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Structures, Rotation Barrier, and Thermodynamic Properties $\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$ of Chloromethyl Hypochlorites CH_3OCl, CH_2ClOCl, $CHCl_2OCl$, and CCl_3OCl

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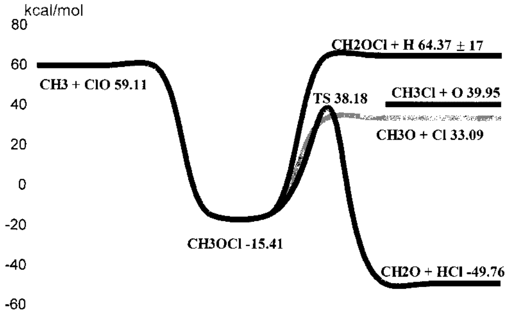
Hypochlorites are formed from reactions of chlorine monoxide (ClO) addition to unsaturates and association with radicals. ClO is a prevalent and an important species in the chemistry of the atmosphere and in combustion systems where chlorine is present. Thermochemical property data on these oxychlorocarbon species are important to understanding the reaction pathways and kinetics in these environments. Enthalpy, $\Delta H_f°_{298}$, entropy, $S°_{298}$, and heat capacities, $C_p(T)$ from 300 to 1500 K are determined for methyl hypochlorite and three chloromethyl hypochlorites 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 $\Delta H°_{rxn}$ and known enthalpies of other reactants in each of several working reactions (up to seven). Barriers for intramolecular rotation are calculated and contributions to entropy and heat capacity from internal rotation in the chloromethyl hypochlorite are determined. Evaluation of enthalpy data from reaction schemes and the statistical distribution of rotation conformers results in $\Delta H_f°_{298}$ values for CH_3OCl of −15.41 ± 1.48 kcal/mol, CH_2ClOCl of −22.05 ± 2.47 kcal/mol, $CHCl_2OCl$ of −26.14 ± 3.61 kcal/mol, and CCl_3OCl of −26.72 ± 4.68 kcal/mol in the CBS-Q//B3LYP/6-31G(d,p) method.

Introduction

CH_3OCl has been considered an important atmospheric species since the severe depletions in stratospheric ozone were first observed during the Antarctic spring in 1985.[1,2] This ozone depletion is now believed to the result from several reaction sequences involving the chlorine monoxide radical (ClO).[3,4] At low temperature, methyl radical associates with chlorine monoxide radical (ClO) and produces methyl hypochlorite (CH_3OCl) but at higher temperature or low pressure, methoxy radical and Cl atom are dominant initial products from the association, with formaldehyde also observed.[5,6]

Chlorocarbon radicals are the initial intermediates from reaction of chlorocarbons in the atmosphere and in combustion systems. Chlorine substitution in methyl and alkyl radicals results in lower reactivity to products and decreased stability of peroxy adducts formed from reaction of these radicals with O_2. The slower reactions with O_2 permit the chlorinated methyl radicals to build up to higher concentrations in combustion environments, relative to CH_3, where they are more likely to undergo reactions with the radical pool, of which HO_2, OH, and ClO are major species. The association reactions with ClO result in chemically activated oxychlorides (chloromethoxy species) which can be stabilized or further react to lower energy products (Scheme 1). Chlorine monoxide radicals are also active in combustion inhibition (termination reactions) via cycles similar to that for thermal catalytic ozone destruction in the stratosphere[7] and the formaldehyde + HCl channel in Scheme 1.

SCHEME 1



$$\text{termination}\quad H + ClO + M \rightarrow HOCl + M$$

$$OH + HOCl \rightarrow H_2O + ClO$$

$$\text{net}\quad H + OH \rightarrow H_2O$$

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 OH or H_2O which has stronger bonds than H−Cl. This often results in significant levels of atomic and molecular chlorine as well as chlorine oxide in the combustion environment. ClO also serves to convert CO to CO_2.[8]

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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.[9,10] ClO 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.[11]

$$CH_3OO + Cl \rightarrow CH_3OOCl \rightarrow CH_3O + ClO \qquad \Delta H_{rxn} = -3.3\ \text{kcal/mol}$$

Thermochemical properties on the oxygenated chlorocarbon species are needed for evaluation of reaction paths and kinetic processes, as well as stability of intermediate adducts and the oxychlorocarbon species formed as products.[5,12,15] Thermo properties are also needed in kinetic modeling and in equilibrium codes. There is very little or no thermodynamic data of these oxygenated chlorocarbons in the literature, Francisco et al. report a theoretical study on the excited states[14] and $\Delta H_f°_0$ for methyl hypochlorite (CH_3OCl) of −13.5 ± 2 kcal/mol with CCSD(T)/6-311G(2df,2p) level[15] of theory, which we convert to $\Delta H_f°_{298}$ of −15.9 kcal/mol. Elrod et al. report Gaussian-2 ab initio study for $\Delta H_f°_{298}$ of CH_3OCl as −17.69 kcal/mol[16] and separately derive $\Delta H_f°_{298}$ of CH_3OCl as −12.26 kcal/mol by bond additivity based on methods developed by Colussi's work.[17] J. Espinosa-Garcia recently reported[18] $\Delta H_f°_{298}$ for CH_3OCl of −13.2 ± 2.3 kcal/mol by the unweighted average of results from 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 $\Delta H_f°_{298}$ for methyl hypochlorite on his Web site −14.00 kcal/mol,[19] and Crowley et al.[20] used bond additivity values of Benson[21] for estimation of $\Delta H_f°_{298}$ of −14.58 kcal/mol for CH_3OCl.

These estimates exhibit a wide range in enthalpy values at 298 K from −12.26 to −17.69 kcal/mol. There is, in addition, no literature data that we are aware of on thermodynamic properties of chloromethyl hypochlorites (CH_2ClOCl, $CHCl_2OCl$, and CCl_3OCl). We also do not know any published values for heat capacity or entropy on CH_3OCl or any of the chloromethyl hypochlorites. This study estimates fundamental thermodynamic property data, $\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$ and internal rotation barriers on the methyl hypochlorite, and chloromethyl hypochlorites using ab initio and density functional calculations. We also determine group additivity values of the O/C/Cl group, for use in estimation of larger alkyl hypochlorites.

