5420 *J. Phys. Chem. A* **2001,** *105,* 5420−5430

Structure, Torsional Potentials, and Thermodynamic Properties $\Delta H°_{f298}$, $S°_{298}$, and $C_p(T)$ of Chloro-Dimethyl Ethers: CH_2ClOCH_3, $CHCl_2OCH_3$, and CCl_3OCH_3. Density Functional and ab Initio Calculations

Dawoon Jung and Joseph W. Bozzelli*

Department of Chemistry, Chemical Engineering and Environmental Science,
New Jersey Institute of Technology, Newark, New Jersey 07102

Received: August 15, 2000; In Final Form: December 20, 2000

Thermochemical properties of oxygenated chlorocarbons are important in studies on oxidation and kinetics of chlorocarbons and in Cl initiated kinetic studies on oxidation of hydrocarbons. Enthalpy, $\Delta H°_{f298}$, entropy, S_{298}, and heat capacities, $C_p(T)$, from 300 to 1500 K are determined for three chloro-dimethyl ethers 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/6-311+G(3df,2p), QCISD(T)/6-31G(d,p), and CBS-Q//B3LYP/6-31G(d,p) levels of calculation (abbreviated as CBSQ//B3**). Enthalpies of formation are determined at each calculation level using the $\Delta H_{rxn(298)}$ and known enthalpies of other reactants in each of seven different working reactions. Contributions to entropy and heat capacity from internal rotation of the chloro-dimethyl ethers are also determined. Evaluation of data from three isodesmic schemes, and the energies of rotational conformers, result in $\Delta H°_{f298}$ values for CH_2ClOCH_3 of -55.42 ± 0.91, for $CHCl_2OCH_3$ of -62.28 ± 2.10, and for CCl_3OCH_3 of -63.11 ± 2.26 kcal/mol at the CBS-Q//B3** level. We determine enthalpy, entropy, and $C_p(T)$ terms for the three mono-oxygenated carbon chlorine groups, where enthalpy values for use in group additivity are C/Cl/H2/O (−20.90), C/Cl2/H/O (−28.23), and C/Cl3/O (−28.69 kcal/mol), respectively.

Introduction

Chlorocarbons are chemicals widely used as solvents in synthesis and in cleaning agents, as synthesis starting materials, and in polymer, pesticide, and other manufactured products. Chlorocarbons and other halocarbon compounds are present in the atmosphere from evaporation of these solvents and other anthropogenic activities. They often exhibit relatively long troposphere lifetimes because of their slow decay in the atmosphere or low reaction rates with the OH radical.[1] Initial reactions of saturated and unsaturated alkyl chlorides in both atmospheric and in combustion chemistry result in alkyl radical intermediates. Saturated chlorocarbons undergo loss of a H atom via abstraction with OH,[2,3] whereas unsaturated chlorocarbons undergo addition. These radicals rapidly react with O_2[4] 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 chlorocarbons in the combustion and atmospheric environments. The data also allow determination of oxychloro-carbon groups for group additivity of the mono-, di-, and trichloro-methyl oxygen species. There is little or no literature data available on the thermodynamic properties of chlorinated oxygenated hydrocarbons with the exception of acid chlorides and methyl hypochlorites. The thermodynamic values for dimethyl ether are well-known,[5] but there is no literature data, to our knowledge, for any chlorinated ether. This research estimates fundamental thermodynamic property data on these species using ab initio and density functional calculations. These thermodynamic properties on chloro-dimethyl ethers allow estimation of C/Cl/H2/O, C/Cl2/H/O, and C/Cl3/O groups for use in group additivity on larger oxychloro carbons. The thermochemical properties are valuable for use in combustion modeling and in detailed kinetic studies of chlorine-initiated oxidation of hydrocarbons, halocarbons, and oxygenated organics.[6−12]

Computational Methods

All ab initio calculations are performed using the Gaussian 94 program suite.[13] The structural parameters are fully optimized at the 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.[14−16]

B3LYP/6-31G(d,p) is chosen because it is widely used and is reported to yield accurate geometry and reasonable energies.[17,18] Curtiss et al.[19] recently reported that G3 (MP2) enthalpies on alkyl hydrocarbons from working reactions and B3LYP/6-31G(d) geometries show a low overall deviation from experimental values. Durant and co-workers[17,20] have compared density functional calculations BHandH and B3LYP with MP2 and Hartree−Fock methods for geometry and vibration frequencies. They report that these density functional methods provide excellent geometry and vibration frequencies, relative to MP2 at reduced computation expense. Petersson et al.[21] compared energy of density functional methods of B3LYP/6-311+G(3df,2p)//B3LYP/6-31G with G2 study and their CBS calculation methods and report that they have been successful for a wide range of molecules. Radom and co-workers[22,23] indicated that the B3LYP/6-31G(d,p) geometry corresponds closely to

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* To whom correspondence should be addressed. E-mail: bozzelli@tesla.njit.edu.

10.1021/jp0029562 CCC: $20.00

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 the working reaction for $\Delta H°_{f298}$ 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 applicable 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.[18] QCISD(T)/6-31G(d,p) is a configuration interaction method but with a small, economical basis set.[22,24] The 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).[16,25] The CBS-Q method[26] 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, whereas 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 $\Delta H°_{f298}$ values for small (C_1 to C_3) molecules.[26]

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 vibration frequencies scaled (by 0.9806).[27] This is similar to the Radom research group's CBS/RAD[23] method; it has B3LYP/6-31G(d,p) geometry, which they indicate yields geometry similar to QCISD(T), and in place of CCSD(T), we use a QCISD(T). These calculations are referred to as CBSQ//B3** in the present study.

Thermodynamic Properties Using ab Initio Calculations

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[27] by 0.9806 for ZPVEs. 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.[28−39] Barriers for intramolecular rotation about the two carbon−oxygen bonds of chloro-dimethyl ethers are analyzed versus torsional angle using B3LYP/6-31G(d,p).

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.[40−44] 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 diagonalization of the Hamiltonian matrix. In this work, the torsional potential calculated at a discrete torsional angle is represented by eq E1:

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

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

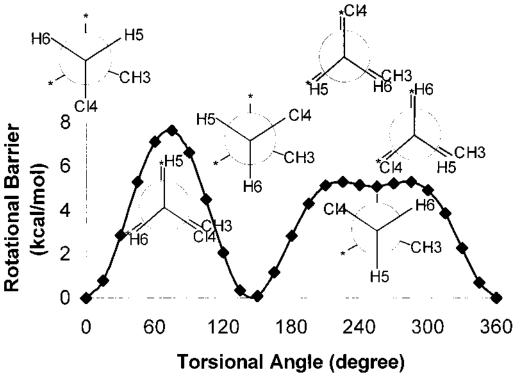


Figure 1. Potential energy for internal rotation about the $CH_2Cl-OCH_3$ bond by torsional angle (* equals a lone pair of O atom).

Results and Discussion

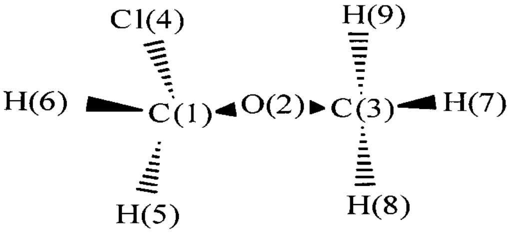
Geometry and Vibration Frequencies. The fully optimized geometries at the B3LYP/6-31G(d, p) density functional calculation level for mono-, 1,1-di-, and 1,1,1-trichloro-dimethyl ethers are presented in Table 1, where effects of increased chlorine α substitution on molecular geometry can be observed. The C−H and C−Cl bond lengths in the equilibrium conformations of three title molecules are similar, whereas the O−C bond lengths of the chloro-methyl groups decrease and the C−O bond length of methyl groups increases slightly with increase of Cl substitution. The Cl−C bond lengths in the chloro-dimethyl ethers also decrease with an increase in number of chlorines. The optimized geometry has lone electron pairs of the oxygen and hydrogen (or chlorine) on the methyl groups in a staggered configuration; the eclipsed geometries have up to 8 kcal/mol higher energy. The geometry is further described in the section on internal rotation barriers.

