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LETTERS

Theoretical Investigation on Stability of the C•H_2OCl Radical

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The reaction of ClO with CH_3OO forms CH_3OCl, which is thought to be an important species in ozone destruction over the Artic and Antarctic polar regions. Principal processes for CH_3OCl loss include abstraction of an H atom by OH or Cl, where the C•H_2OCl radical is formed. This radical can dissociate to Cl + CH_2O products via β scission (elimination) of a Cl atom with formation of a strong carbonyl π bond; or if stable, C•H_2OCl will react with O_2 to form a peroxy radical. Structures and the thermochemical properties (enthalpy, ΔH°_{f298}, entropy S(298), and heat capacity) of the C•H_2OCl radical, a transition state for its dissociation to CH_2O + Cl (TSCH_2O−Cl) and a formaldehyde−Cl atom adduct (ACH_2O∼Cl), are estimated by ab initio and density functional calculations. Geometries are optimized and frequencies are estimated using MP2/6-31G(d,p), B3LYP/6-31G(d,p), or MP2/6-31G(d) level calculations. Single point calculations for estimation of energy are performed with B3LYP/6-311+G(3df,2p) and QCISDT/6-31G(d,p) and with composite methods of CBS-Q and G3/MP2. Density functional calculations do not predict the existence of a stable C•H_2OCl radical; only a lower energy, loosely bound adduct and final products CH_2O + Cl. HF and MP2 calculations optimize to a C•H_2OCl radical structure with an O−Cl bond (MP2) of 1.72 Å. ΔH°_{f298} values on this MP2 structure are calculated using four different working (isodesmic) reactions. Standard enthalpy based on CBS-Q//MP2/6-31G(d,p) energies with isodesmic reaction analysis on this MP2 structure results in ΔH°_{f298} of 32.39 ± 2.21 kcal/mol; this is in excellent agreement with the high level calculations of Espinosa-Garcia (32.0 ± 3.5). MP2 calculations also predict an early transition state for C•H_2OCl dissociation with an O−Cl bond of 1.78 Å. Analysis of the MP2/6-31G transition state structure, using either CBS-Q or G3/MP2, yields an enthalpy some 4.4 kcal/mol lower than the stable radical; i.e., no barrier to C•H_2OCl dissociation is found. Products CH_2O + Cl and a loosely bound adduct of ACH_2O∼Cl have much lower energies at −1.86 ± 2.21 and 0.26 ± 2.21 kcal/mol, respectively. We conclude from analysis of the enthalpy values of the three structures (adduct, TST, and products) that the HF- or MP2-optimized C•H_2OCl structure does not exist as a stable radical and that density functional calculations provide more realistic insight into the chemistry of this species. Abstraction of H atoms from CH_3OCl by active radicals such as OH, Cl, O, H, ..., etc., result in formation of CH_2O plus a Cl atom.

1. Introduction

Chlorocarbons and other halocarbon compounds are present in the atmosphere from evaporation of solvents and other anthropogenic activities.[1,2] The reactions of these species in the atmosphere or combustion environment typically result in chlorocarbon radicals that turn into oxygenated chlorocarbons through reactions with O_2. One of these oxy-chlorocarbons is methyl hypochlorite, which is formed in the atmosphere from reaction of methylperoxy radical with ClO; CH_3OCl is reported to be important in ozone depletion over the polar regions.[3−9]

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TABLE 1: Parameters vs Calculation Method[a]

geometry	$C\cdot H_2OCl$[b]	$TSCH_2OCl$[c]	$ACH_2O{\sim}Cl$ [d]	CH_2O + Cl
MP2/6-31G(d,p)	yes	yes	yes	yes
MP2/6-31G(d)	yes	yes		
B3LYP/6-31G(d,p)	Nf[e]	Nf[f]	yes	yes

energy	$C\cdot H_2OCl$[g]	$TSCH_2OCl$[h]	$ACH_2O{\sim}Cl$[i]	CH_2O + Cl[j]
B3LYP/6-31G(d,p)	yes		yes	yes
B3LYP/6-311+G(3df,2p)	yes		yes	yes
QCISD(T)	yes		yes	yes
CBS-Q	yes	yes	yes	yes
G3/MP2[g]	yes	yes		

[a] Blank = not calculated. Nf = calculation attempted, indicated structure not found (see text). [b] Stable radical ($C\cdot H_2OCl$) → [c]CH_2O-Cl (TS)→ [d]$ACH_2{\sim}OCl$ (adduct) → $CH_2O + Cl$. [e] Stable structure is not found. [f] TST to $CH_2O + Cl$ not found. [g] Energy on MP2/6-31G(d,p) structure. [h] G3/MP2 is on MP2/6-31G(d) structure. [i] Energy on MP2 and density functional structure.