Calculation Methods

Selection of Calculation Methods and Basis Sets. B3LYP/6-31G(d,p) is chosen because it is computationally economical and, thus, possibly applicable to larger molecules, if it is accurate. DFT is also commonly used and is reported to yield accurate geometry and reasonable energies.[22,23] Comparison of calculation results from this level against data from higher calculation levels for $\Delta H_f°_{298}$ will provide some calibration of the B3LYP/6-31G(d,p) values (with similar working reactions) for larger molecules, where this may be one of the few calculation methods available. B3LYP/6-311+G(3df,2p) is chosen to see if this larger basis set results in an improvement to the above commonly used density functional calculation method.[23] QCISD(T)/6-31G(d,p) is a configuration interaction method; but with a small, economical basis set.[24,25] 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).[26,27] This CBS-Q//B3LYP/6-31G(d,p) method is similar to the Radom research group's CBS/RAD[24] 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.

Thermodynamic Properties Using ab Initio Calculations. Enthalpy, $\Delta H_f°_{298,}$ entropy, $S°_{298}$, and heat capacities $C_p(T)$, from 300 to 1500 K are determined for four chloromethyl hypochlorites, CH_3OCl, CH_2ClOCl, $CHCl_2OCl$, and CCl_3OCl using density functional B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), and ab initio QCISD(T)/6-31G(d,p) and CBS-Q calculation methods.[28−31] 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.[32] 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 seven different reaction series.[33−42] Barriers for intramolecular rotation about the CH_3−OCl bond are analyzed versus torsion angle using B3LYP/6-31G(d,p) density functional calculations.

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.[43,44] 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 digonalization of Hamiltonian matrix. In this work, the torsional potential calculated at discrete torsional angles is represented by eq E1.

$$V(\phi) = a_0 + a_1\cos(\phi) + a_2\cos(2\phi) + a_3\cos(3\phi) + b_1\sin(\phi) + b_2\sin(2\phi) + b_3\sin(3\phi) \quad \text{(E1)}$$

Results and Discussion

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 1. They are in good agreement with other calculation[15,18,19] and experimental data.[12,45,46] The ClO stretching frequency mode of CH_3OCl shows 660 cm^{-1} in this work, 667 cm^{-1} in B3LYP/6-311++G(3df,3pd),[15] 692 cm^{-1} in CCSD(T)/6-311G(2df,2p),[15] 704 cm^{-1} in BAC/MP4 theory,[19] and 680 cm^{-1} in the spectra of Crowley et al.[12] The CO stretching frequency mode of CH_3OCl is 1019 cm^{-1} in this calculation, 1007 cm^{-1} in B3LYP/6-311++G(3df,3pd),[15] 1046 cm^{-1} in CCSD(T)/6-311G(2df,2p),[15] 1039 cm^{-1} in BAC/MP4 level,[19] 1006 cm^{-1} in the spectra of Crowley[12] et al., and 1002 cm^{-1} in the experiment of Jungkamp et al.[45]

The optimized B3LYP/6-31G(d,p) geometries for the methyl and three chlorinated methyl hypochlorites are illustrated in Table 2 and show good agreement with literature data.[10,15,18,47] Effects of chlorine α-substitution on molecular geometry can be seen from Table 2. The C−H and O−Cl bond lengths in the equilibrium conformations of CH_3OCl, CH_2ClOCl, $CHCl_2OCl$, and CCl_3OCl optimized at the B3LYP/6-31G(d,p) are similar;

TABLE 1: (a) Vibrational Frequencies[a] (cm^{-1}) for Methyl Hypochlorite, (b) Rotation Constants (GHz) for Methyl Hypochlorite, and (c) Vibrational Frequencies[a] and Rotation Constants for Chloromethyl Hypochlorite

(a) Vibrational Frequencies for Methyl Hypochlorite

CH_3OCl sym	freq mode type	B3LYP/ 6-31G(d,p)[a]	B3LYP/ 6-311++G(3df,3pd)[b]	CCSD(T)/ 6-311G(2df,2p)[b]	BAC/MP4[c]	experiment Crowley[d]	experiment Jungkamp[e]
a″	torsion	259	243	254	230		
a′	COCl bend	364	367	373	360		
a′	ClO stretch	660	677	692	704		680
a′	CO stretch	1019	1007	1046	1039	1006	1002
a″	CH_3 rock	1175	1172	1180	1150		1150
a′	CH_3 rock	1198	1196	1201	1181	1190	1170
a′	CH_3 s-deform	1463	1458	1467	1440	1450	1456
a″	CH_3 d-deform	1471	1466	1479	1454		1471
a′	CH_3 d-deform	1523	1505	1516	1478		
a′	CH_3 s-stretch	3026	3019	3040	2880	2998	2820
a″	CH_3 d-stretch	3104	3092	3117	2951		2920
a′	CH_3 d-stretch	3125	3114	3144	2969		2904

(b) Rotation Constants for Methyl Hypochlorite

CH_3OCl calculation method	rotational constants (GHz) A	B	C
B3LYP/6-31G(d,p)	41.97723	6.06531	5.48635
B3LYP/6-311++G(3df,3pd)	43.101	6.177	5.596
CCSD(T)/6-311G(2df,2p)	41.484	6.280	5.651
BAC/MP4	44.990	6.334	5.751
experimental[f]	42.06435	6.29688	5.67062

(c) Vibrational Frequencies and Rotation Constants for Chloromethyl Hypochlorite

CH_2ClOCl freq	B3LYP/6-31G(d,p) rotation[g]	$CHCl_2OCl$ freq	B3LYP/6-31G(d,p) rotation[g]	CCl_3OCl freq	B3LYP/6-31G(d,p) rotation[g]
124.47	11.39849	112.10	2.73563	115.01	1.80228
321.38	2.27446	182.46	2.01362	166.40	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		390.20	
1063.43		732.07		391.75	
1264.86		767.69		534.36	
1347.11		1060.24		689.10	
1466.70		1217.93		766.45	
3090.95		1311.52		839.81	
3171.11		3144.99		1036.88	

[a] Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d,p) level of theory. [b] Reference 15. [c] Reference 19. [d] Reference 12. [e] Reference 45. [f] Reference 46 [g] The rotational constant units are GHz.

while the C−O bond lengths (R4) decrease in the order 1.425 Å in CH_3OCl, 1.390 Å in CH_2ClOCl, 1.375 Å in $CHCl_2OCl$, 1.383 Å in CCl_3OCl. The Cl−C bond lengths (R1) in the chloromethyl hypochlorites also decrease with increase in number of chlorines, while the Cl−O bond length increases. The geometry of CH_3OCl in this work is similar to values reported by Francisco[15] and Melius[19] and the experimental values of Rigden et al.[46] in Table 2. There is a good agreement of frequency data with B3LYP/6-31G(d,p) in this study, with larger basis set calculations[15] and with experiments[12,45,46] for methyl hypochlorite.