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 rotational constants (GHz) for monochloro-dimethyl ether in this study are compared with the previous experimental data and calculations in Table 2 part a. The frequencies calculated by the B3LYP/6-31G(d,p) density functional method show a good agreement with the spectra of McKean et al.,[45] Guirgis et al.,[46] and Planje et al.[47] and are more accurate than ab initio HF values.[46] Table 2 part b lists the vibration frequencies and the rotational constants for the 1,1-di- and 1,1,1-trichloro-dimethyl ethers.

Rotational Barriers. Potential barriers for the two internal rotations of CH_2ClOCH_3, $CHCl_2OCH_3$, and CCl_3OCH_3 are calculated at the B3LYP/6-31G(d,p) level. The values of the coefficients of the Fourier expansion, a_i and b_i in eq 1, are listed in Table 3.

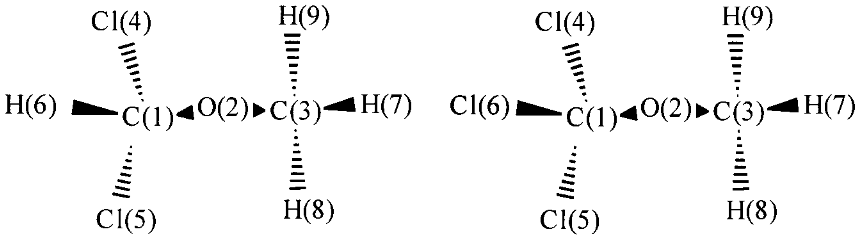
Figure 1 shows calculated rotational structure energies of Cl−C−O−CH_3 versus torsion angle. The asterisks signify a lone electron pair on oxygen. Chloro-dimethyl ether ($CH_2Cl-OCH_3$) has two conformers. The CH_3−Cl anti staggered is 5.09, (3.63) kcal/mol higher in energy by this study and in (Guirgis') study,[46] respectively, than the more stable CH_3−H anti staggered conformer because of the Cl interaction with the oxygen atom's nonbonding electrons. The CH_3−Cl eclipsed rotational barrier is 7.65, (6.91) kcal/mol and the CH_3−H eclipsed rotational barrier is 5.30, (4.24) kcal/mol in this B3LYP/6-31G(d,p) method and (Guirgis') HF/6-31G(d,p)[46] calculations, respec-

TABLE 1: Optimized Geometry of Chlorinated Ethers[a]



(a) Monochloro-Dimethyl Ether

				ref 46	ref 45	ref 47
	CH_2ClOCH_3	B3LYP/6-31G(d,p)	MP2/6-31G*	experimental data		
name	definition	value[a]	value[e]	value[e]	value[f]	value[g]
R(O−C)[b]	R(2,1)	1.3656	1.378	1.371	1.362	1.368
R(C−O)	R(3,2)	1.4262	1.427	1.430	1.421	1.414
R(Cl−C)	R(4,1)	1.8626	1.810	1.818	1.822	1.813
R(H−C)	R(5,1)	1.0952	1.095	1.097	1.097	1.120
R(H−C)	R(6,1)	1.0987	1.088	1.088	1.097	1.120
R(H−C)	R(7,3)	1.0905	1.089	1.077	1.090	1.120
R(H−C)	R(8,3)	1.0952	1.093	1.096	1.126	1.120
R(H−C)	R(9,3)	1.0987	1.097	1.100	1.105	1.120
A(C−O−C)[c]	A(1,2,3)	114.97	113.4	114.0	114.1	113.2
A(O−C−Cl)	A(2,1,4)	113.41	113.4	113.0	112.9	112.3
A(O−C−H)	A(2,1,5)	113.59	112.5	113.6	113.6	
A(Cl−C−H)	A(4,1,5)	103.94				
A(O−C−H)	A(2,1,6)	108.48	107.3	109.5	109.5	106.1
A(Cl−C−H)	A(4,1,6)	105.08				
A(H−C−H)	A(5,1,6)	112.02	111.4	112.3	112.3	
A(O−C−H)	A(2,3,7)	106.48	106.1	107.2	107.2	
A(O−C−H)	A(2,3,8)	110.92	111.0	109.6	109.6	112.3
A(H−C−H)	A(7,3,8)	109.67				
A(O−C−H)	A(2,3,9)	110.99	110.7	109.6	109.6	
A(H−C−H)	A(7,3,9)	109.48	109.8	111.6	111.6	
A(H−C−H)	A(8,3,9)	109.25	109.7	109.5	109.5	
D(C−O−C−Cl)[d]	D(3,2,1,4)	−72.47	73.3	70.2	70.6	74.3
D(C−O−C−H)	D(3,2,1,5)	45.93				
D(C−O−C−H)	D(3,2,1,6)	171.19				
D(H−C−C−C)	D(7,3,2,1)	185.73				
D(H−C−O−C)	D(8,3,2,1)	66.46				
D(H−C−O−C)	D(9,3,2,1)	−55.19				



(b) 1,1-Di- and 1,1,1-Trichloro-Dimethyl Ethers

$CHCl_2OCH_3$			CCl_3OCH_3		
name	definition	value	name	definition	value
R(O−C)[b]	R(2,1)	1.3453	R(O−C)	R(2,1)	1.3405
R(C−O)	R(3,2)	1.4362	R(C−O)	R(3,2)	1.4414
R(Cl−C)	R(4,1)	1.8347	R(Cl−C)	R(4,1)	1.8339
R(Cl−C)	R(5,1)	1.8347	R(Cl−C)	R(5,1)	1.8338
R(H−C)	R(6,1)	1.0863	R(Cl−C)	R(6,1)	1.7908
RH−C)	R(7,3)	1.0893	R(H−C)	R(7,3)	1.0888
R(H−C)	R(8,3)	1.0931	R(H−C)	R(8,3)	1.0924
RH−C)	R(9,3)	1.0931	R(H−C)	R(9,3)	1.0924
A(C−O−C)[c]	A(1,2,3)	118.56	A(C−O−C)	A(1,2,3)	118.83
A(O−C−Cl)	A(2,1,4)	113.47	A(O−C−Cl)	A(2,1,4)	112.53
A(O−C−Cl)	A(2,1,5)	113.47	A(O−C−Cl)	A(2,1,5)	112.53
A(Cl−C−Cl)	A(4,1,5)	108.50	A(Cl−C−Cl)	A(4,1,5)	107.19
A(O−C−H)	A(2,1,6)	108.61	A(O−C−Cl)	A(2,1,6)	106.72
A(Cl−C−H)	A(4,1,6)	106.15	A(Cl−C−Cl)	A(4,1,6)	108.89
A(Cl−C−H)	A(5,1,6)	106.15	A(Cl−C−Cl)	A(5,1,6)	108.90
A(O−C−H)	A(2,3,7)	105.34	A(O−C−H)	A(2,3,7)	104.78
A(O−C−H)	A(2,3,8)	110.49	A(O−C−H)	A(2,3,8)	110.34
A(H−C−H)	A(7,3,8)	110.14	A(H−C−H)	A(7,3,8)	110.4
A(O−C−H)	A(2,3,9)	110.49	A(O−C−H)	A(2,3,9)	110.34
A(H−C−H	A(7,3,9)	110.14	A(H−C−H)	A(7,3,9)	110.40
A(H−C−H)	A(8,3,9)	110.15	A(H−C−H)	A(8,3,9)	110.45
D(C−O−C−Cl)[d]	D(3,2,1,4)	−62.21	D(C−O−C−Cl)	D(3,2,1,4)	−60.63
D(C−O−C−Cl)	D(3,2,1,5)	62.23	D(C−O−C−Cl)	D(3,2,1,5)	60.61
D(C−O−C−H)	D(3,2,1,6)	180.01	D(C−O−C−Cl)	D(3,2,1,6)	179.99
D(H−C−O−C)	D(7,3,2,1)	−179.96	D(H−C−O−C)	D(7,3,2,1)	179.97
D(H−C−O−C)	D(8,3,2,1)	61.12	D(H−C−O−C)	D(8,3,2,1)	61.13
D(H−C−O−C)	D(9,3,2,1)	−61.04	D(H−C−O−C)	D(9,3,2,1)	−61.19

[a] The geometry is optimized at B3LYP/6-31G(d,p) density functional calculation level. [b] Bond length or the distance between two atoms of number in Å. [c] Bond angle or the angle among three atoms of number in degrees. [d] The dihedral angle among the four number atoms. [e] Geometry is estimated in ref 44. [f] Geometry is estimated in ref 45. [g] Geometry is estimated in ref 46.

