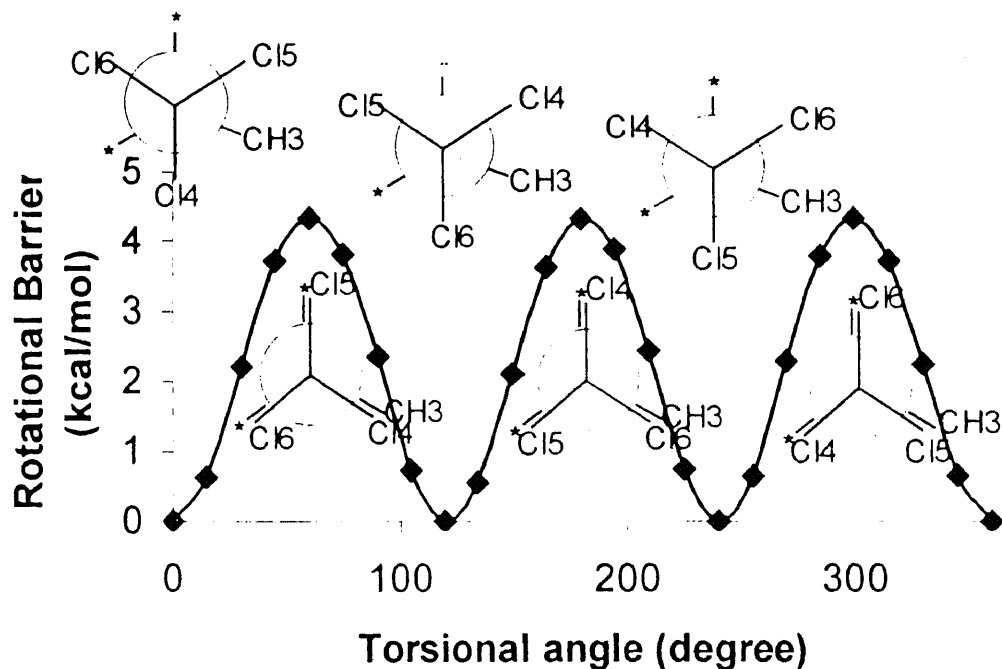


Figure 3.5. Potential energy for internal rotation about  $\text{CCl}_3\text{-OCH}_3$  bond by torsional angle.

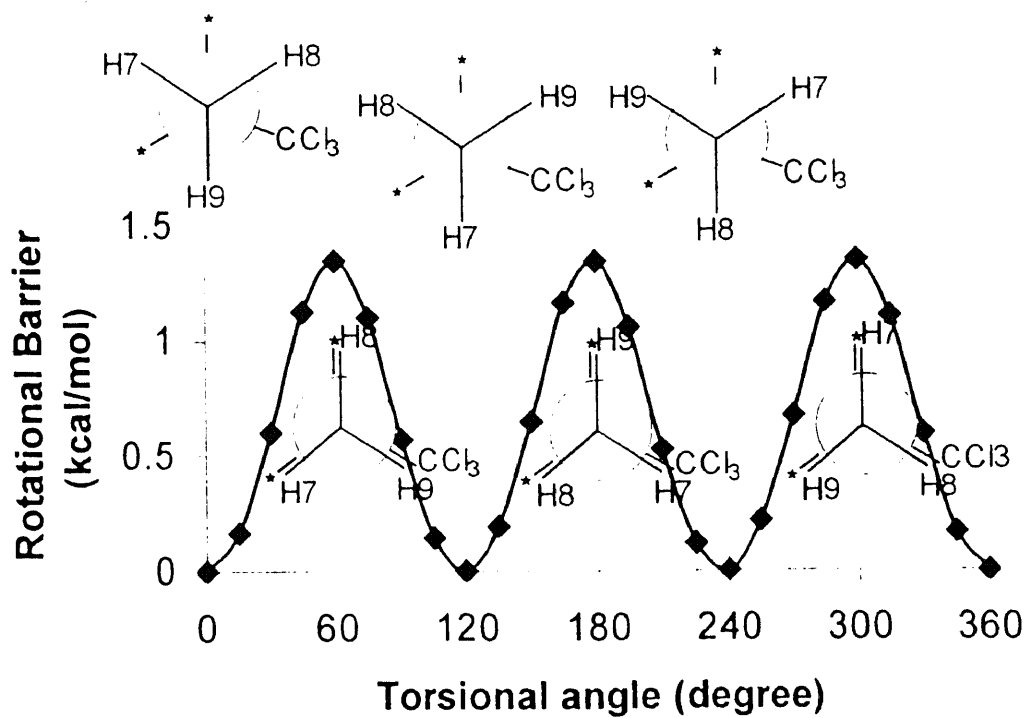


Figure 3.6. Potential energy for internal rotation about  $\text{CCl}_3\text{O-CH}_3$  bond by torsional angle.

**Table 3.10.**  $\Delta H_f^\circ_{298}$  for Rotational Conformers, Relative, Overall  $\Delta H_f^\circ_{298}$  Values and Entropy correction<sup>h</sup>

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

<sup>a</sup> CH<sub>3</sub>-H anti staggered, and <sup>b</sup> CH<sub>3</sub>-Cl anti staggered conformer in Figure 1. <sup>c</sup> CH<sub>2</sub>Cl-H anti staggered, and <sup>d</sup> CH<sub>2</sub>Cl-Cl anti staggered conformer in Figure 3. <sup>e</sup> Energy of conformer = overall value in Table 6 + energy barrier, Energy barrier = energy of conformer- energy of most stable conformer <sup>f</sup> Relative = conformer fraction ÷ total fraction; Conformer fraction =  $e^{(-B/RT)}$ , B = Energy difference, R = 1.987 (cal/mol·K), T = 298K. <sup>g</sup> Final value =  $\Sigma(\text{Energy} \times \text{relative fraction})$ ; Uncertainty is the value in foot note e in Table 6. <sup>h</sup> Entropy correction for CHCl<sub>2</sub>OCH<sub>3</sub> =  $-R\{0.9884 \cdot \ln(0.9884) + 0.0116 \cdot \ln(0.0116)\}$  = 0.13 cal/mol·K.

**TABLE 3.11** Coefficients<sup>a</sup> (kcal/mol) of Truncated Fourier Series Representation Expansion for Internal Rotation Potentials

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

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

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

Figure 3.1 shows calculated rotational barriers of CH<sub>2</sub>Cl-OCH<sub>3</sub> versus torsion angle. The double asterisks, \* \* signify a lone electron pair on oxygen. 1 chloro-dimethyl ether (CH<sub>2</sub>Cl-OCH<sub>3</sub>) has two conformers. The CH<sub>3</sub>-Cl anti staggered is 5.09 kcal/mol higher in energy than the more stable CH<sub>3</sub>-H anti staggered conformer because of the Cl interaction with the oxygen atom's non bonding electrons. The CH<sub>3</sub>-Cl eclipsed

rotational barrier is 7.65 kcal/mol and the CH<sub>3</sub>-H eclipsed rotational barrier is 5.30 kcal/mol. The CH<sub>3</sub>-Cl eclipsed barrier is 2.35 kcal/mol higher in energy than the CH<sub>3</sub>-H eclipsed barrier. The interaction of chlorine and a methyl group appears to exhibit more repulsion or strain compared to that of a methyl interaction with hydrogen.

Calculated rotational barriers and conformer energies in 1,1 dichloro-dimethyl ether (CHCl<sub>2</sub>-OCH<sub>3</sub>) are shown in figure 3.3. The CH<sub>3</sub>-H staggered conformer has 2.63 kcal/mol lower energy than the CH<sub>3</sub>-Cl staggered conformer due to the interaction between an electron lone pair of oxygen and chlorine. The CH<sub>3</sub>-Cl eclipsed structure represents a rotational barrier of 7.00 kcal/mol and the CH<sub>3</sub>-H eclipsed structure represents a barrier of 4.30 kcal/mol. The CH<sub>3</sub>-Cl eclipsed barrier shows higher energy than CH<sub>3</sub>-H eclipsed because the interaction of methyl group and chlorine has more repulsion and strain compared to that of methyl group and hydrogen.

The symmetric rotational barrier of 1,1,1 trichloro-dimethyl ether (CCl<sub>3</sub>-OCH<sub>3</sub>) is illustrated in Figure 3.3. The CH<sub>3</sub>-Cl eclipsed structure shows a rotational barrier of 4.33 kcal/mol above the CH<sub>3</sub>-Cl staggered conformer.

The calculated symmetric rotational barriers for methyl (CH<sub>3</sub>) rotations in the chlorinated dimethyl ethers are shown in Figures 3.2, 3.4, 3.6. The calculations show that the hydrogen and chloromethyl (H-CH<sub>2</sub>-Cl<sub>x</sub>) staggered structure has a rotational barrier of 1.82 kcal/mol in CH<sub>2</sub>ClO-CH<sub>3</sub>, 1.28 kcal/mol in CHCl<sub>2</sub>O-CH<sub>3</sub>, and 1.34 kcal/mol in CCl<sub>3</sub>O-CH<sub>3</sub>.

TABLE 3.12: Ideal Gas Phase Thermodynamic Properties<sup>a</sup>

Species		$\Delta H_f^{\circ}{}_{298}$ <sup>b</sup>	$S^{\circ}{}_{298}$ <sup>c</sup>	$C_{p300}$ <sup>c</sup>	$C_{p400}$	$C_{p500}$	$C_{p600}$	$C_{p800}$	$C_{p1000}$	$C_{p1500}$
CH <sub>2</sub> ClOCH <sub>3</sub> (3) <sup>l</sup>	TVR <sup>d</sup>		64.89	13.90	17.54	21.02	24.07	28.91	32.48	38.01
	Internal(1) <sub>e</sub>		4.93	2.15	2.33	2.48	2.52	2.36	2.02	1.26
	Internal(2) <sub>f</sub>		4.65	1.93	1.73	1.55	1.42	1.26	1.18	1.08
	Total	-55.39	74.47	17.99	21.60	25.05	28.02	32.53	35.68	40.35
	Group add. <sub>k</sub>	-54.65	73.96	18.23	22.16	25.59	28.48	33.02	36.16	
CHCl <sub>2</sub> OCH <sub>3</sub> (3)	TVR		71.23	17.50	21.25	24.58	27.36	31.61	34.66	39.29
	Internal(1) <sub>g</sub>		3.64	3.03	3.85	4.09	3.89	3.04	2.27	1.17
	Internal(2) <sub>h</sub>		4.65	1.93	1.73	1.55	1.42	1.26	1.18	1.08
	Total	-61.79	79.65	22.47	26.83	30.23	32.67	35.92	38.10	41.54
	Group add.	-61.06	79.29	22.33	27.04	30.53	33.03	36.48	38.71	
CCl <sub>3</sub> OCH <sub>3</sub> (18)	TVR		73.78	21.78	25.48	28.50	30.93	34.51	37.01	40.71
	Internal(1) <sup>i</sup>		5.93	2.22	2.27	2.20	2.05	1.66	1.30	0.73
	Internal(2) <sup>j</sup>		5.31	1.73	1.50	1.35	1.26	1.15	1.10	1.04
	Total	-62.79	85.02	25.72	29.25	32.06	34.24	37.32	39.41	42.48
	Group add.	-61.85	84.45	25.83	29.62	32.40	34.55	37.79	39.92	

<sup>a</sup> Thermodynamic properties are referred to standard state of an ideal gas of pure enantiomer at 1atm. One torsion frequency is excluded in the calculation of entropies and heat capacities; instead, the contributions from hindered rotations about the C-O bond are calculated. <sup>b</sup>  $\Delta H_f^{\circ}{}_{298}$  is the average value of CBS-Q level considering the statistical contribution of rotational conformers in kcal/mol. (see footnote c in Table 6 and final value in Table 8) <sup>c</sup> Units in cal/mol·K; mixing of -0.13 cal/mol·K for entropy correction of CHCl<sub>2</sub>OCH<sub>3</sub> is included (see footnote h in Table 10). <sup>d</sup> The sum of contributions from translations, external rotations, and vibrations. <sup>e</sup> Contributions from internal rotation about C-O bond of CH<sub>2</sub>Cl-O-CH<sub>3</sub>. <sup>f</sup> CH<sub>2</sub>ClO-CH<sub>3</sub>. <sup>g</sup> CHCl<sub>2</sub>-O-CH<sub>3</sub>. <sup>h</sup> CHCl<sub>2</sub>O-CH<sub>3</sub>. <sup>i</sup> CCl<sub>3</sub>-O-CH<sub>3</sub> and <sup>j</sup> CCl<sub>3</sub>O-CH<sub>3</sub>. <sup>k</sup> Group additivity; C/13/O and O/C2 come from ref.36; C/C/112/O, C/C/12/11/O and C/C/13/O comes from the average of chloro-methanols (ref.37) and chloro-dimethyl ethers (this work). <sup>l</sup> Symmetry number is taken into account for  $S^{\circ}{}_{298}$ .