Distances between the hypochlorite chlorine and hydrogen on the methyl group in the low-energy conformers are 2.815, 2.772, and 2.744 Å for CH_3OCl, CH_2ClOCl, and $CHCl_2OCl$. Several groups report significant H atom- -Cl interactions can occur over these distances.[47,48]

Enthalpies of Formation ($\Delta H_f°_{298}$). Enthalpies of formation ($\Delta H_f°_{298}$) 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.[32] Thermal correction, 0 K to 298.15 K, is calculated to estimate $\Delta H_f°_{298}$ at 298.15 K.[28] The following seven reaction schemes are selected to determine $\Delta H_f°_{298}$ of each hypochlorite.

$$CH_{4-x}Cl_{x-1}OCl + CH_4 \rightarrow CH_3OH + CH_{4-x}Cl_x \quad (1)$$

$$CH_{4-x}Cl_{x-1}OCl + CH_3CH_3 \rightarrow CH_3OH + CH_3CH_{3-x}Cl_x \quad (2)$$

$$CH_{4-x}Cl_{x-1}OCl + H_2O \rightarrow CH_3OH + xHOCl \quad (3)$$

$$CH_{4-x}Cl_{x-1}OCl + xH_2 \rightarrow CH_3OH + xHCl \quad (4)$$

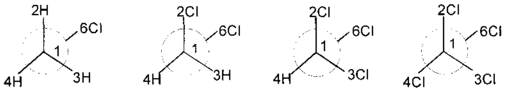
$$CH_{4-x}Cl_{x-1}OCl + x\ H_2 \rightarrow CH_{4-x}Cl_x + xHOCl \quad (5)$$

$$CH_3OCl + HOOH \rightarrow CH_3OOH + HOCl \quad (6)$$

$$CH_3OCl + CH_3OH \rightarrow CH_3OOH + CH_3Cl \quad (7)$$

Density functional and ab initio calculations with ZPVE and thermal correction are performed for all four compounds in each reaction, and enthalpy of reaction $\Delta H_{rxn}°_{298}$ is calculated. Since enthalpies of formation of three compounds have been

TABLE 2: Optimized Geometry of Chloromethyl Hypochlorites[a]



		CH_3OCl				
name	definition	B3LYP/ 6-31G(d,p)[a]	B3LYP/ 6-311++G(3df,3pd)[b]	CCSD(T)/ 6-311G(2df,2p)[c]	BAC/MP4[d]	expt[e]
R1[f]	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(6,3)	2.815				
A1[g]	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[h]	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_2ClOCl			$CHCl_2OCl$			CCl_3OCl		
name	definition	value[a]	name	definition	value[a]	name	definition	value[a]
R1[f]	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(6,3)	2.772	R6	R(6,3)	2.744	R6	R(6,3)	3.271
A1[g]	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[h]	D(6,5,1,2)	74.68	D1	D(6,5,1,2)	−63.92	D1	D(6,5,1,2)	62.13
D2	D(6,5,1,3)	−47.43	D2	D(6,5,1,3)	−63.92	D2	D(6,5,1,3)	−62.12
D3	D(6,5,1,4)	−169.23	D3	D(6,5,1,4)	−180.07	D3	D(6,5,1,4)	−180.00

[a] Geometry is optimized in B3LYP/6-31g(d,p) density functional calculation level. [b] B3LYP/6-311++G(3df,3pd) level in ref 15. [c] CCSD(T)/6-311(2df,2p) level in ref 15. [d] BAC/MP4 level in ref 19. [e] Experimental value in ref 46. [f] Bond length or the distance between two atoms of number in Å. [g] Bond angle or the angle among three atoms of number in degrees. [h] Dihedral angle among the four number atoms.

experimentally determined or theoretically calculated, the unknown enthalpies of formation of CH_3OCl, CH_2ClOCl, $CHCl_2OCl$, and CCl_3OCl are obtained. As example, $\Delta H_f°_{298}(CH_3OCl)$ is calculated from (1) and the known enthalpies of CH_3OH, CH_3Cl, and CH_4.[32−34]

$$\Delta H_{rxn\,298} = \Delta H_f°_{298}(CH_3OH) + \Delta H_f°_{298}(CH_3Cl) - \Delta H_f°_{298}(CH_3OCl) - \Delta H_f°_{298}(CH_4) \quad (I)$$

The enthalpies of reaction from the reaction schemes are listed in Table 3. $\Delta H_f°_{298}$ of the standard compounds are listed in Table 4 and determined $\Delta H_f°_{298}$ of chloromethyl hypochlorites are in Table 5.

Data in Table 5 shows that the enthalpy of formation at the CBS-Q//B3** calculation level is relatively consistent for each species, except for values determined using reaction scheme (4). $\Delta H_f°_{298}$ for CH_3OCl is −15.41 kcal/mol, using CBS-Q//B3** values over all reactions in Table 5, on the other hand, $\Delta H_f°_{298}$ for CH_3OCl is −15.91 kcal/mol, using the average of B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), and QCISD(T)/6-31g(d,p) values. Francisco et al.[15] used CCSD(T) calculation with a large basis set 6-311G(2df,2p) determine $\Delta H_f°_0$ for -13.5 ± 2 kcal/mol from the reaction

$$CH_3OCl + H_2O \rightarrow CH_3OH + HOCl$$

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

$${}^3/_2H_2 + {}^1/_2O_2 + {}^1/_2Cl_2 + C(s) \rightarrow CH_3OCl$$

Elord et al.[16] report $\Delta H_f°_{298}$ of CH_3OCl at −17.69 kcal/mol from G2 analysis on the isodesmic reaction:

$$CH_3OH + ClO \rightarrow CH_3OCl + OH$$

They also calculated $\Delta H_f°_{298}$ of CH_3OCl at −12.26 kcal/mol from bond additivity by Colussi's values.[17] Espinosa-Garcia recently reported[18] $\Delta H_f°_{298}$ for CH_3OCl of -13.2 ± 2.3 kcal/mol by the unweighted average of the results of MP4/6-31G(d,p)//MP2/6-31G(d), CCSD(T)/6-311G(3d,2p), CCSD/cc-

TABLE 3: Reaction Enthalpies (in kcal/mol) at 298 K[a]