TABLE 2: Vibrational Frequencies (cm^{-1}) and Rotational Constants (GHz) for Chlorinated Ethers[a]

(a) Monochloro-Dimethyl Ether

	B3LYP/6-31G(d,p)		experimental data		HF/3-21G*	MP2/6-31G*
	this work	this work	ref 45	ref 46	ref 46	ref 46
frequencies	freq[b]	*I*[c]	freq	*I*	freq	*I*
CH_3 torsion/A	145.44	11.39849	133	14.211	148	14.358
CH_2Cl torsion/B	187.44	2.27446	180	3.488	200	3.457
ClCO bend/C	350.14	1.99297	352	3.037	342	3.024
COC bend	450.49		457		466	
CCl stretch	636.57		679		676	
COC sym. str.	951.90		933		970	
CH_2 rock	1010.37		999		1090	
COC antisym. str.	1162.94		1125		1228	
CH_3 rock	1184.46		1160		1272	
CH_3 rock	1228.94		1197		1305	
CH_2 twist	1307.75		1278		1413	
CH_2 wag	1354.44		1323		1496	
CH_3 antisym. def.	1480.56		1449		1623	
CH_2 deformation	1498.64		1458		1664	
CH_3 antisym. def.	1514.21		1467		1671	
CH_3 sym. str.	1520.76		1471		1689	
CH_3 antisym. str.	3019.38		2839		3197	
CH_2 antisym. str.	3059.57		2937		3272	
CH_2 sym. str.	3097.21		2956		3271	
CH_3 antisym. str.	3159.16		3020		3332	
CH_2 antisym. str.	3180.26		3034		3377	

(b) 1,1-Di- and 1,1,1-Trichloro-Dimethyl Ethers

	CH_3OCHCl_2		CH_3OCCl_3	
	freq[b]	*I*[c]	freq	*I*
v1/A	106.90	3.38433	99.90	1.80228
v2/B	179.64	1.60156	188.21	1.14561
v3/C	245.44	1.11949	206.94	1.09308
v4	286.60		244.18	
v5	376.67		278.00	
v6	506.19		330.28	
v7	669.08		382.23	
v8	730.70		425.67	
v9	942.92		502.60	
v10	1174.23		713.75	
v11	1190.93		837.99	
v12	1230.71		976.58	
v13	1234.06		1171.49	
v14	1366.68		1182.51	
v15	1485.75		1211.39	
v16	1500.15		1483.26	
v17	1515.16		1498.36	
v18	3061.84		1512.40	
v19	3142.64		3068.13	
v20	3177.92		3153.12	
v21	3189.44		3187.26	

[a] Nonscaled. Frequencies and the moment of inertia are optimized at the B3LYP/6-31G(D,P) level of theory. [b] Frequencies unit in cm^{-1}. [c] The rotational constants unit in GHz.

TABLE 3: Coefficients[a] **(kcal/mol) of Truncated Fourier Series Representation Expansion for Internal Rotation Potentials**

rotors	a0	a1	a2	a3	b1	b2	b3
$CH_2Cl-OCH_3$	3.692	−0.089	−2.254	−1.288	−0.265	1.578	−0.981
$CH_2ClO-CH_3$	0.896	0.010	−0.006	−0.908	−0.006	−0.019	0.024
$CHCl_2-OCH_3$	3.971	−0.298	−1.996	−1.821	0.034	−0.021	−0.061
$CHCl_2O-CH_3$	0.620	0.005	−0.007	−0.642	−0.007	−0.015	0.039
CCl_3-OCH_3	2.218	−0.011	−0.026	−2.178	−0.021	0.043	−0.070
CCl_3O-CH_3	0.641	0.006	−0.008	−0.670	−0.007	−0.017	0.040

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

tively. The CH_3-Cl eclipsed barrier is 2.35 and 2.67 kcal/mol higher in energy than the CH_3-H eclipsed barrier by this study and Guirgis' study,[46] respectively. The interaction of chlorine and a methyl group exhibits more repulsion or strain compared to that of a methyl interaction with hydrogen.

The calculated symmetric rotational barriers for methyl (CH_3) rotations in the chlorinated dimethyl ethers are shown in Figures 2, 4, and 6. The calculations show that the hydrogen and chloromethyl ($H-CH_{3-x}Cl_x$) staggered structure has a rotational barrier of 1.82 kcal/mol in $CH_2ClO-CH_3$, 1.28 kcal/mol in $CHCl_2O-CH_3$, and 1.34 kcal/mol in CCl_3O-CH_3.

Calculations to discern the full three-dimensional surface include the following: freezing the torsional angle (dihedral angle Cl−C−O−C) at intervals of 15 degrees and rotating the

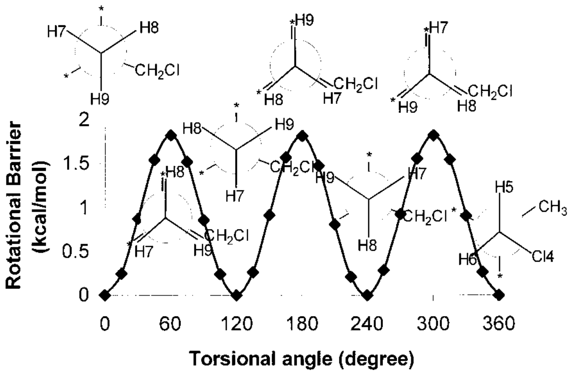


Figure 2. Potential energy for internal rotation about the $CH_2ClO-CH_3$ bond by torsional angle (* equals a lone pair of O atom).

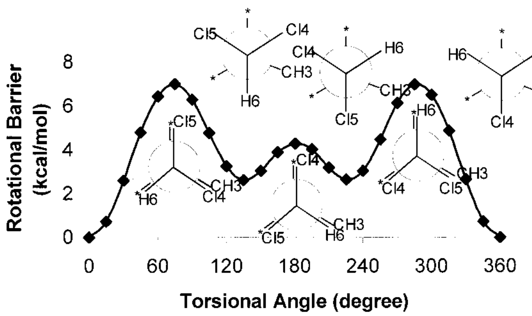


Figure 3. Potential energy for internal rotation about the $CHCl_2-OCH_3$ bond by torsional angle (* equals a lone pair of O atom).

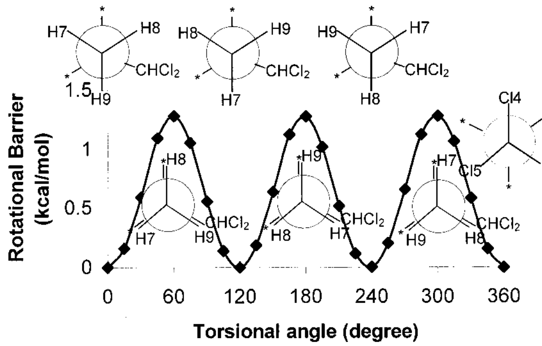


Figure 4. Potential energy for internal rotation about the $CHCl_2O-CH_3$ bond by torsional angle (* equals a lone pair of O atom).

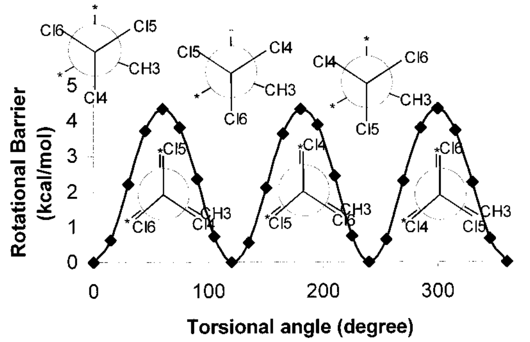


Figure 5. Potential energy for internal rotation about the CCl_3-OCH_3 bond by torsional angle (* equals a lone pair of O atom).

CH_3 methyl (H−C−O−C) through 15° intervals between 0 and 180°. Structures were completely optimized with the exception of the two locked torsion angles. The three-dimensional contour plot of torsional angle (Cl−C−O−C) vs torsional angle (H−C−O−C) vs relative energy is illustrated in Figure 7. It confirms that the optimized geometry in Table 2 is the most stable structure, but it is difficult to interpret quantitatively. Detailed three-dimensional plot data are included in the Supporting Information.