### 3.3.8 Entropy, $S^{\circ}{}_{298}$ and Heat Capacity, $C_p(T)$ from 300 to 1500 K

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

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

### 3.3.9 Group Values and Group Additivity Estimation

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

$$(\text{CH}_2\text{ClOCH}_3) = (\text{C/H3/O}) + (\text{O/C/2}) + (\text{C/Cl/H2/O}) \quad (3.10)$$

Values for C/Cl/H2/O, C/Cl2/H/O and C/Cl3/O are taken from recent work in this laboratory on chlorinated methanols<sup>38</sup> and this study. The properties of the C/Cl/H2/O, C/Cl2/H/O and C/Cl3/O groups for example, are derived from chloro-methanol ( $\text{CH}_2\text{ClOH}$ ), 1,1-dichloro-methanol ( $\text{CHCl}_2\text{OH}$ ), and 1,1,1-trichloro-methanol ( $\text{CCl}_3\text{OH}$ ), respectively and from chloro-dimethyl ether ( $\text{CH}_2\text{ClOCH}_3$ ), 1,1-dichloro-dimethyl ether ( $\text{CHCl}_2\text{OCH}_3$ ), and 1,1,1-trichloro-dimethyl ether ( $\text{CCl}_3\text{OCH}_3$ ), respectively. Group values for of C/Cl/H2/O, C/Cl2/H/O, C/Cl3/O are -20.9, -27.3, -28.1 kcal/mol for enthalpy of formation at 298 K. The group additivity determined  $\Delta H_f^{\circ}_{298}$  values for  $\text{CH}_2\text{ClOCCCH}_3$  of -54.7,  $\text{CHCl}_2\text{OCH}_3$  of -61.1, and  $\text{CCl}_3\text{OCH}_3$  of -61.9 kcal/mol. These enthalpy values are slightly higher than our recommended CBS-Q//B3\*\* values in Table 3.12. The reason is that the oxygenated chlorocarbon groups are an average of values from alcohols and ethers. The recommended  $\Delta H_f^{\circ}_{298}$  values

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

The entropy,  $S^\circ_{298}$  of the C/Cl/H<sub>2</sub>/O is calculated on the basis of the equation 3.10.

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

$R = 1.987$  cal/mol K, and  $\sigma$  is symmetry number, which is 3 for  $\text{CH}_2\text{ClOCH}_3$ . Entropy of mixing =  $-R \sum \{(n_i) \times \ln(n_i)\}$ ; where  $n_i$  is fraction of conformer  $i$ . Mixing entropy is included in the (C/Cl<sub>2</sub>/H/O) group, as it is in hydrocarbon and other molecular groups. For  $\text{CHCl}_2\text{OCH}_3$ , the mixing term for entropy is:  $-R \{0.9884 \times \ln(0.9884) + 0.1161 \times \ln(0.1161)\} = 0.13$  cal/mol K in Table 3.10. Thermodynamic properties of the C/Cl/H<sub>2</sub>/O, C/Cl<sub>2</sub>/H/O, and C/Cl<sub>3</sub>/O groups are calculated using two sets of thermodynamic property data; where the two data from chloro-methanols and chloro-dimethyl ethers are listed in Table 3.13-a. Table 3.13-b lists the average of group values in Table 3.13-a. Group values of C/Cl/H<sub>2</sub>/O, C/Cl<sub>2</sub>/H/O, C/Cl<sub>3</sub>/O are 37.1, 42.4, 51.1 cal/mol·K for entropy at 298 K and 8.6, 12.7, 16.2 cal/mol·K for heat capacity at 300 K, respectively in Table 3.13-b which are values we recommend. Table 3.14 lists groups for use in oxychlorocarbon by our modified group additivity method.

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

**TABLE 3.13-a.** Thermodynamic Properties of C/Cl<sub>x</sub>/H<sub>3-x</sub>/O from chloro-methanol and from this work

Groups	H <sub>f</sub> <sup>o</sup> <sub>298</sub> <sup>a</sup>	S <sup>o</sup> <sub>298</sub> <sup>b</sup>	C <sub>p300</sub> <sup>b</sup>	C <sub>p400</sub>	C <sub>p500</sub>	C <sub>p600</sub>	C <sub>p800</sub>	C <sub>p1000</sub>	C <sub>p1500</sub>	Ref
C/Cl/H2/O	-20.10	36.55	8.88	11.18	13.02	14.35	16.09	17.27	19.19	37 <sup>c</sup>
C/Cl/H2/O	-21.59	37.56	8.40	10.06	11.95	13.43	15.10	16.31		this work
C/Cl2/H/O	-26.52	42.03	12.61	15.71	17.73	18.80	19.62	19.94	20.60	37
C/Cl2/H/O	-27.99	42.74	12.88	15.29	17.13	18.08	18.49	18.73		this work
C/Cl3/O	-27.11	50.54	16.34	18.45	19.65	20.28	20.82	21.06	21.46	37
C/Cl3/O	-28.99	51.67	16.13	17.71	18.96	19.65	19.89	20.04		this work
C/H3/O <sup>d</sup>	-10.00	30.41	6.19	7.84	9.40	10.79	13.03	14.77	17.58	36
O/C2 <sup>e</sup>	-23.80	8.68	3.40	3.70	3.70	3.80	4.40	4.60		36

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

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

Groups	H <sub>f</sub> <sup>o</sup> <sub>298</sub> <sup>a</sup>	S <sup>o</sup> <sub>298</sub> <sup>b</sup>	C <sub>p300</sub> <sup>b</sup>	C <sub>p400</sub>	C <sub>p500</sub>	C <sub>p600</sub>	C <sub>p800</sub>	C <sub>p1000</sub>	C <sub>p1500</sub>	Ref
C/Cl/H2/O	20.85	37.05	8.64	10.62	12.49	13.89	15.59	16.79	19.19	this work
C/Cl2/H/O-27.26	42.38	12.74	15.50	17.43	18.44	19.05	19.34	20.60		this work
C/Cl3/O	-28.05	51.11	16.24	18.08	19.30	19.96	20.36	20.55	21.46	this work

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

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

Compounds	CH <sub>2</sub> ClOCH <sub>3</sub>	CHCl <sub>2</sub> OCH <sub>3</sub>	CCl <sub>3</sub> OCH <sub>3</sub>
Group 1	C/H3/O	C/H3/O	C/H3/O
Group 2	O/C2	O/C2	O/C2
Group 3	C/Cl/H2/O	C/Cl2/H/O	C/Cl3/O

C<sub>p</sub>(T) or All<sup>o</sup><sub>298</sub> of compounds = All<sup>o</sup><sub>298</sub> of Group 1 + All<sup>o</sup><sub>298</sub> of Group 2 + All<sup>o</sup><sub>298</sub> of Group 3. S<sup>o</sup><sub>298</sub> of compounds = S<sup>o</sup><sub>298</sub> of Group 1 + S<sup>o</sup><sub>298</sub> of Group 2 + S<sup>o</sup><sub>298</sub> of Group 3 - Rln(symmetry); R = 1.987 cal/mol-K, Symmetry = see the foot note 1 in the Table 12. Entropy of mixing = -R Σ{(n<sub>i</sub>) × ln(n<sub>i</sub>)}; where n<sub>i</sub> is fraction of conformer i. For CHCl<sub>2</sub>OCH<sub>3</sub>, the mixing term is: -R {0.9014 × ln(0.9014) + 0.0986 × ln(0.0986)} = 0.64 cal/mol K in Table 3.10.



and  $\text{CCl}_3\text{OCH}_3$  is 18.0, 22.5, 25.7 cal/mol·K at 300 K, and 25.1, 30.2, 32.1 cal/mol at 500 K from B3LYP/6-31G(d,p) calculation. The comparison values from group additivity are 18.2, 22.3, 25.8 cal/mol·K at 300 K, 25.6, 30.5, 32.4 cal/mol·K at 500 K.

### 3.4 Summary

Structure, torsion potentials and thermodynamic properties of three chlorinated dimethyl ethers are calculated using density function and *ab initio* calculations. Enthalpies,  $\Delta H_f^\circ_{298}$  are presented as average data using up to seven reaction schemes based on CBS-Q//B3\*\* theory and considering statistical distribution of rotational conformers. CBS-Q//B3\*\* calculation values of  $\Delta H_f^\circ_{298}$  show consistency for all reaction schemes except the reaction:  $\text{CHCl}_2\text{OCH}_3 + 2\text{H}_2 \rightarrow 2\text{HCl} + \text{CH}_3\text{OCH}_3$ . Enthalpy of formation at 298 K,  $\Delta H_f^\circ_{298}$ , entropies,  $S^\circ_{298}$  and heat capacities,  $C_p(T)$  from 300 K to 1500 K are reported along with values of thermodynamic properties on C/Cl/H<sub>2</sub>/O, C/Cl<sub>2</sub>/H/O, C/Cl<sub>3</sub>/O groups needed for use in group additivity.

## CHAPTER 4

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

#### 4.1 Overview

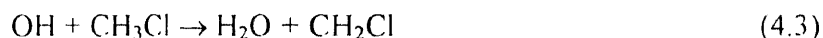
The initial product of chlorocarbon reaction in atmospheric chemistry and in combustion is a chlorocarbon (ClC) radical. One of the important reaction of these ClC radicals is reaction with  $O_2$  then the NO in atmosphere to form ClCO· radical or reaction in high temperature combustion with  $O_2$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

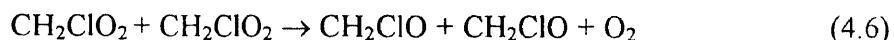
Enthalpy,  $\Delta H_f^\circ_{298}$ , entropy,  $S^\circ_{298}$  and heat capacities,  $C_p(T)$  from 300 to 1500K of chloro methoxy radicals ( $CH_2ClO\cdot$ ,  $CHCl_2O\cdot$ ,  $CCl_3O\cdot$ ) and that of formaldehyde – Cl atom complex radicals ( $CH_2O\text{--}Cl$ ,  $C^*HClO\text{--}Cl$ ,  $CCl_2O\text{--}Cl$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

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

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

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





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

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

loss of a hydrogen on  $\text{CH}_3\text{OCl}$  (formation of  $\text{C}\cdot\text{H}_2\text{OCl}^*$ ) results in rapid cleavage of the weak  $\text{O}-\text{Cl}$  bond and formation of the PI (double) bond of  $\text{CH}_2=\text{O}$ .