		ΔH_{rxn} (theory level[b])			
	reaction	B3LYP6-31	B3LYP6-311	QCISD(T)	CBS-Q//B3**
1	$CH_3OCl + CH_4 \rightarrow CH_3OH + CH_3Cl$	−32.16	−33.94	−32.25	−35.23
	$CH_2ClOCl + CH_4 \rightarrow CH_3OH + CH_2Cl_2$	−26.46	−29.13	−27.18	−30.82
	$CHCl_2OCl + CH_4 \rightarrow CH_3OH + CHCl_3$	−23.33	−26.55	−24.07	−28.83
	$CCl_3OCl + CH_4 \rightarrow CH_3OH + CCl_4$	−21.64	−25.33	−21.93	−28.30
2	$CH_3OCl + CH_3CH_3 \rightarrow CH_3OH + CH_3CH_2Cl$	−36.15	−38.06	−36.67	−40.22
	$CH_2ClOCl + CH_3CH_3 \rightarrow CH_3OH + CH_3CHCl$	−32.33	−35.07	−34.32	−39.29
	$CHCl_2OCl + CH_3CH_3 \rightarrow CH_3OH + CH_3CCl_3$	−29.30	−32.41	−32.32	−39.12
	$CCl_3OCl + CH_3CH_3 \rightarrow CH_3OH + CH_2ClCCl_3$	−32.31	−35.12	−34.24	−40.37
3	$CH_3OCl + H_2O \rightarrow CH_3OH + HOCl$	4.39	5.66	5.63	6.72
	$CH_2ClOCl + 2H_2O \rightarrow CH_3OH + 2HOCl$	45.87	50.17	48.68	54.44
	$CHCl_2OCl + 3H_2O \rightarrow CH_3OH + 3HOCl$	82.17	90.29	88.13	99.67
	$CCl_3OCl + 4H_2O \rightarrow CH_3OH + 4HOCl$	112.75	125.12	123.24	141.66
4	$CH_3OCl + H_2 \rightarrow CH_3OH + HCl$	−51.17	−54.51	−51.56	−53.96
	$CH_2ClOCl + 2H_2 \rightarrow CH_3OH + 2HCl$	−65.25	−70.18	−65.69	−66.91
	$CHCl_2OCl + 3H_2 \rightarrow CH_3OH + 3HCl$	−84.50	−90.23	−83.43	−82.36
	$CCl_3OCl + 4H_2 \rightarrow CH_3OH + 4HCl$	−109.49	−115.58	−105.50	−101.04
5	$CH_3OCl + H_2 \rightarrow CH_4 + HOCl$	−18.51	−20.90	−18.79	−19.31
	$CH_2ClOCl + H_2 \rightarrow CH_3Cl + HOCl$	−13.59	−15.99	−13.62	−13.54
	$CHCl_2OCl + H_2 \rightarrow CH_2Cl_2 + HOCl$	−13.06	−15.56	−12.15	−11.61
	$CCl_3OCl + H_2 \rightarrow CCl_3H + HOCl$	−15.66	−18.28	−13.37	−12.87
6	$CH_3OCl + HOOH \rightarrow CH_3OOH + HOCl$	−1.85	−1.73	−1.44	−1.33
7	$CH_3OCl + CH_3OH \rightarrow CH_3OOH + CH_3Cl$	8.75	12.74	10.32	12.43

[a] Reaction enthalpies include thermal correction and zero-point energy correction at 298 K. [b] See calculation methods in text for explanation.

TABLE 4: Enthalpy Data Used in Reactions to Determine $\Delta H_f°_{298}$ of Target Oxychlorides

compound	$\Delta H_f°_{298}$[a]	source	uncertainty	source
CH_4	−17.89	ref 33	±0.1	ref 33 (38)
CH_3Cl	−19.60	ref 34	±0.2	ref 34 (39)
CH_2Cl_2	−22.83	ref 33	±0.3	ref 33
$CHCl_3$	−24.20	ref 35	±0.3	ref 37
CCl_4	−22.94	ref 33	±0.5	ref 33
C_2H_6	−20.24	ref 35	±0.1	ref 35 (39)
CH_3CH_2Cl	−26.84	ref 34	±0.2	ref 34 (39)
CH_3CHCl_2	−31.09	ref 34	±0.3	ref 37
CH_3CCl_3	−34.01	ref 34	±0.3	ref 34 (40)
CH_2ClCCl_3	−35.71	ref 34	±2.0[b]	ref 39
CH_3OH	−48.08	ref 35	±0.1	ref 35 (41)
CH_3OOH	−31.80	ref 36	±0.9	ref 36[c]
HCl	−22.06	ref 33	±0.1	ref 33
HOCl	−17.80	ref 33	±0.5	ref 33
HOOH	−32.53	ref 33		
H_2O	−57.80	ref 35	±0.01	ref 42

[a] Units in kcal/mol. [b] The uncertainty comes from 1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$). [c] The standard deviation of Table 5 in ref 36.

pVTZ, and Truhlar's basis-set limit method using hydrogenation reactions.

$$CH_3OCl + H_2 \rightarrow CH_3OH + HCl$$

$$CH_3OCl + H_2 \rightarrow CH_4 + HOCl$$

Melius reports $\Delta H_f°_{298}$ of −14.0 kcal/mol based on BAC/MP4[19] calculation. The available literature data on CH_3OCl show a variation in standard enthalpies of formation, −12.3 to −17.7 kcal/mol at 298 K.

The 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 $\Delta H_f°_{298}$ values through the reaction schemes excluding data obtained from reaction scheme (3). With the exception of CBS-Q//B3** level results, enthalpies calculated from use of reaction scheme (3) are not consistent with data from the other six reaction schemes. Deviation for $\Delta H_f°_{298}$ across reaction scheme (3) 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 5.

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) is the only isodesmic reaction, but we cannot apply reaction scheme (6) to chloromethyl hypochlorites because $\Delta H_f°_{298}$ values for chloromethyl peroxides are unknown. The values from all calculation levels using reaction scheme (6) for CH_3OCl, where we can apply it, show good agreement.

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.

Test of Calculation Method: Enthalpy of HOCl. Methyl hypochlorite and hypochlorous acid both have the oxychloride bond and an electron donor group, methyl and H atom, respectively. We analyze $\Delta H_f°_{298}$ of HOCl by similar reaction sets to try and evaluate the accuracy of our calculation methods; data are illustrated in Table 6. The evaluated $\Delta H_f°_{298}$ of HOCl is −17.80 kcal/mol,[33] with a more recent value of −18.5 ± 0.5 recommended by Espinosa-Garcia.[18] Our calculated $\Delta H_f°_{298}$ for hypochlorous acid are −19.19, −17.56, −17.61, −17.61, −17.46, and −17.87 kcal/mol using CBS-Q//B3** and reaction schemes 1−6 as shown in Table 6. Data from the reaction schemes in Table 6 obtained at the other calculation levels do not show this good agreement with the experimental value of HOCl. The next most reasonable values for $\Delta H_f°_{298}$ of HOCl are not the QCISD(T) but the density function values with the large basis set (Table 6).