The methyl hypochlorite radical, $C\cdot H_2OCl$, formed by abstraction of a hydrogen from the methyl group, has estimates or theoretical determinations for its enthalpy[6,7,10] but no experimental data that we are aware of. Carl et al.[8] suggest that the radical thermally decomposes in their analysis of experiments on Cl atom reaction with CH_3OCl.[8] The $C\cdot H_2OCl$ radical is somewhat unique in that its dissociation products from β scission of the weak O−Cl bond, CH_2O + Cl atom, are 27 kcal/mol lower in energy than the reported enthalpy for the radical. Carl et al.[8] et al. estimate ΔH°_{f298} of $C\cdot H_2OCl$ as 29.9 kcal/mol by bond additivity methods, while Messer and Elrod[6] report an ΔH°_{f298} of 23.83 kcal/mol by G2 calculation analysis. Espinosa-Garcia[10] recently calculated ΔH°_{f298} of $C\cdot H_2OCl$ as 32.0 ± 3.5 kcal/mol using G2 analysis and Truhlar's basis set limit method. Wang et al.[11] report a number of isomers and reaction paths for $O(^3P)$ with CH_2Cl but do not include isomerization of the CH_2ClO- radical or $C\cdot H_2OCl$. Calculations in this study support the suggestions of Carl et al.

2. Calculation Methods

All ab initio calculations are performed using the Gaussian 98 or Gaussian 94 program suites.[12] The widely used second-order Møller−Plesset (MP2) method[13] and hybrid density functional method of Becke, the three-parameter/Lee, Yang, and Parr (B3LYP),[14] which is reported to yield accurate geometry and reasonable energies,[15,16] are chosen for structure optimizations. B3LYP/6-311+G(3df,2p),[17] QCISD(T)/6-31G(d,p),[18] CBS-Q//B3LYP/6-31G (d,p), CBS-Q//MP2/6-31G(d,p), and G3(MP2) are used for energy calculations. CBS-Q is a high level composite method[9,19] with empirical corrections; it is reported to be comparable with QCISD(T)/6-311++G(3df,2p).[20,21] These calculations are referred to as CBS-Q//B3** and CBS-Q//MP2** in the present study.

Gaussian-3 (G3/MP2) theory[22] is a composite ab initio method with geometry optimization at the MP2/6-31g(d) level. It also includes two higher level single-point energy calculations; a QCISD(T)/6-31G(d) calculation for energy and an MP2(fc)/G3-(MP2) large calculation to determine the energy difference between MP2/6-31g(d) and the MP2/high-level basis sets. The difference is applied to correct the QCISD(T)/6-31G(d) energy. G3(MP2) also includes a four-parameter high-level correction and a core-correlation term. The G3MP2 large basis set differs from the 6-311+G(3df,2p) basis set used in G2(MP2) theory by using 2df polarization functions on the atoms (Li−Ne), 3d2f polarization functions on (Na−Ar), and a special 6-311G basis set for S, Cl, and Ar optimized for the neutral atoms, plus diffuse functions on hydrogens. We have performed the optimization and the frequency and ZPVE calculations all at the MP2/6-31G(d,p) level. Harmonic vibrational frequencies are calculated for $C\cdot H_2OCl$ at the MP2/6-31G(d,p) level theory on the basis of optimized geometry at the same level of theory. B3 calculations were further run with OPT=NOEIGEN in case an inversion frequency or transition state (TS) was present.