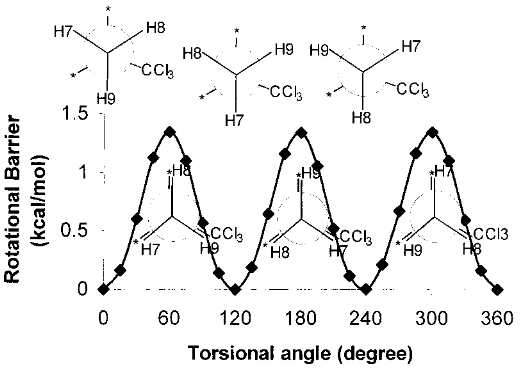


Figure 6. Potential energy for internal rotation about the CCl_3O-CH_3 bond by torsional angle (* equals a lone pair of O atom).

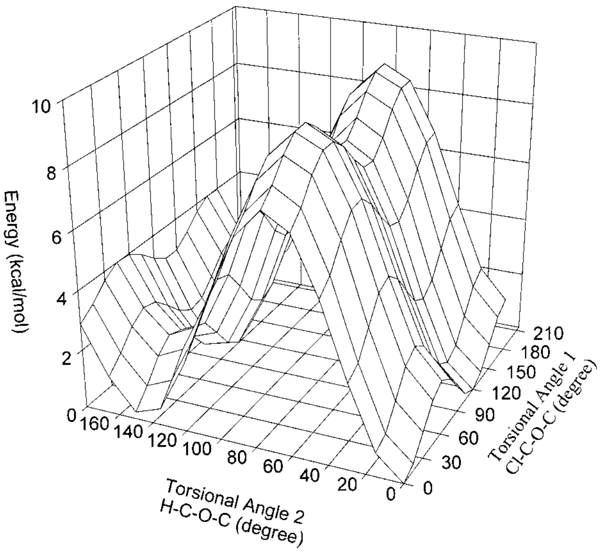


Figure 7. Potential energy (kcal/mol) for internal rotation about the CH_2ClOCH_3 bond by torsional angle 1 (Cl−C−O−C) and torsional angle 2 (H−C−O−C) in degrees.

Calculated rotational barriers and conformer energies in 1,1-dichloro-dimethyl ether ($CHCl_2-OCH_3$) are shown in Figure 3. The CH_3-H staggered conformer has a 2.63 kcal/mol lower energy than the CH_3-Cl staggered conformer because of the interaction between an electron lone pair of oxygen and chlorine. The CH_3-Cl eclipsed structure represents a higher rotational barrier, 7.00 kcal/mol, than the CH_3-H eclipsed structure, 4.30 kcal/mol.

The symmetric rotational barrier of 1,1,1-trichloro-dimethyl ether (CCl_3-OCH_3) is illustrated in Figure 3. The CH_3-Cl eclipsed structure shows a rotational barrier of 4.33 kcal/mol above the CH_3-Cl staggered conformer.

Test of the Calculation Method: Enthalpy of CH_3OCH_3. In an earlier work,[48] we studied $\Delta H°_{f298}$ for methyl hypochlorite and observed that isodesmic and some nonisodesmic reactions result in accurate $\Delta H°_{f298}$ of target molecules when using the CBS-Q//B3** method and reasonable $\Delta H°_{f298}$ values of target molecules by B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), and QCISD(T)/6-31G(d,p) levels of theory. A test of calculation method for $\Delta H°_{f298}$ of dimethyl ether is performed with our selected working reactions, before $\Delta H°_{f298}$ analysis on the chloro-dimethyl ethers is completed. Two working reaction

TABLE 4: Total Energies at Different Levels of Theory, Composite CBS-Q, Zero-Point Vibrational Energy, and Thermal Correction (in Hartree)

	total energies					
	B3lyp6−31[a]	B3lyp6−311[b]	Qcisd(t)[c]	CBS-Q[d]	ZPE[e]	therm. corr[f]
CH_3OCH_3	−155.0329666	−155.0885135	−154.6002123	−154.7428736	0.0783558	0.0052490
CH_3OCH_2Cl	−614.6343156	−614.7229552	−613.6374661	−613.9098084	0.0703718	0.0059450
CH_3OCHCl_2	−1074.2255172	−1074.3483312	−1072.6674820	−1073.0705568	0.0610178	0.0069350
CH_3OCCl_3	−1533.8043626	−1533.9626027	−1531.6876816	−1532.2232547	0.0506088	0.0080850
CH_4	−40.5240144	−40.5367468	−40.3895577	−40.4053008	0.0441427	0.0038100
CH_3Cl	−500.1125454	−500.1588917	−499.4146950	−499.5567137	0.0371844	0.0039640
CH_3OH	−115.7239624	−115.7729014	−115.4123794	−115.5342419	0.0503989	0.0042490
CH_2ClOH	−575.3265536	−575.4076554	−574.4501957	−574.6987353	0.0426973	0.0046320
$CHCl_2OH$	−1034.9193503	−1035.0341002	−1033.4813828	−1033.8597902	0.0334081	0.0054200
CCl_3OH	−1494.497447	−1494.647355	−1492.500597	−1493.0111533	0.0228529	0.0065690
CH_2Cl_2	−959.6989037	−959.7802630	−958.4390436	−958.7102821	0.0288944	0.0045180
$CHCl_3$	−1419.2803335	−1419.3974234	−1417.4600091	−1417.8637645	0.0194826	0.0054130
CCl_4	−1878.8542563	−1879.0076351	−1876.4749422	−1877.0143867	0.0091235	0.0065880
C_2H_6	−79.8387377	−79.8614929	−79.5855303	−79.6247780	0.0734705	0.0044200
CH_3CH_2Cl	−539.4330408	−539.4896189	−538.6171237	−613.9098084	0.0655247	0.0049740
CH_3CHCl_2	−999.0218923	−999.1134044	−997.6453262	−997.9432661	0.0564894	0.0057830
CH_3CCl_3	−1458.6031122	−1458.7300519	−1456.6676728	−1457.0996327	0.0465540	0.0068200
C_2H_5OH	−155.9628217	−155.0210006	−154.532637	−154.7628412	0.0786686	0.0051800
H_2	−1.1785393	−1.1800138	−1.1651440	−1.1625321	0.0099737	0.0033050
H_2O	−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

[a] B3LYP/6-31G(d,p). Total energies are in Hartree at 0 K. [b] B3LYP/6-311+G(3df,2p). Total energies are in Hartree at 0 K. [c] QCISD(T)/6-31G(d,p). Total energies are in Hartree at 0 K. [d] CBS-Q enthalpies are in Hartree, which include thermal correction and zero-point energy at 298.15 K. [e] ZPE is in Hartree and scaled by 0.9806. [f] Thermal corrections are in Hartree.

TABLE 5: Enthalpies of Formation[a] (in kcal/mol) at 298.15 K for CH_3OCH_3

	$\Delta H^\circ_{f\,298}$ (theory level[b])			
reaction	B3LYP[c] /6-31G(d,p)	B3LYP/6−311[d] +G(3df,2p)	QCISD(t)[e] /6-31G(d,p)	CBS-Q[f] //B3**
1. $CH_3OCH_3 + H_2O \rightarrow 2\ CH_3OH$	−41.96	−42.70	−43.41	−42.97
2. $CH_3OCH_3 + H_2 \rightarrow CH_3OH + CH_4$	−46.64	−43.75	−46.60	−44.55
average	−44.30	−43.23	−45.01	−43.76

[a] Reaction enthalpies include thermal correction and zero-point energy correction at 298 K. [b] See foot notes of Table 4 for the explanation of theory levels. [c] B3LYP/6-31G(d,p). [d] B3LYP/6-311+G(3df,2p). [e] QCISD(T)/6-31G(d,p). [f] CBS-Q//B3** method.

schemes are used to evaluate ΔH°_{f298} of dimethyl ether (CH_3OCH_3):

$$CH_3OCH_3 + H_2O \rightarrow 2CH_3OH$$

$$CH_3OCH_3 + H_2 \rightarrow CH_3OH + CH_4$$

The recommended ΔH°_{f298} for dimethyl ether is −43.99 kcal/mol,[30] and the calculated average ΔH°_{f298} over the two working equations for CH_3OCH_3 are −44.30, −43.23, −45.01, and −43.76 kcal/mol in B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p), and CBS-Q/B3** calculation methods, respectively. Total energies of the species in these reactions are listed in Table 4, and enthalpy data for dimethyl ether for the reaction and the calculation methods are in Table 5. The density functional, ab initio, and composite methods all calculate accurate values for CH_3OCH_3. Similar reactions are used to estimate ΔH°_{f298} of the chloro-dimethyl ethers (CH_2ClOCH_3, $CHCl_2OCH_3$, and CCl_3OCH_3).