TABLE 5: Comparison of Enthalpies of Formation[a] at 298 K (in kcal/mol)

species theory[b]	rxn 1[c]	rxn 2	rxn 3	rxn 4	rxn 5	rxn 6	rxn 7	avg[d]	overall[e]
CH_3OCl									
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 ± 1.48
max error[f]	±0.4	±0.4	±0.61	±0.2	±0.6	±1.4	±1.2	±0.69	
CH_2ClOCl									
B3lyp6-31	−26.56	−26.60	***−13.95***	−26.95	−23.81			−25.98 ± 1.46	
B3lyp6-311	−23.89	−23.86	***−18.25***	−22.02	−21.41			−22.80 ± 1.27	
Qcisd(t)	−25.84	−24.61	***−16.76***	−26.51	−23.78			−25.19 ± 1.22	
CBS-Q//B3**	−22.20	−19.64	−22.52	***−25.29***	−23.86			−22.06 ± 1.76	−22.05 ± 2.47
max error	±0.5	±0.5	±1.12	***±0.3***	±0.7			±0.7	
$CHCl_2OCl$									
B3lyp6-31	−31.06	−32.55	***−10.25***	−29.76	−27.57			−30.24 ± 2.11	
B3lyp6-311	−27.84	−29.44	***−18.37***	−24.02	−25.07			−26.59 ± 2.49	
Qcisd(t)	−30.32	−29.53	***−16.21***	−30.83	−28.48			−29.79 ± 1.02	
CBS-Q//B3**	−25.56	−22.73	−27.75	***−31.90***	−29.02			−26.27 ± 2.76	−26.14 ± 3.61
max error	±0.5	±0.50	±1.63	***±0.4***	±0.80			±0.86	
CCl_3OCl									
B3lyp6-31	−31.48	−31.24	***−0.83***	−26.83	−26.34			−28.98 ± 2.76	
B3lyp6-311	−27.80	−28.43	***−13.20***	−20.74	−23.72			−25.17 ± 3.61	
Qcisd(t)	−31.20	−29.31	***−11.32***	−30.82	−28.63			−29.99 ± 1.22	
CBS-Q//B3**	−24.83	−23.18	−29.74	***−35.28***	−29.13			−26.72 ± 3.22	−26.72 ± 4.68
max error	±0.7	±2.2	±2.14	***±0.5***	±0.8			±1.46	

[a] Enthalpies of formation are calculated by different seven reactions in Table 3. [b] See Table 2 footnote for the explanation of theory levels. [c] CBS-Q//B3** results, see the reactions in Table 3, includes conformers. [d] Average values do not include bold italic data. [e] Average of CBS-Q//B3** values by all reaction schemes except reaction set 4 and adopted statistical conformer analysis. Uncertainty = the standard deviation of average (footnote d) + the average maximun error of all reaction schemes except reaction set 4. [f] The maximum error from uncertainty in values of the 3 standard molecules of reaction scheme; values from Table 5.

TABLE 6: Enthalpies of Formation of HOCl at 298 K (in kcal/mol)[a]

		$\Delta H_f^\circ{}_{298}$ (theory level[b])			
	reaction	B3LYP6-31	B3LYP6-311	QCISD(T)	CBS-Q//B3**
1	$HOCl + H_2 \rightarrow H_2O + HCl$	−24.27	−19.69	−22.68	−19.69
2	$HOCl + CH_4 \rightarrow CH_3Cl + H_2O$	−22.95	−19.90	−21.63	−17.56
3	$HOCl + CH_4 \rightarrow CH_3OH + HCl$	−19.59	−18.64	−19.49	−17.49
4	$HOCl + CH_3CH_3 \rightarrow CH_3CH_2OH + HCl$	−19.85	−19.38	−19.65	−17.61
5	$HOCl + CH_3CH_3 \rightarrow CH_3CH_2Cl + H_2O$	−23.85	−20.68	−22.10	−17.46
6	$HOCl + H_2O \rightarrow HOOH + HCl$	−11.29	−17.24	−13.67	−17.87

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

TABLE 7: Enthalpies of Formation at 298 K (in kcal/mol) for B3LYP/6-311+G(3df,2p) and CBS-Q//B3LYP6-31G(d,p)

	CH_3OCl[a]	CH_2ClOCl[a]	$CHCl_2OCl$[a]	CCl_3OCl[a]	HOCl[b]
B3LYP/6-311+G(3df,2p)	−15.43	−22.80	−26.59	−25.17	−17.24
CBS-Q//B3LYP/6-31G(d,p)	−15.41	−22.06	−26.27	−26.72	−17.87

[a] The average values from the selected reaction in Table 5. [b] Value from working reaction 6 in Table 6.

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 7; data suggest this level of density functional theory is reasonable for enthalpy determinations of oxy-halocarbons using selected working reactions. Radom et al.[49] also 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.

Enthalpies of Rotational Conformers. There are two staggered structures, in CH_2ClOCl and $CHCl_2OCl$, as shown in Figures 2 and 3, which show different enthalpies. We calculate the correction to enthalpy of formation using statistical analysis of the conformer values listed in Table 9. The $\Delta H_f^\circ{}_{298}$ of CH_3OCl, CH_2ClOCl, $CHCl_2OCl$, and CCl_3OCl are −15.41 ± 1.52, −22.05 ± 2.41, −26.14 ± 3.59, and −26.72 ± 4.65 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 9. The error analysis includes the standard deviation from CBS-Q//B3** calculations and the average maximum error from use of standard molecules.

There still exists a significant discrepancy in the $\Delta H_f^\circ{}_{298}$ for CH_3OCl. 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 chlorocarbon species, i.e., for estimation of thermodynamic properties of higher molecular weight hypochlorites. The very high level ab initio calculation values of Espinosa-Garcia[18] with one working reaction are 2.2 kcal/mol above our value; but our values for a number of calculation levels and reactions appear consistent, and are close to other reported data.