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

## 4.2 Methods

### 4.2.1 Selection of Calculation Methods and Basic Sets

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

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

#### 4.2.2 *Ab Initio*, Density Functional and Composite Calculations

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

#### 4.2.3 Calculation of Hindered Rotation Contribution to Thermodynamic Parameters

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

subsequent calculation of energy levels by direct diagonalization of Hamiltonian matrix. In this work the torsion potential calculated at discrete torsion angle is represented by equation 4.7.

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

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

**TABLE 4.1-a.** Vibrational Frequencies<sup>a</sup> (cm<sup>-1</sup>) for Methoxy Radical

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

**TABLE 4.1-b.** Rotation Constants (amu·Bohr<sup>2</sup>) for Methoxy Radical

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

**TABLE 4.1-c.** Vibrational Frequencies<sup>a</sup> (cm<sup>-1</sup>), for Chloro-methoxy and Formaldehyde (CH<sub>2</sub>=O) -- Cl complex Radicals

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

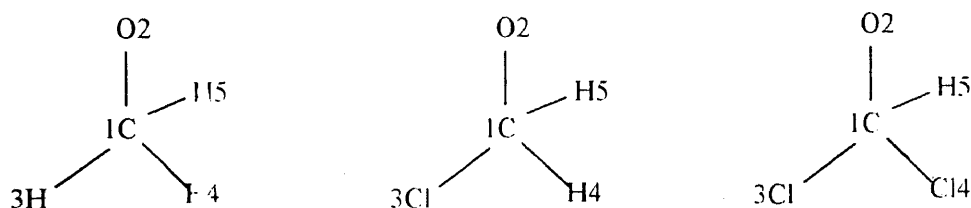
**TABLE 4.1-d.** Moment of Inertia (amu·Bohr) for Chloro-methoxy and Formaldehyde (CH<sub>2</sub>=O)--Cl complex Radicals

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

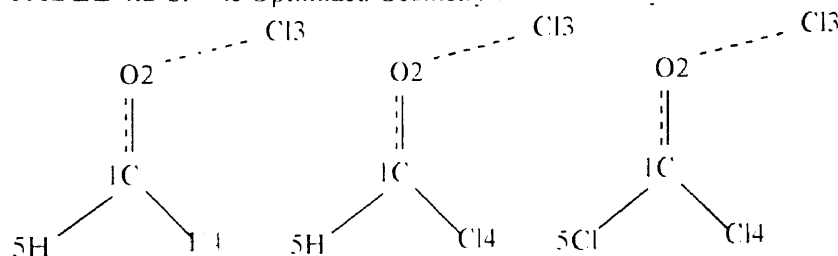
<sup>a</sup> Nonscaled. frequencies are calculated at the B3LYP/6-31G(d,p) level of theory; <sup>b</sup> Reference 15; <sup>c</sup> Reference 18; <sup>d</sup> Reference 10; <sup>e</sup> Reference 46; <sup>f</sup> Reference 47 <sup>g</sup> The rotational constant units are Ghz.



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



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

TABLE 4.2-b. The Optimized Geometry of Formaldehyde-Cl atom complex radicals<sup>b</sup>

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

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

## 4.3 Results and Discussion

### 4.3.1 Vibrational frequencies and geometry

Harmonic vibrational frequencies are calculated for the methoxy, chlorinated methoxy, formaldehyde-Cl atom complex, chlorinated formaldehyde-Cl atom complex radicals at the B3LYP/6-31G(d, p) level of theory on the basis of optimized geometry at the same level of theory in Table 4.1. The vibrational frequencies and rotational constants for the methoxy radicals are given in Table 4.1-a. They are in good agreement with other reported calculations<sup>18,71</sup> and experimental reports.<sup>72,73,74</sup> The CO stretching frequency mode of CH<sub>3</sub>O• shows 737 cm<sup>-1</sup> in this work, 728 cm<sup>-1</sup> in HF/6-31G\*<sup>18,71</sup> of 662 cm<sup>-1</sup> in the laser-excited fluorescence spectra of Powers et al.<sup>72</sup>, 657 cm<sup>-1</sup> in the laser-excited fluorescence spectra of Chiang et al.<sup>73</sup> and 630 cm<sup>-1</sup> in the photoelectron spectra of Ramond et al.<sup>74</sup> In this work, The CH<sub>2</sub> scissoring frequency mode of CH<sub>3</sub>O• shows 1382 cm<sup>-1</sup> in this work, 1423 cm<sup>-1</sup> in HF/6-31G\*,<sup>18,71</sup> 1403 cm<sup>-1</sup> in the laser-excited fluorescence spectra of Powers et al., 1410 cm<sup>-1</sup> in the laser-excited fluorescence spectra of Chiang et al.<sup>73</sup> and 1465 cm<sup>-1</sup> in the photoelectron spectra of Ramond et al.<sup>74</sup> The CH<sub>3</sub> stretching frequency mode of CH<sub>3</sub>O• shows 2978 cm<sup>-1</sup> in this work, 2901 cm<sup>-1</sup> in HF/6-31G\*,<sup>18,71</sup> 2948 cm<sup>-1</sup> in the laser-excited fluorescence spectra of Powers<sup>72</sup> et al., 3077 cm<sup>-1</sup> in the laser-excited fluorescence spectra of Chiang<sup>73</sup> et al. and 2895 cm<sup>-1</sup> in the photoelectron spectra of Ramond et al.<sup>74</sup> The vibrational frequencies and rotational constants for multiple chloro-methyl hypochlorites are given in Table 4.1.

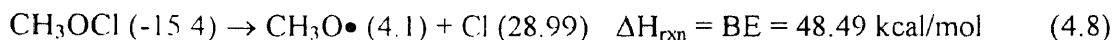
The optimized B3LYP/6-31G(d, p) geometries for radicals are illustrated in Table 4.2. Methoxy and chloro methoxy radicals are tetrahedral structures. HF/6-31G\* study by Melius<sup>18,71</sup> et al. shows similar structure with this study in Table 3.2 The

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

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

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

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



Where the gain in energy from forming the R<sub>2</sub>C=O from R<sub>2</sub>C•-O• is about 80 kcal/mol.

TABLE 4.4. Reaction Enthalpies (in kcal/mol) at 298 K<sup>a</sup>

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

**TABLE 4.4.** Reaction Enthalpies (in kcal/mol) at 298 K<sup>a</sup> (cont'd)

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

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

**TABLE 4.5.** Enthalpy Data Used in Reactions to Determine ΔH<sub>f,298</sub><sup>o</sup> of Target Radicals

Compound		source
CH <sub>3</sub>	-17.89	Ref.32
CH <sub>3</sub>	4.10	Ref. 71
CH <sub>3</sub> Cl	-19.60	Ref.33
CH <sub>2</sub> Cl	26.75	This Study
C <sub>2</sub> H <sub>5</sub>	-20.24	Ref.34
C <sub>2</sub> H <sub>5</sub>	29.30	Ref.77
CH <sub>3</sub> OH	-48.08	Ref.34
CH <sub>2</sub> ClOH	-58.00	Ref.38
CHCl <sub>2</sub> OH	-64.42	Ref.38
CCl <sub>3</sub> OH	-65.01	Ref.38
CH <sub>3</sub> OCl	-15.41	This Study
CH <sub>2</sub> ClOCl	-22.05	This Study
CCl <sub>2</sub> OCl	-26.14	This Study
C <sub>2</sub> H <sub>5</sub> OH	-56.12	This Study
C <sub>2</sub> H <sub>5</sub> O•	-3.30	Ref.75

**TABLE 4.6.** Enthalpies of Formation<sup>a</sup> for Standard Radicals at 298 K (kcal/mol)<sup>a</sup>

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

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

**TABLE 4.7.** Comparison of Enthalpies of Formation<sup>a</sup> for Standard Radicals  
298 K (kcal/mol)

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





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

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

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

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

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

and the listed known enthalpies of  $\text{CH}_3\text{O}\cdot$ ,  $\text{CH}_2\text{ClOH}$  and  $\text{CH}_3\text{OH}$ . The enthalpies of reaction are obtained by the reaction schemes tabulated in Tables 4.4. The  $\Delta H_f^\circ_{298}$  on the standard compounds in reaction sets are from literature in Table 4.5 and are used to determine  $\Delta H_f^\circ_{298}$  values in Table 4.6.

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

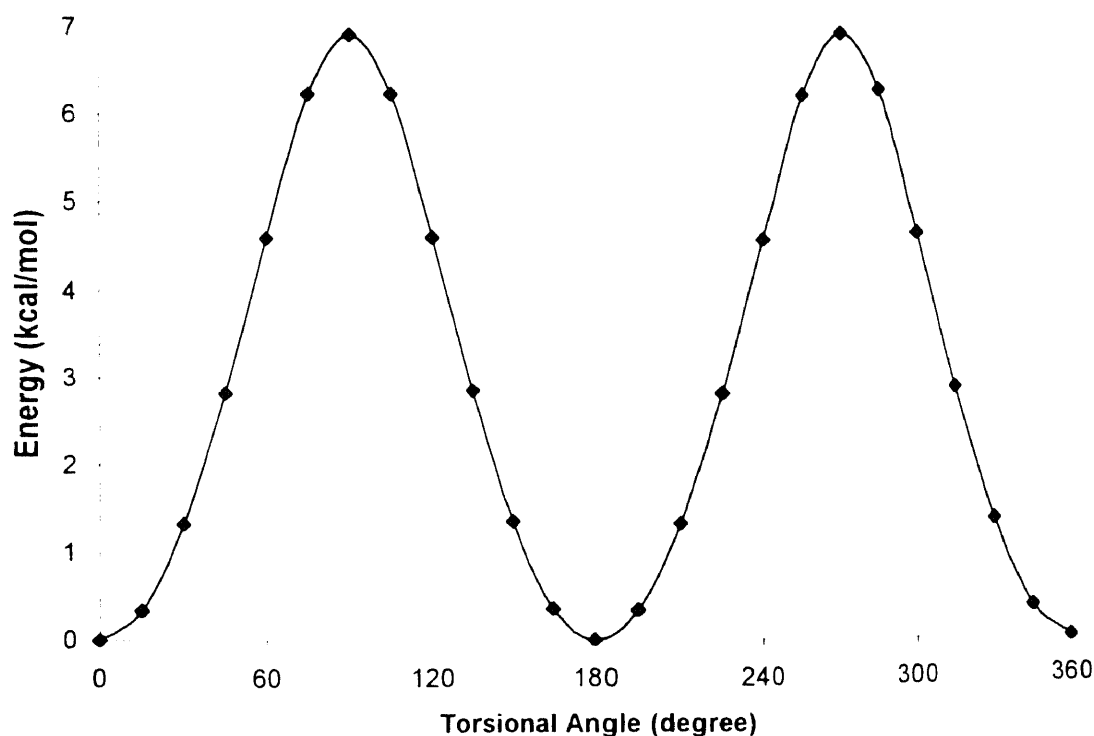
using the CBS-Q//B3\*\* method through all reaction schemes in Table 3.6, Tsang et al.<sup>15</sup> report enthalpy of formation for  $-4.1 \pm 1$  kcal/mol at 298 K. Melius et al.<sup>16</sup> report  $\Delta H_f^\circ_{298}$  of  $\text{CH}_3\text{O}\cdot$  at  $-3.9$  kcal/mol from BAC/MP4 analysis.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