Chloro-dimethyl Ether Enthalpies of Formation (ΔH°_{f298}). Enthalpies of formation (ΔH°_{f298}) are estimated using total energies in Table 4 and calculated $\Delta H_{rxn(298)}$ for the seven reaction series in Table 6. The calculated $\Delta H_{rxn(298)}$ and known ΔH°_{f298} of reference species are utilized to estimate ΔH°_{f298} of the target chlorinated dimethyl ethers in each of the reaction schemes. ΔH°_{f298} for the reference species comes from literature thermodynamic properties, reported in Table 7. Enthalpies of reaction ($\Delta H_{rxn\ (298)}$) are estimated using total energies obtained by the density functional and ab initio calculations. ZPVEs and thermal correction to 298 K are taken into account. The total energies at 0 K, scaled ZPVEs, 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 4.

ΔH°_{f298} (CH_2ClOCH_3) calculated from the reaction scheme 1 is

$$\Delta H_{rxn(298)} = \Delta H^\circ_{f298}(CH_3OCH_3) + \Delta H^\circ_{f298}(CH_3Cl) - \Delta H^\circ_{f298}(CH_2ClOCH_3) - \Delta H^\circ_{f298}(CH_4) \quad (1)$$

and the listed known enthalpies of CH_3OCH_3, CH_3Cl, and CH_4.

Reaction Schemes:

$$CH_{3-x}Cl_xOCH_3 + CH_4 \rightarrow CH_3OCH_3 + CH_{4-x}Cl_x \quad (1')$$

$$CH_{3-x}Cl_xOCH_3 + CH_3CH_3 \rightarrow CH_3OCH_3 + CH_3CH_{3-x}Cl_x \quad (2)$$

$$CH_{3-x}Cl_xOCH_3 + xH_2O \rightarrow xHOCl + CH_3CH_2OH \quad (3)$$

$$CH_{3-x}Cl_xOCH3 + xH_2O \rightarrow CH_3OCH_3 + xHOCl \quad (4)$$

$$CH_{3-x}Cl_xOCH_3 + xH_2 \rightarrow CH_3OCH_3 + xHCl \quad (5)$$

$$CH_{3-x}Cl_xOCH_3 + H_2 \rightarrow CH_3CH_{4-x}Cl_{x-1} + HOCl \quad (6)$$

$$CH_{3-x}Cl_xOCH_3 + CH_3OH \rightarrow CH_3OCH_3 + CH_{3-x}Cl_xOH \quad (7)$$

ΔH°_{f298} values are reported in Table 8.

TABLE 6: Reaction Enthalpies (in kcal/mol) at 298.15 K[a]

	$\Delta H_{\mathrm{rxn(298)}}$ (theory level)[b]			
reaction[b]	B3LYP/ 6-31G(d,p)	B3LYP/ 6−311+G(3df,2p)	QCISD(t)/ 6-31G(d,p)	CBS-Q// B3**
1. $CH_2ClOCH_3 + CH_4 \rightarrow CH_3OCH_3 + CH_3Cl$	8.35	8.02	7.91	9.74
$CHCl_2OCH_3 + CH_4 \rightarrow CH_3OCH_3 + CH_2Cl_2$	11.78	10.93	11.86	14.25
$CCl_3OCH_3 + CH_4 \rightarrow CH_3OCH_3 + CHCl_3$	10.62	9.58	11.84	13.75
2. $CH_2ClOCH_3 + CH_3CH_3 \rightarrow CH_3OCH_3 + CH_3CH_2Cl$	4.36	3.90	3.49	4.75
$CHCl_2OCH_3 + CH_3CH_3 \rightarrow CH_3OCH_3 + CH_3CHCl_2$	5.92	4.98	4.71	5.77
$CCl_3OCH_3 + CH_3CH_3 \rightarrow CH_3OCH_3 + CH_3CCl_3$	4.65	3.72	3.59	3.47
3. $CH_2ClOCH_3 + H_2O \rightarrow HOCl + CH_3CH_2OH$	36.46	37.52	35.73	39.16
$CHCl_2OCH_3 + 2H_2O \rightarrow 2HOCl + CH_3CH_2OH$	75.67	80.13	77.66	86.97
$CCl_3OCH_3 + 3H_2O \rightarrow 3HOCl + CH_3CH_2OH$	107.68	116.33	113.98	129.73
4. $CH_2ClOCH_3 + H_2O \rightarrow CH_3OCH_3 + HOCl$	44.90	47.62	45.79	51.69
$CHCl_2OCH_3 + 2H_2O \rightarrow CH_3OCH_3 + 2HOCl$	84.11	90.23	87.71	99.50
$CCl_3OCH_3 + 3H_2O \rightarrow CH_3OCH_3 + 3HOCl$	116.13	126.43	124.04	142.26
5. $CH_2ClOCH_3 + H_2 \rightarrow CH_3OCH_3 + HCl$	−10.69	−12.56	−11.40	−8.98
$CHCl_2OCH_3 + 2H_2 \rightarrow CH_3OCH_3 + 2HCl$	−27.07	−30.13	−26.66	−21.85
$CCl_3OCH_3 + 3H_2 \rightarrow CH_3OCH_3 + 3HCl$	−50.65	−54.10	−47.52	−39.77
6. $CH_2ClOCH_3 + H_2 \rightarrow CH_3CH_3 + HOCl$	19.00	15.95	16.88	18.86
$CHCl_2OCH_3 + H_2 \rightarrow CH_3CH_2Cl + HOCl$	17.66	14.83	16.50	19.73
$CCl_3OCH_3 + H_2 \rightarrow CH_3CHCl_2 + HOCl$	12.09	9.51	12.12	15.69
7. $CH_2ClOCH_3 + CH_3OH \rightarrow CH_3OCH_3 + CH_2ClOH$	−0.80	−0.22	−0.37	1.53
$CHCl_2OCH_3 + CH_3OH \rightarrow CH_3OCH_3 + CHCl_2OH$	−1.89	−0.97	−1.19	1.34
$CCl_3OCH_3 + CH_3OH \rightarrow CH_3OCH_3 + CCl_3OH$	−1.51	−0.43	−0.67	2.17

[a] Reaction enthalpies include thermal correction and zero-point energy correction at 298 K. [b] See Table 4 foot note for the explanation of theory levels. Reactions 1, 2, and 7 are isodesmic.

TABLE 7: Enthalpy Data Used in Reactions to Determine ΔH°_{f298} of Target Ethers

compound	ΔH°_{f298}[a]	source	uncertainty	source
CH_4	−17.89	ref 28	±0.1	ref 28 (32)
CH_3Cl	−19.60	ref 29	±0.2	ref 29 (33)
CH_2Cl_2	−22.83	ref 28	±0.3	ref 28 (34)
$CHCl_3$	−24.20	ref 30	±0.3	ref 30 (35)
C_2H_6	−20.24	ref 28	±0.1	ref 28 (32)
CH_3CH_2Cl	−26.84	ref 29	±0.2	ref 29 (33)
CH_3CHCl_2	−31.09	ref 29	±0.3	ref 29 (34)
CH_3CCl_3	−34.01	ref 29	±0.3	ref 29 (36)
CH_3OH	−48.08	ref 30	±0.1	ref 29 (37)
CH_2ClOH	−58.07	ref 31	±0.7	ref 31
$CHCl_2OH$	−65.88	ref 31	±0.8	ref 31
CCl_3OH	−65.96	ref 31	±0.8	ref 31
CH_3OCH_3	−43.99	ref 30	±0.1	ref 22 (38)
CH_3CH_2OH	−56.12	ref 30	±0.4	ref 22 (35)
HCl	−22.06	ref 28	±0.1	ref 28
HOCl	−17.80	ref 28	±0.5	ref 28
HOOH	−32.53	ref 28		
H_2O	−57.80	ref 30	±0.01	ref 39

[a] Units in kcal/mol.

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.