3. Results and Discussion

3.1. Geometries and Vibrational Frequencies. Structures and energies determined at the different calculation levels are summarized in Table 1. The MP2/6-31G(d,p) optimized $C\cdot H_2OCl$ structure has an O−Cl bond of 1.72 Å and a C−O bond of 1.37 Å. Frequencies are listed in Table 2; they are in good agreement with data from other reported calculations.[6,10] HF/6-31g(d,p) calculations determine a radical structure with a

TABLE 2: Vibrational Frequencies (cm^{-1}), Rotational Constants (GHz), Geometries (Å or deg), and Spin Ontaminations for CH_2OCl

param	CH_2OCl[a] HF/6-31G(d,p)	CH_2OCl[a] MP2/6-31G(d,p)	CH_2OCl[a] MP2/6-31G(d)	CH_2OCl[a] ref 10	CH_2OCl[a] ref 6	$TSCH_2OCl$[d] B3LYP/ 6-31G(d,p)	$TSCH_2O-Cl$[b] MP2/6-31G(d,p)	$TSCH_2O-Cl$[b] MP2/6-31G(d)	$ACH_2O{\sim}Cl$[c] B3LYP/ 6-31G(d,p)	$ACH_2O{\sim}Cl$[c] MP2/6-31G(d,p)
					Frequencies					
	230.815	289.654		287.000		−455.729[e]	−1158.929[f]		166.903	87.076
	423.230	397.454		398.000		392.641	281.124		246.591	135.469
	779.527	691.963		691.000		652.035	394.112		280.622	152.407
	842.561	789.328		784.000		672.258	801.126		1197.160	1271.775
	1241.945	1158.861		1162.000		1135.026	1138.825		1241.034	1302.291
	1282.762	1207.152		1209.000		1197.595	1224.224		1507.110	1603.975
	1577.554	1505.838		1509.000		1438.049	1565.631		1796.616	2668.060
	3291.080	3227.285		3231.000		3138.040	3198.514		2968.496	3117.375
	3431.395	3384.277		3388.000		3281.272	3342.681		3068.678	3162.147
					Rotational					
A	56.008	52.165				53.680	54.302		50.386	49.698
B	6.667	6.498				6.370	6.178		4.041	3.397
C	6.004	5.819				5.710	5.702		3.741	3.179
					Geometry					
$R(O-Cl)$	1.668	1.724	1.722	1.721	1.722	1.733	1.781	1.780	2.479	2.737
$R(C-H)$	1.074	1.079	1.082	1.078	1.082	1.086	1.083	1.086	1.105	1.100
$R(C-O)$	1.368	1.378	1.378	1.377	1.378	1.375	1.301	1.301	1.213	1.213
∠COCl	113.451	111.300	111.381	111.350	111.400	113.368	115.131	115.164	108.002	108.658
∠HCOCl	174.621	−183.956	175.582			−195.357	53.474	53.592	179.833	179.965
$\langle S2 \rangle$	0.76	0.76	0.76	0.76		0.75	0.93	0.93	0.75	0.76

[a,b,c] Free radical, TS or adduct in the reaction path: [a] CH_2OCl (radical) → [b] CH_2O-Cl (TS)→ [c] $ACH_2{\sim}OCl$ (adduct) → $CH_2O + Cl$. [d] CH_2OCl optimized in TS by B3LYP/6-31G(d,p). [e] Imaginary frequency to CH_3-OCl rotational torsion. [f] Imaginary frequency to O−Cl stretching.

TABLE 3: Enthalpy Data Used in Isodesmic Reactions to Determine ΔH°_{f298} of CH_2OCl

compound	ΔH°_{f298}[a]	source	uncertainty	source
CH_4	−17.89	ref 25	±0.1	ref 33 (38)
CH_3•	34.82	ref 25	±0.2	ref 25 (31)
CH_3Cl	−19.60	ref 26	±0.2	ref 34 (39)
CH_2Cl•[a]	28.12	this study	±0.8	this study (31)
CH_3CH_3	−20.24	ref 35	±0.1	ref 35 (39)
CH_3CH_2	29.30	ref 31	±0.5	ref 31
CH_3OH	−48.08	ref 35	±0.1	ref 35 (41)
C•H_2OH[a]	−3.55	this study	±0.7	this study
CH_3OCl	−15.41	ref 9	±1.5	ref 9

[a] See Supplement 3 (Supporting Information).

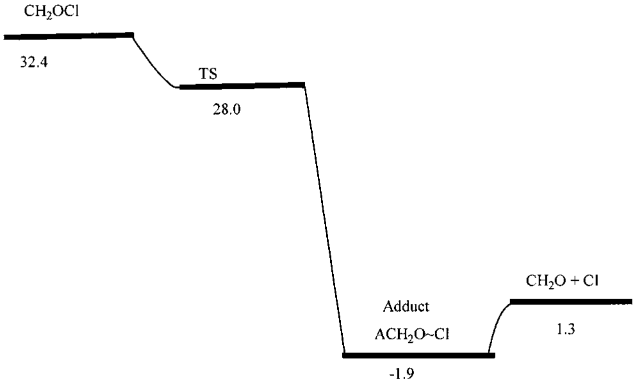

Figure 1. Potential energy for the life of C•H_2OCl (C•H_2OCl, CBS-Q//MP2**; TS, the average of CBS-Q//MP2** and G3/MP2; adduct, CBS-Q//B3**).