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

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

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

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



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

**Table 4.9.** Total Energy<sup>a</sup> (Hartrees) of Molecules by Torsion angle

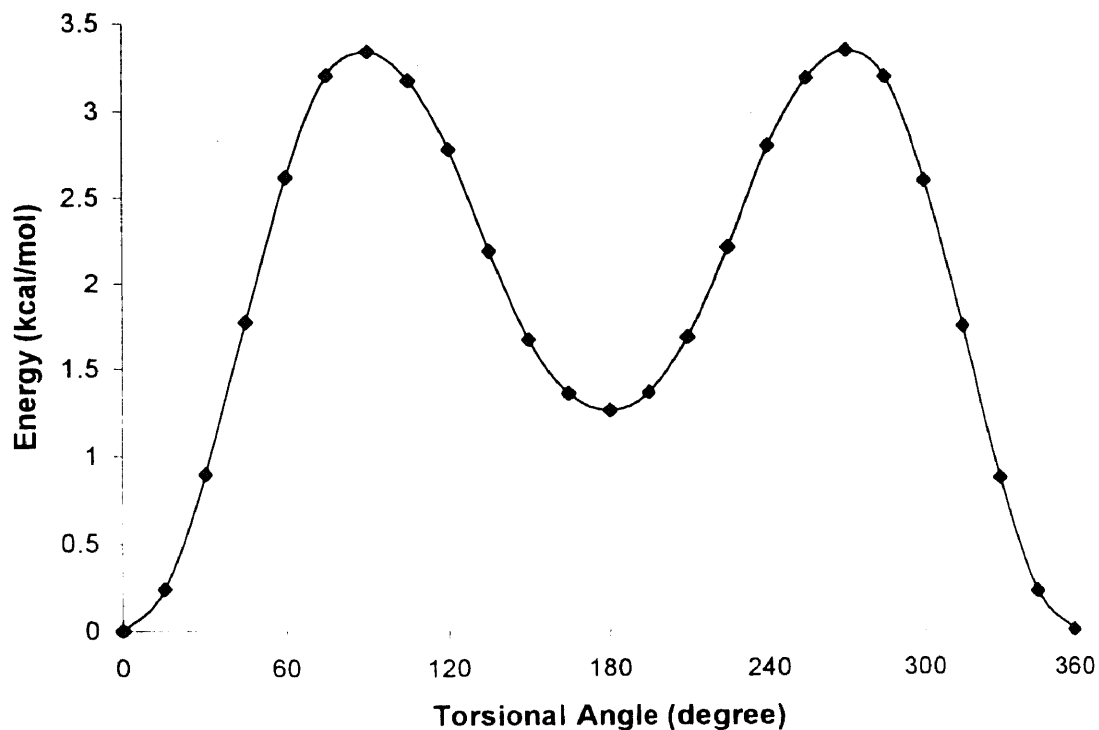
Angle( gree)	CH <sub>2</sub> O--Cl	CHClO--Cl	CCl <sub>2</sub> O--Cl
0	-574.65382	-1034.26023	-1493.85431
15	-574.65327	-1034.26005	-1493.85423
30	-574.65169	-1034.25953	-1493.85397
45	-574.64930	-1034.25868	-1493.85350
60	-574.64649	-1034.25776	-1493.85300
75	-574.64388	-1034.25715	-1493.85268
90	-574.64280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

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

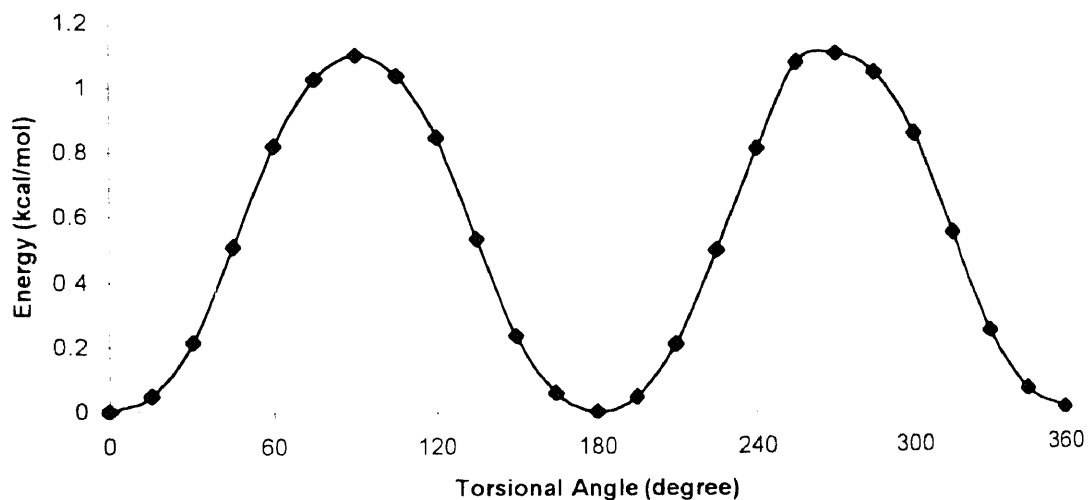
**Table 4.10.**  $\Delta H_f^{\circ}_{298}$  for Rotational Conformers, Relative fraction, and Overall  $\Delta H_f^{\circ}_{298}$  Values

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

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



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



**Figure 4.3.** Potential energy for internal rotation about C-O bond of CCl<sub>2</sub>O--Cl versus torsion angle (0=Optimized Geometry)

**TABLE 4.11:** Coefficients<sup>a</sup> (kcal/mol) of Truncated Fourier Series Representation  
Expansion for Internal Rotation Potentials

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

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

**TABLE 4.12.** Ideal Gas Phase Thermodynamic Properties<sup>a</sup>

		$H_f^\circ_{298}$ <sup>b</sup>	$S^\circ_{298}$ <sup>c</sup>	$C_{p300}$	$C_{p400}$	$C_{p500}$	$C_{p600}$	$C_{p800}$	$C_{p1000}$	$C_{p1500}$
CH <sub>2</sub> Cl (2) <sup>d</sup>	TVR <sup>e</sup>	26.75	58.61	10.08	11.45	12.53	13.38	14.66	15.64	17.3
CH <sub>3</sub> O (3)	TVR	4.10 <sup>e</sup>	54.41	9.61	11.26	12.92	14.42	16.88	18.77	21.73
CH <sub>2</sub> ClO	TVR	-4.51	64.68	12.18	14.27	15.99	17.38	19.42	20.86	23
CHCl <sub>2</sub> O	TVR	-5.56	72.17	15.58	17.71	19.27	20.4	21.93	22.9	24.23
CCl <sub>3</sub> O (3)	TVR	-7.49	76.85	19.8	21.65	22.8	23.56	24.44	24.9	25.4
C-H <sub>2</sub> O-Cl	TVR		65.37	11.93	13.01	14.15	15.23	17.07	18.5	20.75
(2)	Int. <sup>f</sup>		2.9	1.82	2.02	2.16	2.25	2.27	2.17	1.81
	Tot.	-2.1	68.27	13.75	15.03	16.31	17.48	19.34	20.67	22.56
CHClO--Cl	TVR		74.74	14.41	15.82	16.99	17.95	19.4	20.42	21.91
	Int.		6.48	3.2	2.67	2.11	1.65	1.05	0.7	0.33
	Tot.	-17.5	81.22 <sup>h</sup>	17.61	18.49	19.1	19.6	20.45	21.12	22.24
C-Cl <sub>2</sub> O--Cl	TVR		81.12	17.67	19.17	20.18	20.91	21.86	22.44	23.15
(2)	Int.		8.42	1.2	0.8	0.56	0.41	0.25	0.16	0.08
	Tot.	-24.67	89.54	18.87	19.97	20.74	21.32	22.11	22.6	23.23

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

### 4.3.3 Rotational Barriers

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

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

### 4.3.4 Entropy, $S^\circ_{298}$ and Heat Capacity, $C_p(T)$ from 300 to 1500 K

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

contributions from translations, external rotations and vibrations for  $S_{298}^0$  and  $C_p(T)$ . The torsion frequency corresponding to the internal rotor is not included in TVR. Instead, a more exact contribution from the hindered rotation is calculated and listed under I.R. in Table 4.12. I.R. represents the contributions from internal rotation about C-O bond for  $S_{298}^0$  and  $C_p(T)$ 's for formaldehyde (CH<sub>2</sub>O)~Cl complex or chloro-formaldehyde (CHClO)~Cl, (CHCl<sub>2</sub>O)~Cl complex radicals.  $R = 1.987$  cal/mol K, and  $\sigma$  is symmetry number, Entropy of mixing =  $-R \sum \{ (n_i) \times \ln(n_i) \}$ ; where  $n_i$  is fraction of conformer  $i$ . Mixing entropy is included in CHClO--Cl, chloro-formaldehyde~Cl atom complex radical as  $-R\{0.944 \times \ln(0.056) + 0.056 \times \ln(0.056)\} = 0.43$ . There is no published data on entropy and heat capacity values for CH<sub>2</sub>ClO•, CHCl<sub>2</sub>O•, CCl<sub>3</sub>O•, CH<sub>2</sub>O--Cl, CHClO--Cl, or CCl<sub>2</sub>O--Cl.



#### 4.4 Summary

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

## CHAPTER 5

### KINETIC STUDY FOR THE REACTION OF METHYL RADICAL AND CHLORINE MONOXIDE

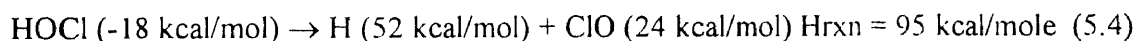
#### 5.1 Overview

Thermochemical properties and thermochemistry of the reaction path are reported by CBS-Q//B3LYP/6-31g(d,p) calculations and methods fully described in chapters 1 to 3. Stable molecule and radical structures are optimized in B3LYP/6-31G(d,p) for the geometries, vibrational frequencies and rotational constants. The total energies are calculated using B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q methods with single point calculation. The reaction system ( $\text{CH}_3 + \text{ClO} \leftrightarrow \text{CH}_3\text{OCl}^* \leftrightarrow \text{Products}$ ) is important because monochlorine monoxide radical ( $\text{ClO}$ )<sup>1-4</sup> is a known chemical that strongly effects ozone depletion in the Antarctic and Arctic polar regions after nocturnal winters. There is a significant amount of literature data on methyl and methyl halide radicals and chlorine oxide radical. However, chlorinated radicals are relatively unstable and some of the kinetics have been not studied. Atomic chlorine reacts with ozone to form the chlorine oxide radical plus  $\text{O}_2$ . The chlorine oxide radical ( $\text{ClO}$ ) is not as active as hydroxyl radical ( $\text{OH}$ ), hydrogen atom ( $\text{H}$ ), or oxygen atom ( $\text{O}$ ) and is not rapidly converted at low temperature,

#### Chlorine Oxide Catalytic Destruction of Ozone Cycle



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



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



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



## 5.2. RRK Theory

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

The Slater theory<sup>81</sup> is a dynamical theory concerned with the detailed treatment of molecular vibrations and the behavior of particular molecular coordinates as a function of time. A reaction is postulated to occur in Slater theory when a chosen coordinate achieves a critical extension by the phase-coincidence of certain modes of vibration. The rate

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

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

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

### 5.2.1 Lindemann-Hinshelwood Mechanism for Unimolecular Reactions

The theory known as Lindemann theory, which forms the basis for all modern theories of unimolecular reactions, has been developed from ideas published almost simultaneously by Lindemann<sup>82</sup> and Christiansen<sup>83</sup>. The concept is that: (a) By collision, a certain fraction of the molecules become energized, i.e., the molecule gains energy in excess of a critical quantity  $E_0$ . The rate of the energization process depends upon the rate of

bimolecular collision. (b) This energized molecule terms  $A^*$ . Energized molecules are de-energized by collision, which is a reverse reaction. This de-energized rate is taken to be energy-independent and is equated with the collision number  $Z_2$  by assuming that every collision of  $A^*$  leads to a de-energized start. (c) There is a time-lag between the energization and unimolecular dissociation or isomerization of the energized molecules.