Analysis of Data Trends by Isodesmic vs Nonisodesmic Reaction. Reaction schemes 1, 2, and 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 may have errors because of the uncertainty in ΔH°_{f298} of the di- and trichloro-methanols. The isodesmic reactions 1, 2, and 7 show uniform results for 1-chloro-methyl ether and 1,1-dichloro-methyl ether, whereas the nonisodesmic reactions show significantly higher error and less uniformity (see Table 7). The average error values over the three isodesmic reactions are ±0.57, 0.63, and 0.63 kcal/mol for CH_2ClOCH_3, $CHCl_2OCH_3$, and CCl_3OCH_3, respectively, in Table 8.

Only reaction scheme 2 shows good consistency for 1,1,1-trichloro-dimethyl ether with a standard deviation of ±0.54 over the four calculation methods; the average value of isodesmic reactions 1, 2, and 7 over the four calculation levels is 1.4 kcal/mol above the CBS-Q results. Isodesmic reactions 1 and 7 also show good consistency only in the noncomposite calculations methods. Nonisodesmic reactions 3 and 4, which use H_2O and HOCl, are unacceptable for the noncomposite calculation methods on 1,1-di- and 1,1,1-trichloro-dimethyl ethers.

Recommended Values for ΔH°_{f298}. The ΔH°_{f298} of CH_2ClOCH_3, $CHCl_2OCH_3$, and CCl_3OCH_3 are −55.42, −62.28, and −63.11 kcal/mol, respectively, before statistical analysis of conformers. These enthalpies are the average value of ΔH°_{f298} by the three isodesmic reactions at the CBS-Q/B3** calculation level.

Two conformers of CH_2ClOCH_3 and $CHCl_2OCH_3$ are illustrated in Figures 1 and 3 and show differences in enthalpies of 5.1 and 2.6 kcal/mol, respectively. In our analysis of energy by torsional angle, the most stable conformer in Figures 1−6 and Table 9 is the optimized geometry shown in Table 1. The D(C−O−C−Cl) dihedral angle, D(3,2,1,4), is −72.47, −62.21, −60.63 E in CH_2ClOCH_3, $CHCl_2OCH_3$, and CCl_3OCH_3, respectively, for the low energy conformers. The ΔH°_{f298} considering statistical distribution of rotation conformers of CH_2ClOCH_3, $CHCl_2OCH_3$, and CCl_3OCH_3 are -55.42 ± 0.91, -62.28 ± 2.10, and -63.11 ± 2.26 kcal/mol, respectively. The uncertainty in Table 10 is the standard deviation of the reaction sets (1, 2, and 7) plus the average of maximum error from standard compounds in the reaction schemes.

Comparison of Calculated ΔH°_{f298} with Semiempirical (MOPAC) Data. The AM1[49,50] and PM3[51] methods in the MOPAC 6.0 package[52] are used to perform the semiempirical

TABLE 8: Comparison of Enthalpies of Formation[a] (in kcal/mol)

species theory[b]	rxn 1[c]	rxn 2[c]	rxn 3[c]	rxn 4[c]	rxn 5[c]	rxn 6[c]	rxn 7[c]	avg.[d]	recomm.[e]
CH_2ClOCH_3									
B3lyp6-31[f]	−54.05	−54.91	−52.58	**−48.89**	−55.36	−57.00	−53.18	−54.51	
B3lyp6-311[g]	−53.72	−54.45	−53.64	**−51.61**	−53.50	−53.95	−53.76	−53.84	
Qcisd(t)[h]	−53.61	−54.04	−51.85	**−49.78**	−54.66	−54.88	−53.61	−53.78	
CBS-Q[i]	−55.44	−55.3	−55.28	−55.68	−57.07	−56.86	−55.51	−55.88	−55.42 ± 0.91
overall[j]	−54.21	−54.68	−53.34		−55.15	−55.67	−54.02		
max err stds.[k]	0.4	0.4	0.9	0.6	0.2	0.6	0.9		0.57 + 0.34
$CHCl_2OCH_3$									
B3lyp6-31[f]	−60.71	−60.76	**−51.79**	**−48.10**	−61.04	−62.26	−59.90	−59.41	
B3lyp6-311[g]	−59.86	−59.82	**−56.25**	**−54.22**	−57.98	−59.43	−60.82	−59.03	
Qcisd(t)[h]	−60.79	−59.55	**−53.78**	**−51.7**	−61.45	−61.10	−60.60	−59.55	
CBS-Q[i]	−63.18	−60.61	−63.09	−63.49	−66.26	−64.33	−63.13	−63.44	−62.28 ± 2.10
overall[j]	−61.14	−60.19			−61.68	−61.78	−61.11		
max err stds.[k]	0.5	0.5	1.4	1.12	0.3	0.7	0.9		0.63 + 1.47
CCl_3OCH_3									
B3lyp6-31[f]	−60.92	−62.41	**−43.8**	**−40.12**	−59.52	−60.98	−60.36	−58.00	
B3lyp6-311[g]	−59.88	−61.48	**−52.45**	**−50.42**	−56.07	−58.4	−61.44	−58.29	
Qcisd(t)h	−62.14	−61.35	**−50.10**	**−48.03**	−62.65	−61.01	−61.2	−59.74	
CBS-Q[i]	−64.05	−61.23	−65.85	−66.25	−70.4	−64.58	−64.05	−65.20	−63.11 ± 2.26
overall[j]	−61.75	−61.62			−62.16	−61.24	−61.76		
max err stds.[k]	0.5	0.5	1.9	0.4	0.1	0.8	0.9		0.63 + 1.63

[a] Enthalpies of formation are calculated by seven different reactions in Table 6. [b] See Table 4 footnote for the explanation of theory levels. [c] See the reactions in Table 6. Reactions 1, 2, and 7 are isodesmic. [d] Average values do not include bold italic data. [e] Average of values in CBS-Q level by isodesmic reactions 1, 2, and 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 reactions 1, 2, and 7 sets. [f] B3LYP/6-31G(d,p). [g] B3LYP/6-311+G(3df,2p). [h] QCISD(T)/6-31G(d,p). [i] CBS-Q//B3** method. [j] Average of overall theory's enthalpies of formation. [k] The maximum error from uncertainty in values of the three standard molecules of the reaction scheme, values from Table 5.

TABLE 9: Total Energy[a] (Hartrees) of Molecules by Torsional Angle

angle	$CH_2Cl-OCH_3$[b]	$CH_2ClO-CH_3$[c]	$CHCl_2-OCH_3$[b]	$CHCl_2O-CH_3$[c]	CCl_3-OCH_3[b]	CCl_3O-CH_3[c]
0	−614.6343159	−614.6343156	−1074.2255172	−1074.2255172	−1074.2255172	−1533.8043626
15	−614.6330616	−614.6339271	−1074.2243767	−1074.2252622	−1074.2252622	−1533.8033554
30	−614.6297728	−614.6329192	−1074.2213612	−1074.2245698	−1074.2245698	−1533.8008319
45	−614.6258583	−614.6318585	−1074.2178362	−1074.2237757	−1074.2237757	−1533.7984387
60	−614.6229417	−614.6314129	−1074.2152227	−1074.2234769	−1074.2234769	−1533.7974553
75	−614.6221322	−614.6318943	−1074.2143534	−1074.2238355	−1074.2238355	−1533.7982959
90	−614.6237312	−614.6329492	−1074.2154511	−1074.2246271	−1074.2246271	−1533.8006089
105	−614.6271423	−614.6339314	−1074.2179066	−1074.2252979	−1074.2252979	−1533.8031884
120	−614.6310369	−614.6343150	−1074.2203145	−1074.2255152	−1074.2255152	−1533.8043553
135	−614.6337560	−614.6338927	−1074.2213283	−1074.2252190	−1074.2252190	−1533.8034764
150	−614.6341790	−614.6328621	−1074.2206580	−1074.2245052	−1074.2245052	−1533.8009977
165	−614.6324536	−614.6318096	−1074.2193224	−1074.2237215	−1074.2237215	−1533.7985752
180	−614.6297869	−614.6314170	−1074.2186662	−1074.2234830	−1074.2234830	−1533.7974678
195	−614.6274419	−614.6319596	−1074.2190991	−1074.2238896	−1074.2238896	−1533.7981773
210	−614.6261374	−614.6330298	−1074.2204164	−1074.2246888	−1074.2246888	−1533.8004658
225	−614.6258609	−614.6339801	−1074.2213106	−1074.2253279	−1074.2253279	−1533.8031606
240	−614.6260893	−614.6343125	−1074.2206472	−1074.2255104	−1074.2255104	−1533.8043611
255	−614.6262031	−614.6338541	−1074.2183656	−1074.2251873	−1074.2251873	−1533.8033374
270	−614.6259969	−614.6328387	−1074.2157211	−1074.2244685	−1074.2244685	−1533.8006931
285	−614.6258665	−614.6318299	−1074.2143728	−1074.2237252	−1074.2237252	−1533.7983133
300	−614.6264497	−614.6314123	−1074.2151341	−1074.2234767	−1074.2234767	−1533.7974549
315	−614.6281335	−614.6318498	−1074.2177545	−1074.2238170	−1074.2238170	−1533.7984214
330	−614.6307055	−614.6328714	−1074.2212987	−1074.2245871	−1074.2245871	−1533.8007732
345	−614.6332104	−614.6338840	−1074.2243440	−1074.2252647	−1074.2252647	−1533.8033142
360	−614.6343158	−614.6343155	−1074.2255172	−1074.2255173	−1074.2255173	−1533.8043630

[a] The unit of total energies is Hartree in B3LYP/6-31G(d,p) theory. [b] The torsional angle of D(4123) in Table 1. [c] The torsional angle of D(8321) in Table 1.