1.63 Å O−Cl bond. The optimized geometries for transition state (TSCH_2O-Cl) and adduct (ACH_2O~Cl) are also listed in Table 2; with MP2-predicted O−Cl bond lengths of 1.78 and 2.73 Å, respectively. Density functional methods only identified the existence of an adduct with an O−Cl bond length of 2.48 Å; they do not predict C•H_2OCl to exist. The B3LYP/6-31G-(d,p) calculations also find a transition state with an imaginary frequency corresponding to internal rotation of the CH_2 group about the CH_2−OCl bond. This TS structure is similar to the MP2 structure for stable radical but varies in dihedral angles and reaction coordinate frequency.

3.2. Enthalpies of Formation (ΔH°_{f298}) for C•H_2OCl and ACH_2O~Cl. Enthalpies of formation (ΔH°_{f298}) for radical (C•H_2OCl) and adduct (ACH_2O~Cl) are estimated using total energies obtained by the B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p), and CBS-Q calculation methods in four working reactions:

$$\mathrm{C{\bullet}H_2OCl + CH_4 \rightarrow CH_3{\bullet} + CH_3OCl} \quad (1a)$$

$$\mathrm{ACH_2O{\sim}Cl + CH_4 \rightarrow CH_3{\bullet} + CH_3OCl} \quad (1b)$$

$$\mathrm{C{\bullet}H_2OCl + CH_3Cl \rightarrow CH_2Cl{\bullet} + CH_3OCl} \quad (2a)$$

$$\mathrm{ACH_2O{\sim}Cl + CH_3Cl \rightarrow CH_2Cl{\bullet} + CH_3OCl} \quad (2b)$$

$$\mathrm{C{\bullet}H_2OCl + CH_3CH_3 \rightarrow C_2H_5{\bullet} + CH_3OCl} \quad (3a)$$

$$\mathrm{ACH_2O{\sim}Cl + CH_3CH_3 \rightarrow C_2H_5{\bullet} + CH_3OCl} \quad (3b)$$

$$\mathrm{C{\bullet}H_2OCl + CH_3OH \rightarrow C{\bullet}H_2OH + CH_3OCl} \quad (4a)$$

$$\mathrm{ACH_2OCl + CH_3OH \rightarrow C{\bullet}H_2OH + CH_3OCl} \quad (4b)$$

Total energies are corrected by zero-point vibration energies (ZPVE), which are scaled by 0.9608 as recommended by Scott[23] et al. for the MP2/6-31G(d,p) method. Thermal correction, 0−298.15 K, is calculated to estimate ΔH°_{f298} at 298.15 K.[24]

TABLE 4: Enthalpies of Formation at 298 K (in kcal/mol)

(a) For C•H_2OCl[a]

molecule reacn	B3LYP/6-31G(d,p)//MP2** [b]	B3LYP/6-311+(3df,2p)//MP2**	QCISD(T)/6-31G(d,p)//MP2**	CBS-Q//MP2**	max error from reacn[c]
		C•H_2OCl [f]			
1	30.09	30.34	32.30	32.40	1.8
2	31.13	31.48	32.36	32.39	2.5
3	31.63	31.83	32.07	32.37	2.1
4	32.48	31.82	32.40	32.39	2.3
av	31.33	31.37	32.28	32.39	2.2
total error[e]	3.06	2.81	2.33	2.21	

(b) Others for C•H_2OCl

molecule	this study	ref 10	ref 6	ref 8
		ref 10	ref 6	ref 8
C•H_2OCl	32.39 ± 2.33	32.0 ± 3.5	23.83	29.9