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



where M can represent a product molecule, an added “inert” gas molecule, or a second molecule of reactant. In the simple Lindemann theory  $k_1$ , along with  $k_2$  and  $k_3$  are taken to be energy-independent and are calculated from the simple collision theory. By application of the steady-state hypothesis to the concentration of  $A^*$ , the unimolecular rate constant and high pressure limit and low pressure limit rate and rate constants are then given as follows.

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

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

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

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

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

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

Based on Lindemann's suggestion that  $k_1$  could be increased by assuming that the required energy (energize molecules) could be drawn in part from the internal degrees of freedom (mainly vibration) of the reactant molecule, Hinshelwood<sup>84</sup> increases  $k_1$  by using a much higher chance of a molecule possessing total energy  $\geq E_0$  in  $s$  classical degrees of freedom,  $k_1 = Z_1 \exp(-E_0/kT) = [Z_1 / (s-1)!] (E_0/kT)^{s-1} \exp(-E_0/kT)$ , when  $\exp(-E_0/kT) = (E_0/kT)^{s-1} \exp(-E_0/kT) / (s-1)!$ . and replace  $k_1$  and  $A^*$  as  $k_1(E \rightarrow E + \delta E)$  and  $A^*_{(E \rightarrow E + \delta E)}$  in mechanism above.

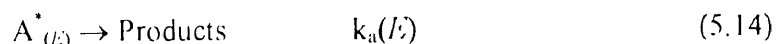
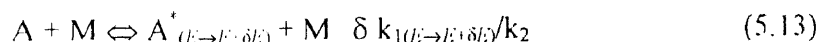
### 5.2.2 RRK Theory of Unimolecular Reactions

In order to make accurate quantitative predictions of the fall-off behavior of a unimolecular reaction it is essential to take into account the energy dependence of the rate constant  $k_a$  ( $k_3$ ) for the conversion of energized molecules into activated complexes and hence products. One of accepted theories is the RRK theory, a statistical theory used in this thesis because it is more computable and needed parameters are readily obtained.

The RRK theory was developed virtually simultaneously by Rice and Ramsperger<sup>85</sup> and Kassel<sup>86-88</sup> with very similar approaches. Both consider that for reaction to occur a critical energy  $E_0$  must become concentrated in one part (one vibration mode) of the molecule. They used the basic Lindemann-Hinshelwood mechanism of

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

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



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

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

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

Hence,

$$k_1(nh\nu) = A \frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!} \quad (5.15)$$

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

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

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

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

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

### 5.2.3 Chemical Activation Reactions

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

This molecular collision at a given temperature produces energized molecules with an equilibrium distribution of energy which enables or produces the fraction of molecules energized into a particular energy range or quantum state. Other energization methods, other than by molecular collision, such as photoactivation and chemical activation, may produce a non-equilibrium situation in which molecules acquire energies far in excess of the average thermal energy. This amount of excess of energy contained in energized



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

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

The basic idea of the treatment of a chemical activation system is that a vibration excited molecule  $A^*$  by an association of reactants can reform reactants with a rate constant  $k'_{-1}(I)$ , form decomposition products with a rate constant  $k_a(I)$  or be de-energized to stable molecules  $A$  by collisions with bath gas  $k_{\text{stab}}(m)$ .

On the strong collision assumption the first order rate constant for de-energization is equal to the collision frequency,  $\omega = Zp$  where  $p$  is the total pressure and  $Z$  is collision number

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

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

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

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

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

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

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

So,

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

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

distribution  $K(E)\delta E$ , so the rate of dissociation to reactants is then  $k'_a(E)K(E)\delta E$ , and by the principle of detailed balancing this also gives the rate of combination of reactants to give  $A^*$  in this energy range. The total rate of energization to all levels above the minimum energy  $E_{\min}$  (the minimum energy of  $A^*$ ) is:

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

Therefore, the distribution function is given by:

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

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

#### 5.2.4 QRRK Analysis for Unimolecular and Chemical Activation Reactions

QRRK analysis, as initially presented by Dean<sup>89-91</sup> combined with the modified strong collision approach of Gilbert et al<sup>92-94</sup>, are used to compute rate constants for both chemical activation and unimolecular reactions, over a range of temperature and pressure. The computer program CHEMDIS, based on the QRRK theory outlined as above, and unimolecular dissociation and chemical activation formalism carries out all unimolecular and chemical activation reactions involved in this thesis. The input parameters for CHEMDIS are: (1) High pressure limit rate constants (Arrhenius A factor and activation energy  $E_a$ ) for each reaction included for analysis; (2) A reduced set of three vibration frequencies and their associated degeneracy; (3) Lennard-Jones transport parameters, ( $\sigma$  (Angstroms) and  $\epsilon/k$  (Kelvin)), and (4) molecular weight of adduct species. All these

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

### 5.2.5 Input Information Requirements for QRRK Calculation

Pre-exponential factors ( $A_{\infty}$ s), are calculated using canonical TST<sup>95</sup> along with CBS-Q//B3LYP/6-31G(d,p), determined entropies of intermediates and TSs for the reactions where thermodynamic properties of TS are available. High-pressure limit pre-exponential factors for combination reactions are obtained from the literature and from trends in homologous series of reactions. Activation energies come from complete basis model calculations CBS-Q plus evaluated thermodynamic properties and literature data.

Reduced sets of three vibration frequencies and their associated degeneracies are computed from fits to heat capacity data, as described by Ritter and Bozzelli et al.<sup>96,97</sup> These have been shown by Ritter to accurately reproduce molecular heat capacities,  $C_p(T)$ , and by Bozzelli et al.<sup>97</sup> to yield accurate ratios of density of states to partition coefficient,  $\rho(E)/Q$ .

Lennard-Jones parameters, sigma (Angstroms) and  $\epsilon/k$  (Kelvins), are obtained from tabulations<sup>98</sup> and from a calculation method based on molar volumes and compressibility.<sup>99</sup> When necessary, estimation is done in a consistent and uniform manner via use of generic reaction rate constants with reference to literature, experiment or theoretical calculation in each case. The QRRK calculation input parameters and their references are listed in the table associated with the respective reaction system.

### 5.2.6 Recent Modifications to the Quantum RRK Calculation Include

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

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

### 5.3. Thermodynamic Properties Using *ab initio* Calculations

Enthalpy,  $\Delta H_f^\circ_{298}$ , entropy,  $S^\circ_{298}$  and heat capacities  $C_p(T)$ , from 300 to 1500 K are determined for methyl hypochlorites ( $\text{CH}_3\text{OCl}$ ), formaldehyde~Cl atom complex radical ( $\text{CH}_2=\text{O}\cdots\text{Cl}$ ) and transition state (TS) using density functional B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p) and *ab initio* QCISD(T)/6-31G(d,p) and CBS-Q calculation methods.<sup>25-30</sup> Thermodynamic properties of  $\text{CH}_3$ ,<sup>32</sup>  $\text{CH}_2\text{O}$ ,<sup>32</sup>  $\text{HCl}$ ,<sup>32</sup>  $\text{ClO}$ ,<sup>32</sup>  $\text{Cl}$ ,<sup>32</sup> and  $\text{ClO}^\bullet$ <sup>32</sup> are taken from literature data. Enthalpy,  $\Delta H_f^\circ_{298}$ , for methoxy radical ( $\text{CH}_3\text{O}$ ) is used from literature data,<sup>78</sup> and its entropy,  $S^\circ_{298}$  and heat capacities  $C_p(T)$ , from 300 to 1500 K used are the values evaluated in this study, in chapter 4.

Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) density functional calculation level, with single point calculations for energy at the B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q levels of calculation. Vibration frequencies are scaled by 0.9806<sup>31</sup> for zero point energies (ZPVE) and for thermal corrections. Enthalpies of formation ( $\Delta H_f^\circ_{298}$ ) for transition state is calculated in CBS-Q//B3\*\* by the difference of the total energy for CH<sub>3</sub>OCl and transition state (TS).

## 5.4 QRRK Input Parameter

### 5.4.1 CH<sub>3</sub>OCl → CH<sub>2</sub>O + HCl

Methyl radical (CH<sub>3</sub>) reacts with chlororine monoxide to form methyl hypochlorite. This adduct, methyl hypochlorite goes to formaldehyde and hydrogen chloride through a saddle point transition state (TS). It is the path way, which has transition state (TS) and pre-exponential factors ( $A_\infty$ s), calculated using canonical TST<sup>16</sup> along with CBS-Q//B3LYP/6-31G(d,p), determined enthalpies of intermediates and TS for the reaction (CH<sub>3</sub>OCl → CH<sub>2</sub>O + HCl) system. B3LYP/6-31G(d,p) is used to determine entropies and heat capacities. The thermodynamic properties are listed in Table 5.1. The frequency, moment of inertia, and geometry of transition state is displayed in Table 5.2. We calculate three parameters (A, n, and Ea) for the model equation of  $A(T) = A \times T^n \times \exp(-E_a/RT)$  ;  $A = 2.58 \times 10^{10}$  (1/sec),  $n = 1.0$ ,  $E_a = 54.2$  (kcal/mol)

**TABLE 5.1.** Ideal Gas Phase Thermodynamic Properties<sup>a</sup> at 298 K

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

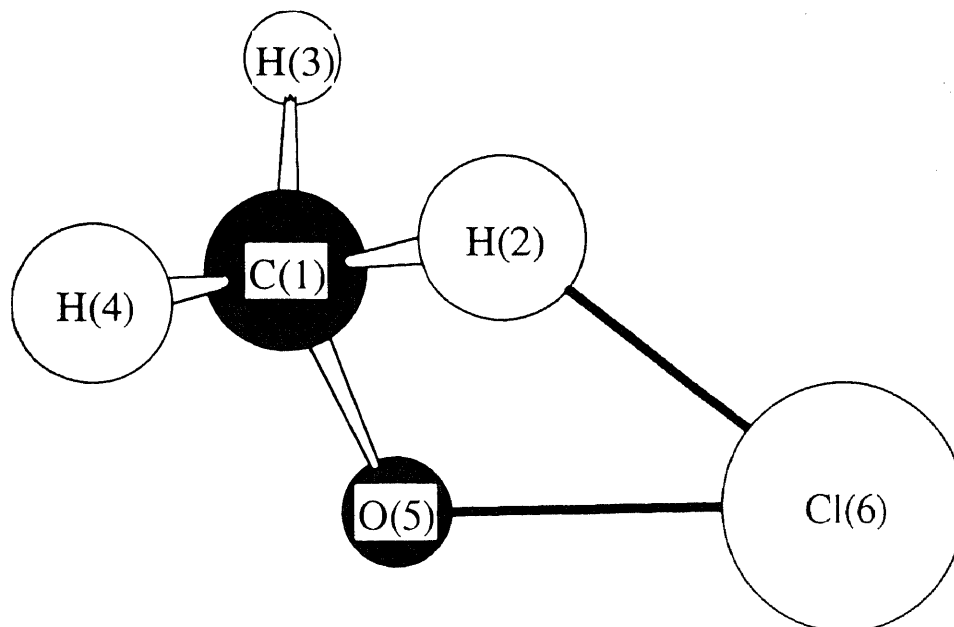
<sup>a</sup> Thermodynamic properties are referred to standard state of an ideal gas of pure enantiomer at 1atm. Units enthalpy in kcal/mol; entropy and heat capacity in cal/mol·K. <sup>b</sup>  $MI_1^{\circ}{}_{298}$  is the average value of CBS-Q level in kcal/mol (see footnote e in Table 2.13 and 4.13). <sup>c</sup> Units in cal/mol·K. <sup>d</sup> This study in Table 4.13. <sup>e</sup>  $MI_1^{\circ}{}_{298}$  is from Reference 78; entropy and heat capacity come from 4.13 in this study.