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 in Table 11. Direct results from the MOPAC calculations, as well as results from reaction analysis with MOPAC data, are presented. The results, listed in Table 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 between these two semiempirical methods. Use of MOPAC results obtained from isodesmic or other working reactions is not satisfactory.

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 12. TVR represents the sum of the contributions from translations, external rotations, and vibrations for S^o_{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 "internal" in Table 12. "Internal" represents the contributions from internal rotation about C−O bonds for S^o_{298} and $C_p(T)$'s. There are two rotors in the chloro-dimethyl ethers and we calculate and list

TABLE 10: ΔH°_{f298} for Rotational Conformers, Relative, Overall ΔH°_{f298} Values, and Entropy Correction[h]

compound	energy (kcal/mol)[e]	relative (%)[f]	final value (kcal/mol)[g]
$CH_2ClOCH_3(1)$[a]	−55.42	99.99	
$CH_2ClOCH_3(2)$[b]	−50.35	0.01	−55.42 ± 0.91
$CHCl_2OCH_3(1)$[c]	−62.31	98.84	
$CHCl_2OCH_3(2)$[d]	−59.68	1.16	−62.28 ± 2.10
CCl_3OCH_3	−63.11	100.00	−63.11 ± 2.26

[a] CH_3−H anti staggered conformer in Figure 1. [b] CH_3−Cl anti staggered conformer in Figure 1. [c] CH_2Cl−H anti staggered conformer in Figure 3. [d] CH_2Cl−Cl anti staggered conformer in Figure 3. [e] Energy of conformer = overall value in Table 6 + energy barrier; energy barrier = energy of conformer- energy of most stable conformer. [f] Relative = conformer fraction/total fraction; conformer fraction = $e^{(-B/RT)}$, B = energy difference, R = 1.987 (cal/mol K), and T = 298 K. [g] Final value = σ(energy × relative fraction); uncertainty is the value in foot note e in Table 6. [h] Entropy correction for $CHCl_2OCH_3 = -R\{0.9884 \ln(0.9884) + 0.0116 \ln(0.0116)\} = 0.13$ cal/mol K.

their contribution individually in Table 12. Entropy correction for conformers resulting from the symmetric (3-fold) CH_3 rotation is accounted for by a $-R \ln(3)$ symmetry correction.[53]

Group Values and Group Additivity Estimation. The group values for thermodynamic properties of C/H3/O and O/C2 are from existing literature.[53,54] In the present work, we improve the group value for C/Cl/H2/O, C/Cl2/H/O, and C/Cl3/O. Enthalpy of formation (ΔH°_{f298}) and heat capacities, $C_p(T)$, of the O/C/H group are calculated on the basis of the eq 2 for each of the thermodynamic properties:

$$CH_2ClOCH_3 = C/H3/O + O/C/2 + C/Cl/H2/O \quad (E2)$$

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[31] and this study. The properties of the C/Cl/H2/O, C/Cl2/H/O, and C/Cl3/O groups, for example, are derived from chloro-methanol (CH_2ClOH), 1,1-dichloro-methanol ($CHCl_2OH$), and 1,1,1-trichloro-methanol (CCl_3OH), respectively, and from chloro-dimethyl ether (CH_2ClOCH_3), 1,1-dichloro-dimethyl ether ($CHCl_2OCH_3$), and 1,1,1-trichloro-dimethyl ether (CCl_3OCH_3), respectively. Group values for of C/Cl/H2/O, C/Cl2/H/O, and C/Cl3/O are −20.90, −28.23, and −28.69 kcal/mol for enthalpy of formation at 298 K. The group additivity determined ΔH°_{f298} values for $CH_2ClOCCH_3$ of −54.70, for $CHCl_2OCH_3$ of −62.03, and for CCl_3OCH_3 of −62.49 kcal/mol. These enthalpy values are slightly higher (ca. 1 kcal/mol) than our recommended CBS-Q//B3** values in Table 12. The reason is that these oxygenated chloro-carbon groups are an average of values from the above alcohols and ethers. The recommended ΔH°_{f298} values determined in this study for $CH_2ClOCCH_3$, $CHCl_2OCCH_3$, and CCl_3OCCH_3 are −55.42 ± 0.91, −62.28 ± 2.10, and −63.11 ± 2.26 kcal/mol.

TABLE 11: 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]	CBS-Q//B**[c]
				CH_2ClOCH_3					
PM3	−49.77	-52.36	-30.58	-28.86	−64.72	-53.02	-53.29	-54.05	−55.42±0.91
AM1	-43.49	-53.86	-50.51	-49.43	−54.58	-65.13	-53.71	-61.12	
				$CHCl_2OCH_3$					
PM3	-55.92	-57.57	-15.10	-13.38	−85.08	-61.07	-62.55	-59.43	−62.28±2.10
AM1	-42.84	-52.13	-51.01	-49.93	−60.23	-70.11	-64.18	-64.15	
				CCl_3OCH_3					
PM3	-57.21	-58.76	2.11	3.83	-103.72	-52.32	-59.37	-63.08	−63.11±2.26
AM1	-36.84	-50.02	-44.28	-43.19	−58.65	-57.13	-60.48	-59.03	

[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 values in CBS-Q calculations by isodesmic reaction schemes (1, 2, and 7) with statistical analysis of conformers.

TABLE 12: Ideal Gas Phase Thermodynamic Properties[a]

species		ΔH°_{f298}[b]	S_{298}[c]	C_{p300}[c]	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
CH_2ClOCH_3	TVR[d]		64.89	13.90	17.54	21.02	24.07	28.91	32.48	38.01
(3)[l]	internal (1)[e]		4.93	2.15	2.33	2.48	2.52	2.36	2.02	1.26
	internal (2)[f]		4.65	1.93	1.73	1.55	1.42	1.26	1.18	1.08
	total	−55.42	74.47	17.99	21.60	25.05	28.02	32.53	35.68	40.35
	group add.[k]	−54.70	73.96	18.23	22.16	25.59	28.48	33.02	36.16	
$CHCl_2OCH_3$	TVR		71.23	17.50	21.25	24.58	27.36	31.61	34.66	39.29
(3)	internal(1)[g]		3.64	3.03	3.85	4.09	3.89	3.04	2.27	1.17
	internal(2)[h]		4.65	1.93	1.73	1.55	1.42	1.26	1.18	1.08
	total	−62.28	79.65	22.47	26.83	30.23	32.67	35.92	38.10	41.54
	group add.	−62.03	79.24	22.33	27.04	30.53	33.03	36.48	38.71	
CCl_3OCH_3	TVR		73.78	21.78	25.48	28.50	30.93	34.51	37.01	40.71
(18)	internal(1)[i]		5.93	2.22	2.27	2.20	2.05	1.66	1.30	0.73
	internal(2)[j]		5.31	1.73	1.50	1.35	1.26	1.15	1.10	1.04
	total	−63.11	84.45	25.72	29.25	32.06	34.24	37.32	39.41	42.48
	group add.	−62.49	84.45	25.83	29.62	32.40	34.55	37.79	39.92	