Comparison to Semiempirical (MOPAC) Data. A comparison of enthalpies of formation calculated using density functional and ab initio theory with the semiempirical MO

TABLE 8: Comparison of Enthalpies of Formation Calculated by Semiemprical Methods (in kcal/mol)

species theory	rxn 1[a]	rxn 2	rxn 3	rxn 4	rxn 5	rxn 6	rxn 7	output[b]	overall[c]
CH_3OCl									
PM3	−30.40	−33.04	−9.50	−45.35	−35.94	−20.57	−37.53	−34.16	−15.41 ± 1.48
AM1	−1.30	−11.72	−7.25	−12.40	−29.05	−18.83	−29.60	−18.71	
CH_2ClOCl									
PM3	−35.76	−37.40	6.78	−64.92	−40.57	−38.75		−38.75	−22.05 ± 2.47
AM1	−3.88	−13.17	−10.97	−21.27	−26.83	−24.95		−24.95	
$CHCl_2OCl$									
PM3	−35.17	−36.71	25.87	−81.68	−43.11	−40.52		−40.52	−26.14 ± 3.61
AM1	−0.44	−13.61	−6.79	−22.24	−21.50	−23.29		−23.29	
CCl_3OCl									
PM3	−34.72	−44.32	40.83	−102.57	−46.64	−46.42		−46.42	−26.72 ± 4.68
AM1	1.81	−8.73	−2.40	−23.01	−17.85	−21.42		−21.42	

[a] Enthalpy of formation at 298 K calculated by reaction scheme. [b] Enthalpy of formation at 298 K calculated by MOPAC program directly. [c] Average of CBS-Q//B3** values after statistical conformer analysis by all reaction schemes except reaction set 4 (see footnote e in Table 6)

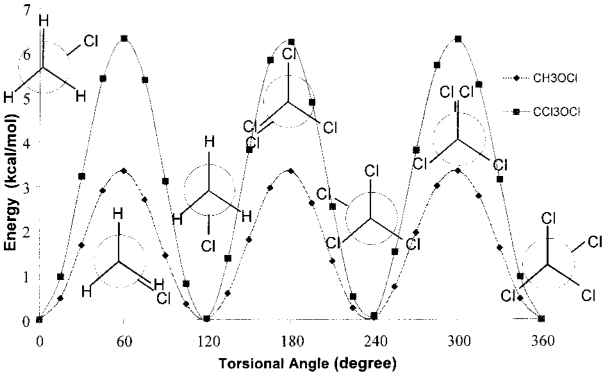


Figure 1. Potential energy for internal rotation about C−O bond of CH_3OCl and CCl_3OCl versus torsional angle.

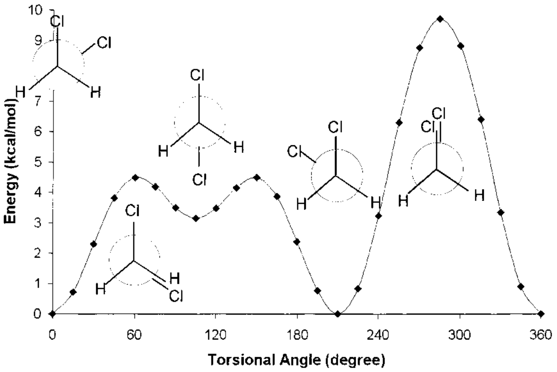


Figure 2. Potential energy for internal rotation about C−O bond of CH_2ClOCl versus torsional angle.

methods,[50] AM1[51,52] and PM3,[53] is also performed. The results listed in Table 8 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 recommend these methods for enthalpies or Gibbs Free Energies of other oxychlorocarbons.

Rotational Barriers. Potential barriers for internal rotations of CH_3OCl, CH_2ClOCl, $CHCl_2OCl$, and CCl_3OCl are calculated at the B3LYP/6-31G(d,p) level. Potential energy as function of torsional 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 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 torsional angle in 15° intervals. Potential energy vs torsion angle diagrams for internal rotations about C−O bond of the methyl and chlorinated methyl hypochlorites are shown in Figures 1, 2, and 3. The values of the coefficients of the Fourier expansion, a_i and b_i in eq E1 are listed in Supplement 3, available as Supporting Information.

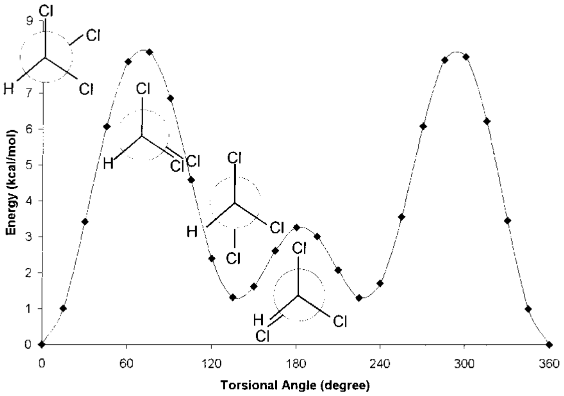


Figure 3. Potential energy for internal rotation about C−O bond of $CHCl_2OCl$ versus torsional angle.

TABLE 9: (a) $\Delta H_f°_{298}$ for Rotational Conformers, Relative Fraction, and Overall $\Delta H_f°_{298}$ Values, and (b) Adjustments for Entropy of Mixing−Rotational Conformers

(a) $\Delta H_f°_{298}$ and Relative Fractions

compound	energy (kcal/mol)[c]	relative (%)[d]	final value (kcal/mol)[e]
CH_3OCl	−15.41	100.00	−15.41 ± 1.48
CH_2ClOCl[a]	−22.06	99.76	
CH_2ClOCl[b]	−18.91	0.24	−22.05 ± 2.47
$CHCl_2OCl$[a]	−26.27	90.14	
$CHCl_2OCl$[b]	−24.96	9.86	−26.14 ± 3.61
CCl_3OCl	−26.72	100.00	−26.72 ± 4.68

(b) Adjustments for Entropy of Mixing−Rotational Conformers

	entropy correction
CH_2ClOCl[f]	$-R\{0.9976 \times \ln(0.9976) + 0.0024 \times \ln(0.0024)\} = 0.03$
$CHCl_2OCl$[g]	$-R\{0.9014 \times \ln(0.9014) + 0.0986 \times \ln(0.0986)\} = 0.64$

[a] H−Cl anti staggered. [b] Cl−Cl anti staggered. [c] Energy of conformer = overall value in Table 5 + energy barrier. Energy barrier = energy of conformer − energy of most stable conformer. [d] Relative (%) = conformer fraction ÷ total fraction. Conformer fraction = $e^{(-B/RT)}$; B = energy difference, R = 1.987 cal/(mol·K), T = 298 K. [e] Final value = Σ(energy × relative fraction). Uncertainty is the value in footnote e in Table 6. [f] Entropy for CH_2ClOCl at 298 K: entropy(CH_2ClOCl) = entropy(C/Cl/H_2/O) + entropy(O/C/Cl) + entropy correction(CH_2ClOCl). [g] Entropy for $CHCl_2OCl$ at 298 K: entropy($CHCl_2OCl$) = entropy(C/Cl_2/H/O) + entropy(O/C/Cl) + entropy correction($CHCl_2OCl$).