**TABLE 5.2-a.** Vibrational Frequencies (cm<sup>-1</sup>) and Rotational constants (Ghz) for TransitionState (CH<sub>3</sub>OCl → TS → HCl + CH<sub>2</sub>O)

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

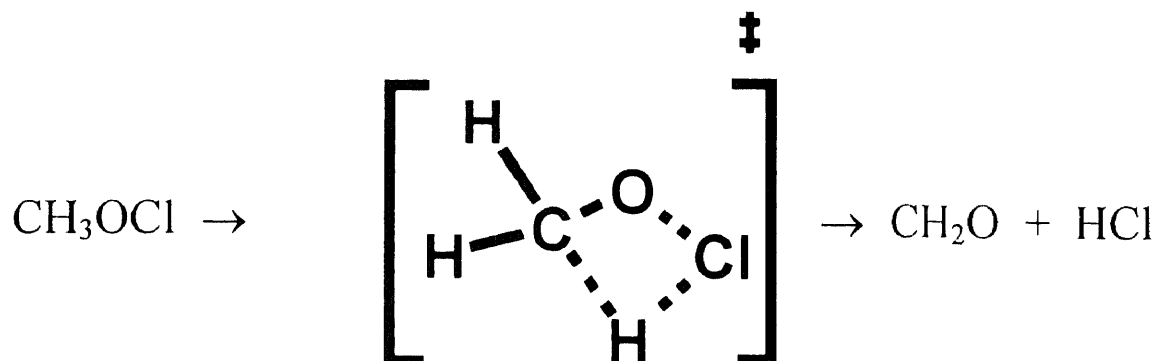
  

TS	Rotational constants (Ghz)		
Calculation method	A	B	C
B3LYP/6-31G(d,p)	32.18664	4.69024	4.21574

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

Name	Definition	Value
H-C	R(3.1)	1.103
H-C	R(4.1)	1.103
O-C	R(5.1)	1.304
Cl-H	R(6.2)	1.919
Cl-O	R(6.5)	2.410
H-C-H	A(3.1.4)	117.218
H-C-O	A(3.1.5)	116.889
H-C-O	A(4.1.5)	116.889
C-O-Cl	A(1.5.6)	92.131
H-O-Cl	A(2.6.5)	49.524
Cl-O-C-H	D(6.5.1.3)	106.842
Cl-O-C-H	D(6.5.1.4)	-106.842
H-Cl-O-C	D(2.6.5.1)	0.000





Transition State

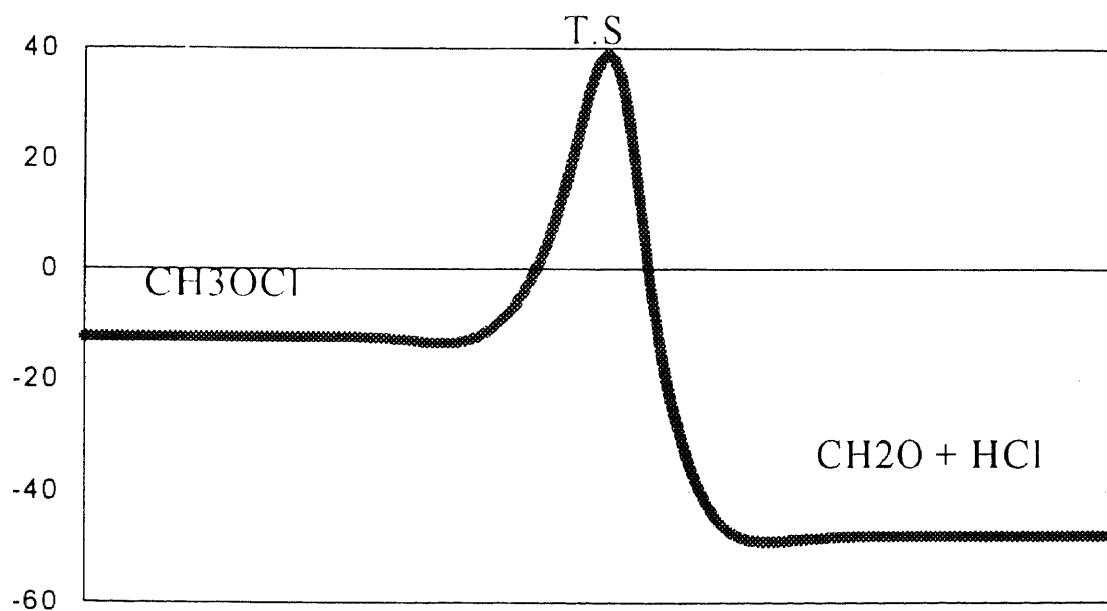
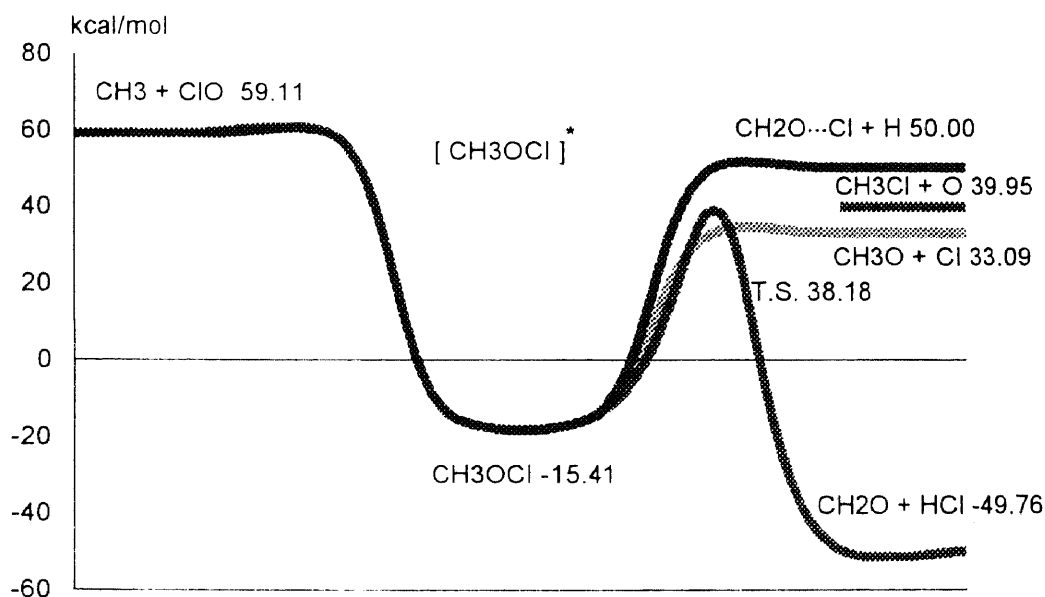


Figure 5.1. Potential energy diagram in the reaction ( $\text{CH}_3\text{OCl} \rightarrow \text{TS} \rightarrow \text{CH}_2\text{O} + \text{HCl}$ ).

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

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

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



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

**Table 5.4.** QRRK Input Parameter<sup>a</sup> for the Reaction of Methyl radical and Chlorine Oxide

	A	n	Ea	Ref
k1				
CH <sub>3</sub> + OCl → CH <sub>3</sub> OCl	7.83E+13	0	0	8
CH <sub>3</sub> OCl → CH <sub>3</sub> + OCl	2.51E+16	0	74.61	b
k2				
CH <sub>3</sub> O + Cl → CH <sub>3</sub> OCl	6.03E+13	0	0	79
CH <sub>3</sub> OCl → CH <sub>3</sub> O + Cl	7.35E+14	0	48.84	b
k3				
CH <sub>2</sub> =OCl + H → CH <sub>3</sub> OCl	1.00E+14	0	0	80
CH <sub>3</sub> OCl → CH <sub>2</sub> =O + Cl + H	6.98E+15	0	67.03	b
k4				
CH <sub>3</sub> OCl → HCl + CH <sub>2</sub> O	2.59E+10	0.9907	54.225	CBSQ/B3**

<sup>a</sup>  $k = AT^n \cdot \text{Exp}(-E_a/RT)$  <sup>b</sup> Microscopic reversibility, L.J Parameter of CH<sub>3</sub>OCl:  $\sigma = 4.63 \text{ \AA}$ ,  $r/k = 380$ . Bath gas = N<sub>2</sub>.

#### 5.4.2 CH<sub>3</sub> + ClO → CH<sub>3</sub>OCl

The reaction CH<sub>3</sub> + ClO system is a chemically activated reaction system. The methyl radical, CH<sub>3</sub>, associates with ClO to form a chemically activated, energized adduct [CH<sub>3</sub>OCl\*]. The adduct contains excess energy from the chemical reaction equal to the energy of the new bond formed. The energized adduct [CH<sub>3</sub>OCl\*] could go back to reactants CH<sub>3</sub> + ClO, or could directly go to products H + CH<sub>2</sub>=O + Cl via formaldehyde + Cl atom complete radical and hydrogen or to Cl + CH<sub>3</sub>O• via a Cl elimination. Both are simple dissociation or simple bond cleavage. Other reactions include molecular HCl elimination forming formaldehyde, CH<sub>2</sub>O + HCl or Cl elimination (cleavage of the weak O~Cl bond). The energized adduct [CH<sub>3</sub>OCl\*] can stay as CH<sub>3</sub>OCl in the well in the Figure 5.2.

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

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

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

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

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

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

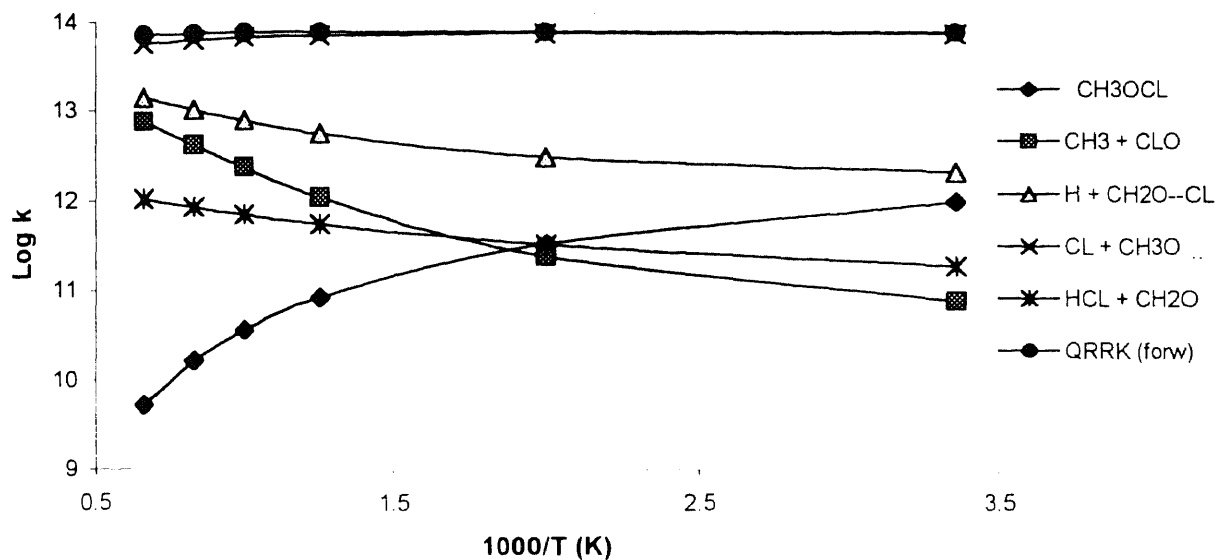


Figure 5.3. QRRK analysis of the reaction in methyl radical and chlorine oxide ( $\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl} \rightarrow \text{Products}$ ) at 1 atm.