(c) For the Adduct, ACH_2O~Cl[a]

molecule reacn	B3LYP/6-31G(d,p)//MP2** [b]	B3LYP/6-311+(3df,2p)//MP2**	QCISD(T)/6-31G(d,p)//MP2**	CBS-Q//MP2** [h]	B3LYP/6-31G(d,p)//B3**[c]	B3LYP/6-311+(3df,2p)//B3**	QCISD(T)/6-31G(d,p)//B3**	CBS-Q//B3**	max error in the reacn[d]
					ACH_2O~Cl[g]				
1	−6.27	−2.49	−5.86	0.28	−8.93	−5.02	−6.95	−1.84	1.8
2	−5.22	−1.34	−5.80	0.26	−7.88	−3.88	−6.88	−1.85	2.5
3	−4.72	−1.00	−6.09	0.25	−7.38	−3.54	−7.18	−1.87	2.1
4	−3.87	−1.00	−5.76	0.26	−6.53	−3.55	−6.85	−1.86	2.3
av	−5.02	−1.46	−5.88	0.26	−7.68	−4.00	−6.97	−1.86	2.2
total error[e]	3.07	2.81	2.33	2.21	3.07	2.81	2.33	2.21	

[a] Enthalpies (ΔH°_{f298}) are calculated by the isodesmic reaction schemes (1-4) in the text; units are in kcal/mol. [b,c] All calculation levels are single point calculations from optimized geometry in [b]MP2/6-31G(d,p) or [c]B3LYP/6-31G(d,p). [d] Maximum error of the reaction = the sum of the uncertainty in other 3 standard compounds except target molecule; the uncertainty comes from literature or this study in Table 2. [e] Total error = the standard deviation through ΔH°_{f298} via 4 different reaction schemes + the average of maximum error. [f] See footnote *b* in Table 2. [g] See footnote *d* in Table 1. [h] All values are higher for MP2 geometry than density functional method.

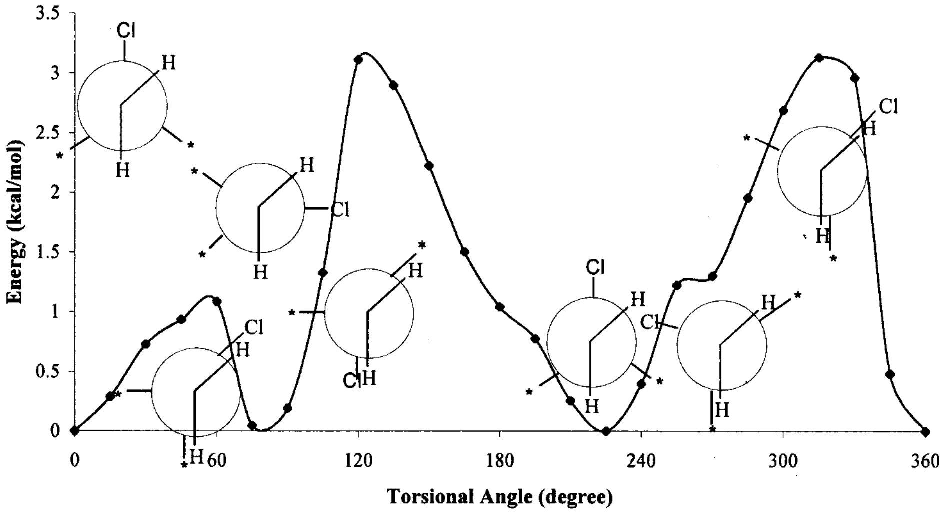

Figure 2. Potential energy for internal rotation about the C−O bond of C•H$_2$OCl versus torsion angle; calculated in MP2/6-31G(d,p).

TABLE 5: Ideal Gas Phase Thermodynamic Properties[a]

		ΔH°_{f892}	S°_{298}	C_{p300}	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
C•H$_2$OCl[b]	TVR[e]		62.69	11.48	13.22	14.66	15.81	17.54	18.79	20.80
	internal[f]		4.16	2.22	2.04	1.85	1.68	1.45	1.32	1.15
	total	32.39	66.85	13.70	15.26	16.51	17.49	18.99	20.11	21.95
TSCH$_2$O−Cl[c]	TVR[e]		65.33	12.32	13.79	15.05	16.09	17.69	18.90	20.86
	internal[f]		4.16	2.22	2.04	1.85	1.68	1.45	1.32	1.15
	total	27.97	69.49	14.54	15.83	16.90	17.77	19.14	20.22	22.01
ACH$_2$O~Cl[d]	TVR[e]	−1.86	65.37	11.93	13.01	14.15	15.23	17.07	18.50	20.75

[a] Thermodynamic properties are referred to standard state of an ideal gas at 1atm. [b] Free radical. [c] transition state, and [d]adduct. [e] The sum of contributions from translations, external rotations, and vibrations. [f] Contributions from internal rotation about C−O bond of CH$_2$O−Cl.