[a] Thermodynamic properties are referred to standard state of an ideal gas of pure enantiomer at 1 atm. Two torsional frequencies are excluded in the calculation of entropies and heat capacities; instead, the contributions from hindered rotations about the C−O bond are calculated. [b] ΔH°_{f298} is the average value of CBS-Q level considering the statistical contribution of rotational conformers in kcal/mol (see footnote e in Table 7 and final value in Table 10). [c] Units in cal/(mol K); mixing of 0.13 cal/(mol K) for entropy correction of $CHCl_2OCH_3$ is included (see foot note h in Table 10). [d] The sum of contributions from translations, external rotations, and vibrations. [e] Contributions from internal rotation about C−O bond of $CH_2Cl-OCH_3$. [f] Contributions from internal rotation about C−O bond of $CH_2ClO-CH_3$. [g] Contributions from internal rotation about C−O bond of $CHCl_2-OCH_3$. [h] Contributions from internal rotation about C−O bond of $CHCl_2O-CH_3$. [i] Contributions from internal rotation about C−O bond of CCl_3-OCH_3. [j] Contributions from internal rotation about C−O bond of CCl_3O-CH_3. [k] Group additivity. C/H3/O and O/C2 come from refs 53 and 54; C/Cl/H2/O, C/Cl2/H/O, and C/Cl3/O come from the average of chloro-methanols (ref 31) and chloro-dimethyl ethers (this work). [l] Symmetry number is taken into account for S_{298}.

TABLE 13: Thermodynamic Properties of Oxy-Chlorocarbon Groups

(a) C/Clx/H3-x/O from Chloro-Methanol and from This Work

groups	$H°_{f298}$[a]	$S°_{298}$[b]	C_{p300}[b]	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}	ref
C/Cl/H2/O	-20.17	36.55	8.88	11.18	13.02	14.35	16.09	17.27	19.19	31[c]
C/Cl/H2/O	-21.62	37.56	8.40	10.06	11.95	13.43	15.10	16.31		this work
C/Cl2/H/O	-27.98	41.93	12.61	15.71	17.73	18.80	19.62	19.94	20.60	31
C/Cl2/H/O	-29.48	42.74	12.88	15.29	17.13	18.08	18.49	18.73		this work
C/Cl3/O	-28.06	50.54	16.34	18.45	19.65	20.28	20.82	21.06	21.46	31
C/Cl3/O	-29.31	51.67	16.13	17.71	18.96	19.65	19.89	20.04		this work
C/H3/O[d]	-10.00	30.41	6.19	7.84	9.40	10.79	13.03	14.77	17.58	53 and 54
O/C2[d]	−23.80	8.68	3.40	3.70	3.70	3.80	4.40	4.60		53 and 54

(b) Averaged Thermodynamic Properties[c]

groups	$H°_{f298}$[a]	S_{298}[b]	C_{p300}[b]	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}	ref
C/Cl/H2/O	-20.90	37.05	8.64	10.62	12.49	13.89	15.59	16.79	19.19	this work
C/Cl2/H/O	-28.23	42.33	12.74	15.50	17.43	18.44	19.05	19.34	20.60	this work
C/Cl3/O	-28.69	51.11	16.24	18.08	19.30	19.96	20.36	20.55	21.46	this work

[a] Units in kcal/mol. [b] Units in cal/(mol K). [c] The group value from chloro-methanols (ref 31). [d] Oxy-hydrocarbon groups of Cohen and Benson used in GA. [e] The average of the values in part a of Table 13.

TABLE 14: Group for Use in Group Additivity of Chloro Ethers[a]

compounds	CH_2ClOCH_3	$CHCl_2OCH_3$	CCl_3OCH_3
group 1	C/H3/OC/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

[a] $C_p(T)$ or $\Delta H°_{f\ 298}$ of compunds $=$ $\Delta H°_{f\ 298}$ of group 1 $+$ $\Delta H°_{f\ 298}$ of group 2 $+$ $\Delta H°_{f\ 298}$ of group 3. $S°_{298}$ of compunds $=$ $S°_{298}$ of group 1 $+$ $S°_{298}$ of group 2 $+$ $S°_{298}$ of group 3 $-$ R ln(symmetry); $R = 1.987$ cal/(mol K), symmetry = see the foot note *l* in the Table 12. Entropy of mixing $= -R\ \sigma\{(n_i)H \ln(n_i)\}$, where n_i is fraction of conformer i. For $CHCl_2OCl$, the mixing term is $-R\ \{0.9883H \ln(0.9883) + 0.0116H \ln(0.0116)\} = 0.13$ cal/(mol K) in Table 10.

The entropy, S_{298}, of the C/Cl/H2/O is calculated on the basis of eq 3:

$$CHCl_2OCH_3 = C/H3/O + O/C/2 + C/Cl2/H/O - R \ln(\sigma) \quad (E3)$$

$R = 1.987$ cal/(mol K), and σ is symmetry number, which is 3 for CH_2ClOCH_3. The entropy of mixing equals $-R\ \Sigma\{(n_i)H \ln(n_i)\}$, where n_i is fraction of conformer i. The mixing entropy is included in the (C/Cl2/H/O) group, as it is in the hydrocarbon and other molecular groups. For $CHCl_2OCl$, the mixing term for entropy is $-R\{0.9884H \ln(0.9884) + 0.0116H \ln(0.0116)\} = 0.13$ cal/(mol K) in Table 10. Thermodynamic properties of the C/Cl/H2/O, C/Cl2/H/O, and C/Cl3/O groups are calculated using two sets of thermodynamic property data; the two data sets from chloro-methanols and chloro-dimethyl ethers are listed in Table 13. The average of group values are also listed in Table 13. Recommended group values for C/Cl/H2/O, C/Cl2/H/O, and C/Cl3/O are 37.05, 42.33, and 51.11 cal/(mol K) for entropy at 298 K and 8.64, 12.74, and 16.24 cal/(mol K) for heat capacity at 300 K. Table 14 lists oxychloro-carbon groups for use with our modified group additivity method.

There are no published data for entropy and heat capacity values of CH_2ClOCH_3, $CHCl_2OCH_3$, or CCl_3OCH_3. We compare our calculated data with the group additivity, where the groups are an average of chloro-methanol and this study. The group additivity shows good agreement for the entropy and heat capacity for all chloro-dimethyl ethers. The entropy at 298 K of CH_2ClOCH_3, $CHCl_2OCH_3$, and CCl_3OCH_3 is 74.47, 79.65, and 85.02 cal/(mol K) in this work and 73.96, 79.24, and 84.45 cal/mol by the group additivity, respectively. The heat capacity of CH_2ClOCH_3, $CHCl_2OCH_3$, and CCl_3OCH_3 is 17.99, 22.47, and 25.72 cal/(mol K) at 300 K and 25.05, 30.23, and 32.06 cal/mol at 500 K from B3LYP/6-31G(d,p) calculation. The comparison values from group additivity are 18.23, 22.33, and 25.83 cal/(mol K) at 300 K and 25.59, 30.53, and 32.40 cal/(mol K) at 500 K, respectively.

Summary

Structure, torsion potentials, and thermodynamic properties of three chlorinated dimethyl ethers are calculated using density function and ab initio calculations. Enthalpies, $\Delta H°_{f298}$, are presented as average data using isodesmic reaction schemes (1, 2, and 7) based on CBS-Q//B3** theory and considering statistical distribution of rotational conformers. CBS-Q//B3** calculation values of $\Delta H°_{f298}$ show consistency for all reaction schemes except the reaction $CCl_3OCH_3 + 3H_2 \rightarrow 3HCl + CH_3OCH_3$. Enthalpy of formation at 298 K, entropies, S_{298}, and heat capacities, $C_p(T)$, from 300 to 1500 K are reported along with values of thermodynamic properties on C/Cl/H2/O, C/Cl2/H/O, and C/Cl3/O groups needed for use in group additivity.

Acknowledgment. We acknowledge the USEPA Northeast Regional Research Center for the funding and Lev N. Krasnoperov, Nikolai V. Shokhirev, and Tsan H. Lay for the rotator program. We thank Chad Sheng (NJIT) for use of his SMCPS (Statistical Mechanics for Heat Capacity and Entropy) computer code to calculate $S°_{298}$ and $C_p(T)$ terms plus ZPVE and thermal energy from Gaussian data files.

Supporting Information Available: Table showing the potential energy for internal rotation about the CH_2ClOCH_3 bond by two different tortional angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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