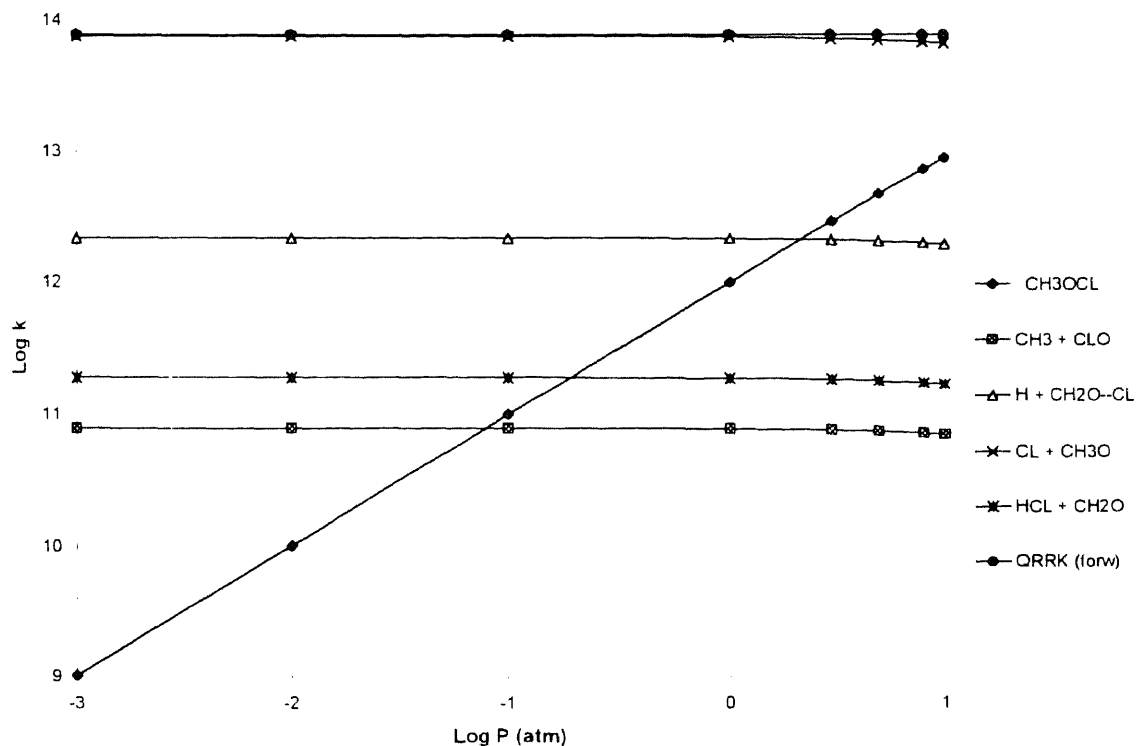


Figure 5.4. QRRK analysis of the reaction in methyl radical and chlorine oxide ( $\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl} \rightarrow \text{Products}$ ) at 298 K.

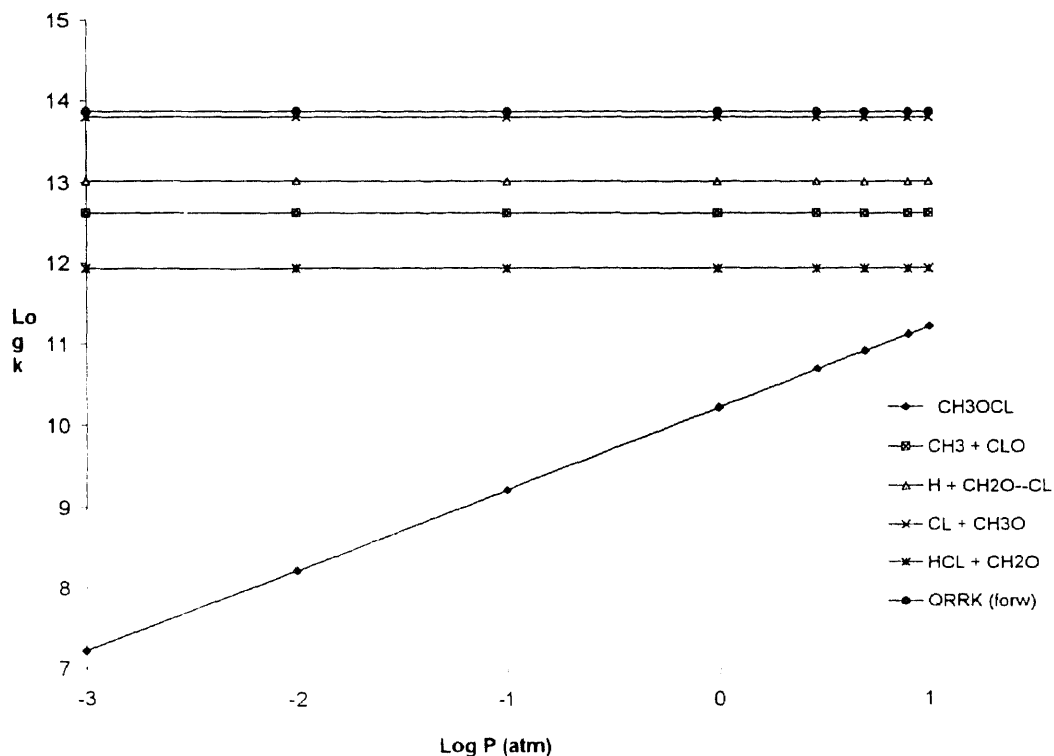


Figure 5.5. QRRK analysis of the reaction in methyl radical and chlorine oxide ( $\text{CH}_3 + \text{ClO} \rightarrow \text{CH}_3\text{OCl} \rightarrow \text{Products}$ ) at 1200 K

### 5.5 Results and Discussion

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

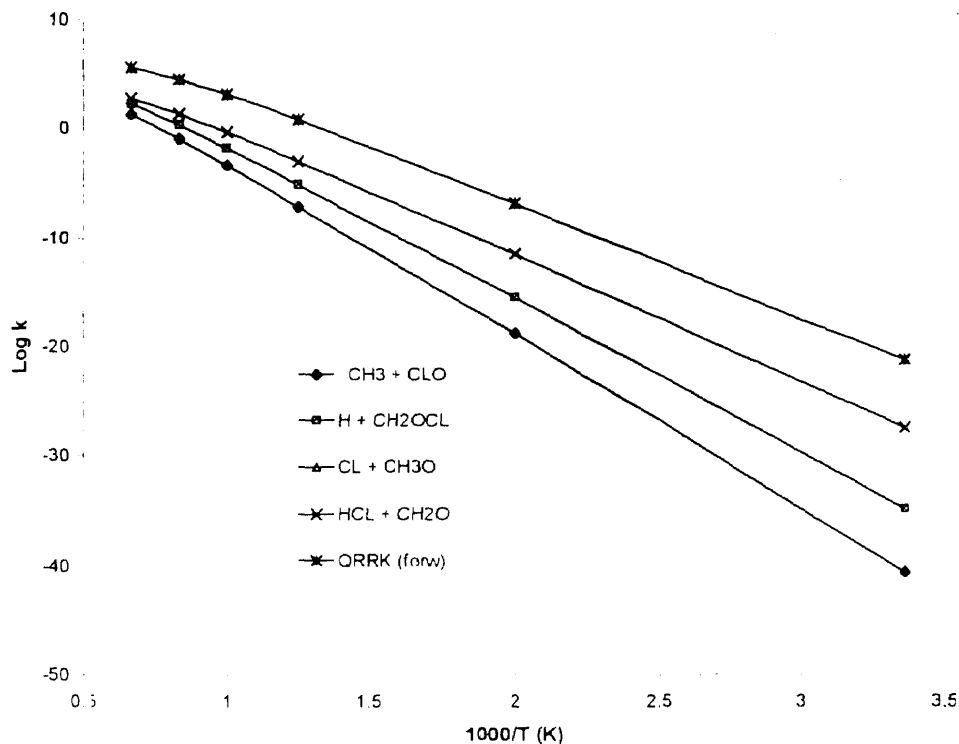


Figure 5.6. QRRK analysis of the dissociation reaction in methyl hypochlorite ( $\text{CH}_3\text{OCl} \rightarrow \text{Products}$ ) at 1 atm.

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

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

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

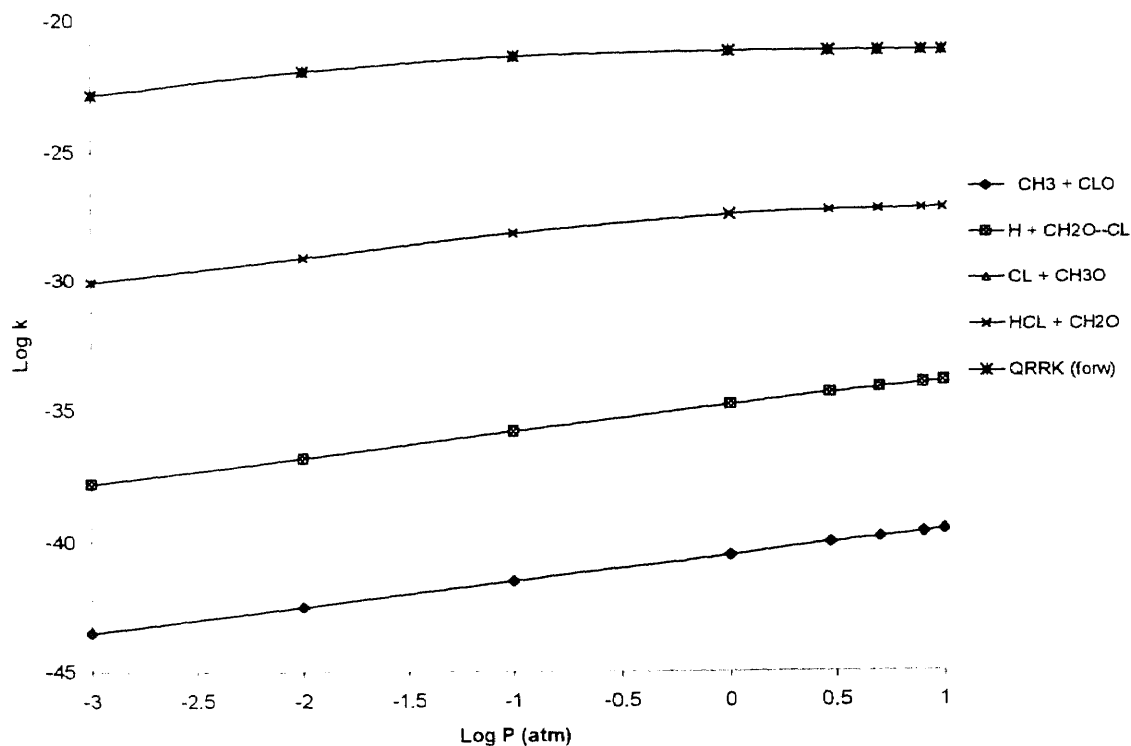
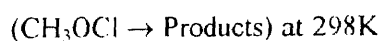
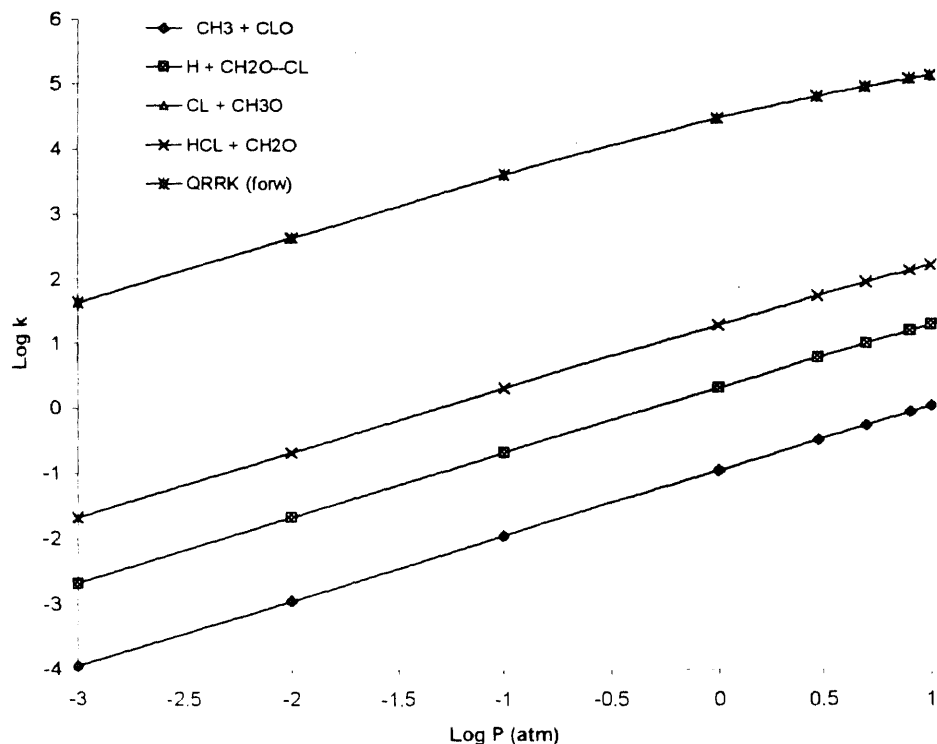