The calculated symmetric rotational barrier for methyl hypochlorite is shown in Figure 1. The calculation shows that

TABLE 10: Ideal Gas Phase Thermodynamic Properties[a] at 298 K

species		$\Delta H_f°_{298}$[b]	$S°_{298}$	C_{p300}[c]	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
CH_3OCl (3)[l]	TVR[d]		60.92	11.46	13.54	15.52	17.25	20.02	22.09	25.31
	internal[e]		4.27	2.13	2.19	2.11	1.98	1.71	1.52	1.26
	total	−15.41	65.19	13.59	15.73	17.63	19.23	21.73	23.61	26.57
	Colussi[f]	−12.26								
	Francisco[g]	−15.9								
	Elord[h]	−17.69								
	Espinosa[i]	−13.2								
	Crowley[j]	−14.58								
	Melius[k]	−14.00	65.40	13.44		17.72		21.89	23.82	26.85
CH_2ClOCl (1)	TVR		68.98	13.85	16.37	18.44	20.08	22.47	24.11	26.54
	internal		5.52	2.24	2.41	2.41	2.28	1.86	1.48	0.88
	total	−22.05	74.53	16.09	18.78	20.85	22.36	24.33	25.59	27.42
$CHCl_2OCl$ (1)	TVR		75.19	17.34	19.98	21.91	23.31	25.16	26.31	27.87
	internal		5.21	3.84	3.27	2.65	2.18	1.62	1.29	0.81
	total	−26.14	81.04	21.18	23.25	24.56	25.49	26.78	27.60	28.68
CCl_3OCl (3)	TVR		79.11	21.70	24.23	25.82	26.85	28.02	28.62	29.26
	internal		6.26	1.84	1.76	1.72	1.67	1.51	1.29	0.81
	total	−26.72	85.37	23.54	25.99	27.54	28.52	29.53	29.91	30.07

[a] Thermodynamic properties are referred to standard state of an ideal gas at 1 atm. Units: enthalpy in kcal/mol; entropy and heat capacity in cal/(mol•K). [b] $\Delta H_f°_{298}$ is the average value of CBS-Q level considering the statistical contribution of rotational conformers in kcal/mol excluding reaction Scheme 4 (see footnote e in Table 6 and final value in Table 8). [c] Units in cal/(mol•K). [d] The sum of contributions from translations, external rotations, and vibrations. [e] Contributions from internal rotation about C−O bond. [f] Reference 17. [g] −15.9 kcal/mol, which we convert to 298 K by this reaction using $\Delta H_f°_0$ of ref 15 and thermal energies of this study; $^3/_2H_2 + ^1/_2O_2 + ^1/_2Cl_2 + C(s) \rightarrow CH_3OCl$. [h] Reference 16. [i] Reference 54. [j] Reference 19. [k] Reference 18b. [l] Symmetry number is taken into account for $S°_{298}$. Entropy corrections for CH_2ClOCl and $CHCl_2OCl$ mixing of 0.03 and 0.64, respectively, are included above.

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 1 also shows the rotational barriers for 1,1,1-trichloromethyl hypochlorite. The Cl−Cl eclipsed structure shows a rotational barrier of 6.30 kcal/mol above the Cl−Cl anti staggered conformer.

Figure 2 shows calculated rotational barriers for 1-chloromethyl hypochlorite. The Cl−Cl anti staggered structure is 3.15 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 4.49 kcal/mol, and the Cl−Cl eclipsed rotational barrier is 9.72 kcal/mol. The Cl/Cl interaction is stronger than H/Cl interaction across the oxygen link on chloromethyl hypochlorite.

Calculated rotational barriers and conformer energies in 1,1 dichloromethyl hypochlorite are shown in Figure 3. The Cl−Cl anti staggered conformer has 1.31 kcal/mol higher energy than the more stable H-Cl anti staggered conformer. The H−Cl eclipsed structure represents a rotational barrier of 3.27 kcal/mol and the Cl−Cl eclipsed structure represents a rotational barrier of 8.08 kcal/mol.

Entropy, $S°_{298}$ and Heat Capacity, $C_p(T)$ from 300 to 1500 K. $S°_{298}$ and $C_p(T)$ calculations use the B3LYP/6-31g(d,p) determined geometry and frequencies with values summarized in Table 10. TVR represents the sum of the contributions from translations, external rotations and vibrations for $S°_{298}$ and $C_p(T)$. The torsion frequency corresponding to the internal rotor is not included in TVR. Instead, a more exact contribution from the hindered rotation is calculated and listed at "internal" in Table 10. Internal represents the contributions from internal rotation about C−O bond for $S°_{298}$ and $C_p(T)$'s.

There is no published data on entropy and heat capacity values for CH_3OCl, CH_2ClOCl, $CHCl_2OCl$, or CCl_3OCl. There is one data set, ab initio calculation, in the web site of Melius for methyl hypochlorite.[19] Our calculation results show a good agreement for the entropy and heat capacity with the BAC/MP4 values of Melius[19] for CH_3OCl; the BAC/MP4 method uses HF/6-31G* structures and frequencies. Table 1 shows a comparison of frequencies among B3LYP/6-31G(d,p), BAC/MP4[19] theory along with experimental data,[12,45] and calculated rotation constants.

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.[54]

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.[55] Previous studies report and explain the use of interaction terms for chlorohydrocarbons[54.56] and fluorohydrocarbons.[57,58]

The group value for thermodynamic properties of C/H3/O are from existing literature.[21,59] Values for C/Cl/H2/O, C/Cl2/H/O and C/Cl3/O are taken from recent work in this research group on chlorinated methanols[60] and ethers.[61] The properties of the C/Cl/H2/O, C/Cl2/H/O and C/Cl3/O groups for example, are derived from chloromethanols (CH_2ClOH, $CHCl_2OH$, CCl_3OH), respectively, and from chlorodimethyl ethers (CH_2ClOCH_3, $CHCl_2OCH_3$, CCl_3OCH_3), respectively. In the present work, we estimate group values for O/C/Cl and chlorine interaction terms across the oxygen link on methyl oxychlorides of OCl/Cl, OCl/Cl2, and OCl/Cl3. There are no chlorines, other halogens, or bulky groups/fragments on the carbon atom adjacent to the oxygen atom containing the chlorine in the defining O/C/Cl group for methyl hypochlorite (CH_3OCl). Enthalpy of formation ($\Delta H_f°_{298}$) and heat capacities, $C_p(T)$ of the O/C/Cl group are calculated on the basis of the eq E2.