Figure 5.7. QRRK analysis of the dissociation reaction in methyl hypochlorite







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

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

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

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

### 5.6 Summary

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

## APPENDIX 5.1

### THERMODYNAMIC ANALYSIS FOR CH<sub>3</sub> + CLO REACTION

#### THERMODYNAMIC ANALYSIS for REACTION

R<sub>x</sub>      CH<sub>3</sub>OCL    =    TCOCL  
Hf {Kcal/mol} -15.410    38.800  
S {cal/mol K}  65.190    65.470

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

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

The model fitted is for uni-molecular reaction.

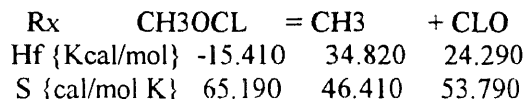
The 3 parameters for the model equation of  $A(T) = A_{\text{prime}} * T^n * \exp(-E_a/RT)$   
A<sub>prime</sub> = 2.5882E+10    n = .99067    E<sub>a</sub> = 5.4225E+04

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

## APPENDIX 5.1

THERMODYNAMIC ANALYSIS FOR CH<sub>3</sub> + CLO REACTION  
(Continued)

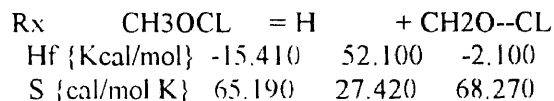
## THERMODYNAMIC ANALYSIS for REACTION



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

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

## THERMODYNAMIC ANALYSIS for REACTION



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

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

## APPENDIX 5.2

KINETIC DATA FOR CH<sub>3</sub> + CLO REACTIONS IN ARREHENIUS FORM
 $k = AT^n \exp(-E_a/RT)$ ; R = 1.987 (cal/mol·K)

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

## APPENDIX 5.2

KINETIC DATA FOR CH<sub>3</sub> + CLO REACTIONS IN ARREHENIUS FORM  
(Continued)

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

Rxn	A	n	Ea(cal/mol)	P(atm)
CH3OCL <=> CH3 + CLO	4.31E+27	-5.65	77923	1.00E-03
CH3OCL <=> CH3 + CLO	4.31E+28	-5.65	77923	1.00E-02
CH3OCL <=> CH3 + CLO	4.33E+29	-5.65	77925	1.00E-01
CH3OCL <=> CH3 + CLO	4.53E+30	-5.66	77939	1.00E+00
CH3OCL <=> CH3 + CLO	1.50E+31	-5.67	77971	3.00E+00
CH3OCL <=> CH3 + CLO	2.73E+31	-5.68	78002	5.00E+00
CH3OCL <=> CH3 + CLO	4.97E+31	-5.7	78047	8.00E+00
CH3OCL <=> CH3 + CLO	6.73E+31	-5.71	78075	1.00E+01
CH3OCL <=> H + CH2O--CL	1.38E+28	-5.87	70092	1.00E-03
CH3OCL <=> H + CH2O--CL	1.38E+29	-5.87	70092	1.00E-02
CH3OCL <=> H + CH2O--CL	1.40E+30	-5.87	70098	1.00E-01
CH3OCL <=> H + CH2O--CL	1.63E+31	-5.89	70148	1.00E+00
CH3OCL <=> H + CH2O--CL	6.63E+31	-5.93	70249	3.00E+00
CH3OCL <=> H + CH2O--CL	1.43E+32	-5.96	70339	5.00E+00
CH3OCL <=> H + CH2O--CL	3.12E+32	-5.99	70458	8.00E+00
CH3OCL <=> H + CH2O--CL	4.63E+32	-6.01	70527	1.00E+01
CH3OCL <=> CL + CH3O	1.54E+37	-8.38	53538	1.00E-03
CH3OCL <=> CL + CH3O	3.56E+38	-8.49	53816	1.00E-02
CH3OCL <=> CL + CH3O	1.22E+40	-8.61	54717	1.00E-01
CH3OCL <=> CL + CH3O	9.69E+37	-7.64	54927	1.00E+00
CH3OCL <=> CL + CH3O	2.72E+35	-6.73	54507	3.00E+00
CH3OCL <=> CL + CH3O	1.05E+34	-6.24	54219	5.00E+00
CH3OCL <=> CL + CH3O	4.26E+32	-5.77	53911	8.00E+00
CH3OCL <=> CL + CH3O	8.83E+31	-5.54	53753	1.00E+01
CH3OCL <=> HCL + CH2O	1.58E+28	-6.26	58367	1.00E-03
CH3OCL <=> HCL + CH2O	1.67E+29	-6.26	58382	1.00E-02
CH3OCL <=> HCL + CH2O	2.59E+30	-6.32	58522	1.00E-01
CH3OCL <=> HCL + CH2O	1.45E+32	-6.52	59260	1.00E+00
CH3OCL <=> HCL + CH2O	3.06E+32	-6.45	59720	3.00E+00
CH3OCL <=> HCL + CH2O	1.57E+32	-6.28	59831	5.00E+00
CH3OCL <=> HCL + CH2O	4.15E+31	-6.04	59840	8.00E+00
CH3OCL <=> HCL + CH2O	1.73E+31	-5.89	59811	1.00E+01

## APPENDIX 5.3

LOG RATE CONSTANTS VS PRESSURE AND TEMPERATURE  
FOR CH<sub>3</sub> + CLO REACTIONChemact reactants CH<sub>3</sub> + CLO Rate constants in log form

P (ATM)	T (K)	1000/T	CH <sub>3</sub> OCl	CH <sub>3</sub> + CLO	H + CH <sub>2</sub> O-Cl	Cl + CH <sub>3</sub> O	HCl + CH <sub>2</sub> O	QRRK
0.00	298.00	3.36	9.01	10.90	12.34	13.88	11.28	13.89
0.00	500.00	2.00	8.53	11.39	12.49	13.87	11.52	13.89
0.00	800.00	1.25	7.93	12.05	12.75	13.85	11.75	13.89
0.00	1000.00	1.00	7.56	12.37	12.90	13.83	11.85	13.88
0.00	1200.00	0.83	7.21	12.62	13.01	13.80	11.93	13.87
0.00	1500.00	0.67	6.72	12.88	13.14	13.75	12.01	13.85

P (ATM)	T (K)	1000/T	CH <sub>3</sub> OCl	CH <sub>3</sub> + CLO	H + CH <sub>2</sub> O-Cl	Cl + CH <sub>3</sub> O	HCl + CH <sub>2</sub> O	QRRK
0.01	298.00	3.36	10.01	10.90	12.34	13.88	11.28	13.89
0.01	500.00	2.00	9.53	11.39	12.49	13.87	11.52	13.89
0.01	800.00	1.25	8.93	12.05	12.75	13.85	11.75	13.89
0.01	1000.00	1.00	8.56	12.37	12.90	13.83	11.85	13.88
0.01	1200.00	0.83	8.21	12.62	13.01	13.80	11.93	13.87
0.01	1500.00	0.67	7.72	12.88	13.14	13.75	12.01	13.85

P (ATM)	T (K)	1000/T	CH <sub>3</sub> OCl	CH <sub>3</sub> + CLO	H + CH <sub>2</sub> O-Cl	Cl + CH <sub>3</sub> O	HCl + CH <sub>2</sub> O	QRRK
0.10	298.00	3.36	11.00	10.90	12.34	13.88	11.28	13.89
0.10	500.00	2.00	10.53	11.39	12.49	13.87	11.52	13.89
0.10	800.00	1.25	9.93	12.05	12.75	13.85	11.75	13.89
0.10	1000.00	1.00	9.56	12.37	12.90	13.83	11.85	13.88
0.10	1200.00	0.83	9.21	12.62	13.01	13.80	11.93	13.87
0.10	1500.00	0.67	8.72	12.88	13.14	13.75	12.01	13.85

P (ATM)	T (K)	1000/T	CH <sub>3</sub> OCl	CH <sub>3</sub> + CLO	H + CH <sub>2</sub> O-Cl	Cl + CH <sub>3</sub> O	HCl + CH <sub>2</sub> O	QRRK
1.00	298.00	3.36	12.00	10.89	12.33	13.87	11.27	13.89
1.00	500.00	2.00	11.53	11.38	12.49	13.87	11.52	13.89
1.00	800.00	1.25	10.93	12.05	12.75	13.85	11.75	13.89
1.00	1000.00	1.00	10.56	12.37	12.90	13.83	11.85	13.88
1.00	1200.00	0.83	10.21	12.62	13.01	13.80	11.93	13.87
1.00	1500.00	0.67	9.72	12.88	13.14	13.75	12.01	13.85

P (ATM)	T (K)	1000/T	CH <sub>3</sub> OCl	CH <sub>3</sub> + CLO	H + CH <sub>2</sub> O-Cl	Cl + CH <sub>3</sub> O	HCl + CH <sub>2</sub> O	QRRK
3.00	298.00	3.36	12.47	10.88	12.32	13.86	11.26	13.89
3.00	500.00	2.00	12.00	11.38	12.49	13.87	11.51	13.89
3.00	800.00	1.25	11.41	12.05	12.75	13.85	11.74	13.89
3.00	1000.00	1.00	11.04	12.37	12.90	13.83	11.85	13.88
3.00	1200.00	0.83	10.69	12.62	13.01	13.80	11.93	13.87
3.00	1500.00	0.67	10.20	12.88	13.14	13.75	12.01	13.85

## APPENDIX 5.3

**LOG RATE CONSTANTS VS PRESSURE AND TEMPERATURE  
FOR CH<sub>3</sub> + CLO REACTION  
(Continued)**

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

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

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



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