$$(CH_3OCl) = (C/H3/O) + (O/C/Cl) \qquad (E2)$$

$S°_{298}$ of O/C/Cl is calculated on the basis of the eq E3.

$$(CH_3OCl) = (C/H3/O) + (O/C/Cl) - R\ln(\sigma) \qquad (E3)$$

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

TABLE 11: (a) Thermodynamic Properties of Chlorine Groups and (b) Thermodynamic Properties of OCl−Cl_x Interactions

(a) Thermodynamic Properties of Chlorine Groups

groups	$\Delta H_{f}^{\circ}{}_{298}{}^{a}$	$S^{\circ}{}_{298}{}^{b}$	$C_{p300}{}^{b}$	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}	ref
C/H_3/O	−10.00	30.41	6.19	7.84	9.40	10.79	13.03	14.77	17.58	59
C/Cl/H_2/O	−20.90	37.05	8.64	10.62	12.49	13.89	15.59	16.79	19.19	other work[c]
C/Cl_2/H/O	−28.23	42.33	12.74	15.50	17.43	18.44	19.05	19.34	20.60	other work[c]
C/Cl_3/O	−28.69	51.11	16.24	18.08	19.30	19.96	20.36	20.55	21.46	other work[c]
O/C/Cl	−5.41	36.96	7.40	7.89	8.23	8.44	8.70	8.84	8.99	this work

(b) Thermodynamic Properties of OCl−Cl_x Interactions

correction	$\Delta H_{f}^{\circ}{}_{298}{}^{a}$	$S^{\circ}{}_{298}{}^{b}$	$C_{p300}{}^{b}$	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}	ref
OCl/Cl	4.26	0.51	0.05	0.27	0.13	0.02	0.04	−0.05	−0.77	this work
OCl/Cl_2	7.50	1.70	1.03	−0.14	−1.10	-1.39	-0.97	-0.58	−0.91	this work
OCl/Cl_3	7.38	−0.52	−0.10	0.02	0.01	0.12	0.47	0.52	−0.38	this work

[a] Units in kcal/mol. [b] Units in cal/(mol·K). [c] The average of group value from chloromethanols (ref 60) and chloro ethers (ref 61). [a] Units in kcal/mol. [b] Units in cal/(mol·K). Groups include entropy of mixing corrections.

Thermodynamic properties of methyl hypochlorite with no chlorine on the carbon atom adjacent to the −OCl are now accurately predicted; but an adjustment needs to be made for chlorooxychlorides where there are chlorine atoms on the adjacent carbon, such as chloromethyl hypochlorite, dichloromethyl hypochlorite, or trichloromethyl 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 interaction values between chlorine(s) on the methyl and the chlorine attached to the oxygen (OCl/Cl, OCl/Cl2, and OCl/Cl3) are calculated from differences between the sum of defined chlorinated oxyhydrocarbon group values and the determined thermodynamic properties of the parent compounds. For example, $\Delta H_f{}^{\circ}{}_{298}$ and C_p's for the OCl/Cl2 interaction term are estimated by the eq E4 and $\Delta H_f{}^{\circ}{}_{298}$ for $CHCl_2OCl$.

$$(\mathrm{CHCl_2OCl}) = (\mathrm{C/Cl2/H/O}) + (\mathrm{O/C/Cl}) + (\mathrm{OCl/Cl2}) \quad \text{(E4)}$$

$$(\mathrm{CHCl_2OCl}) = (\mathrm{C/Cl2/H/O}) + (\mathrm{O/C/Cl}) - R\ln(\sigma) + (\mathrm{OCl/Cl2}) \quad \text{(E5)}$$

$S^{\circ}{}_{298}$ for the OCl/Cl2 interaction term is calculated from eq E5 using the S for the parent molecule. $R = 1.987$ cal/(mol·K), and σ is symmetry number, which is 1 for $CHCl_2OCl$. Entropy of mixing $= -R\sum\{(n_i)\ln(n_i)\}$, 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 $CHCl_2OCl$, the mixing term is $-R\{0.9014\ln(0.9014) + 0.0986\ln(0.0986)\} = 0.64$ cal/(mol·K) in Table 9b. The other interaction values are also estimated in the same manner.

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 chloromethanols and chlorodimethyl ethers. Thermodynamic properties of the O/C/Cl groups are derived from methyl hypochlorite (CH_3OCl) in this work by eqs E2 and E3. All group values and interaction terms are listed in Table 11.

Interaction term values 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 4.26, 7.50, and 7.38 kcal/mol for OCl/Cl, OCl/Cl2, and OCl/Cl3, respectively. Interaction terms for entropies at 298 K and heat capacities are relatively small. Entropy terms are 0.51, 1.70, and −0.52 cal/(mol·K) for OCl/Cl, OCl/Cl2, and OCl/Cl3, respectively, at 298 K. The interaction values for heat capacity at 300 K are 0.05, 1.03, and −0.10 cal/(mol·K) for OCl/Cl, OCl/Cl2, and OCl/Cl3, 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. Table 12 lists groups and interaction terms for use in estimating thermodynamic property of oxychlorocarbons by modified group additivity method.

TABLE 12: Groups and Interaction Terms for Four Oxychlorides

compounds	CH_3OCl	CH_2ClOCl	$CHCl_2OCl$	CCl_3OCl
	C/H_3/O	C/Cl/H_2/O	C/Cl_2/H/O	C/Cl_3/O
	O/C/Cl	O/C/Cl	O/C/Cl	O/C/Cl
interaction		OCl/Cl	OCl/Cl_2	OCl/Cl_3

Summary

Thermochemical properties of CH_3OCl and three chlorinated methyl hypochlorites 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 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), and QCISD(T)/6-31G(d,p) calculations. Entropies, $S^{\circ}{}_{298}$, and heat capacities, $C_p(T)$, from 300 to 1500 K are reported along with groups and oxychloride−chloride interaction group values for use in group additivity. Torsional potentials are presented for intramolecular rotations. Semiempirical methods do not seem satisfactory for estimation of oxychlorocarbon thermochemical properties.

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Supporting Information Available: Tables of total energies at different levels of theory, composite CBS-Q, zero-point vibrational energies, and thermal corrections; total energies of molecules by torsional angle; and coefficients of truncated Fourier series representation expansion for internal rotation potentials. This material is available free of charge via the Internet at http://pubs.acs.org.

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