Standard ΔH°_{f298} for the reactants and products (other than C•H$_2$OCl) in the isodesmic reactions are listed in Table 3 along with their literature reference.[25−31] Their total energies, zero point vibrational energies, and thermal corrections are listed in the Supporting Information (Supplement 1). We note that the enthalpies of CH$_2$Cl• and C•H$_2$OH are from CBS-Q/B3** results described in Supplement 3 (Supporting Information) (this study). The CH$_2$Cl• enthalpy value of Seetula[32] et al. is 28.03 ± 0.74 kcal/mol, and we determine a value of 28.12 ± 0.8 kcal/mol. The ΔH°_{f298} values on C•H$_2$OH by Holmes et al.,[33] Dobe et al.,[34] Ruscic et al.,[35] and Johnson III et al.,[36] are −3.51, −3.97, −3.97, and −4.25 kcal/mol, respectively, while we determine a value of −3.55 ± 0.7 kcal/mol. The geometries, vibrational frequencies, and spin contamination values are listed in Supplement 4 (Supporting Information).

The ΔH°_{f298} of C•H$_2$OCl is 32.39 kcal/mol from CBS-Q//MP2** analysis; average of four working reactions in Table 4. The CBS-Q and the QCISD(T) both show very good consistency (less than 0.1 and 0.4 kcal/mol, respectively) throughout all the isodesmic reactions. The excellent agreement with the value of Espinosa-Garcia supports our calculation methods and our value for standard enthalpy of CH$_3$OCl.[9,10] The ΔH°_{f298} of adduct (ACH$_2$O~Cl) are 0.26 kcal/mol from CBS-Q//MP2** and −1.86 kcal/mol in CBS-Q//B3**, respectively. Figure 1 illustrates an energy diagram of the reaction system.

3.3. Enthalpies of Formation (ΔH°_{f298}) for TSCH$_2$O−Cl. Total energies at 298 K for the transition state (TSCH$_2$O−Cl) are estimated using single point calculations obtained by the B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBS-Q//MP2/6-31G(d,p) methods on the MP2/6-31G(d,p) geometry and the G3/MP2 method with data in Supplement 2 (Supporting Information). All calculations show that the TS has lower energy than the MP2-indicated stable radical C•H$_2$OCl. The difference in energy at 298 K between C•H$_2$OCl and TSCH$_2$O−Cl is 4.41 kcal/mol (average of CBS-Q//MP2 and G3/MP2), resulting in a calculated ΔH°_{f298} for TSCH$_2$O-Cl of 27.97 kcal/mol. The transition state structure is only 0.057 Å longer in the O−Cl bond than the calculated radical structure. The moments of inertial and vibration frequencies, with the exception of the imaginary frequency, are nearly identical;, see Table 2. The difference in enthalpy between these two very similar structures should be of similar accuracy to that obtained from our working reactions, which are only isodesmic.

3.4. Entropy, Heat Capacity, and Rotational Barrier for C•H$_2$OCl. Entropy (S°_{298}) and heat capacity $C_p(T)$ are estimated using the MP2 optimized C•H$_2$OCl structure. The rotational barrier for C•H$_2$OCl is calculated at the MP2/6-31G-(d.p) level with the data in listed Supplement 5 (Supporting Information) and Figure 2. The equation

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

is used to describe the potential versus torsion angle, with coefficients listed in Supplement 6 (Supporting Information). A rotational barrier of 3.1 kcal/mol is calculated for the CH$_2$−OCl rotor. Entropy and heat capacity data are presented in Table 5.

Entropy and heat capacity data are also calculated for the transition state in order to estimate of the $\Delta S^{=}$ and an Arrhenius *A* factor for the radical dissociation reaction using canonical transition state theory. Assuming zero energy of activation, and that the radical is formed with the MP2 calculated structure, a rate constant (*A* factor) is estimated as $k = 3.51 \times 10^{10} T^{1.16}$, as shown in Supplement 7 (Supporting Information).

B3LYP/6-31G(d,p) calculations are applied to calculate variations in enthalpy for moving the Cl about the O in the CH$_2$=O- -Cl to be sure we found the minimum energy; data are in Supplement 5 (Supporting Information) and Figure 3.

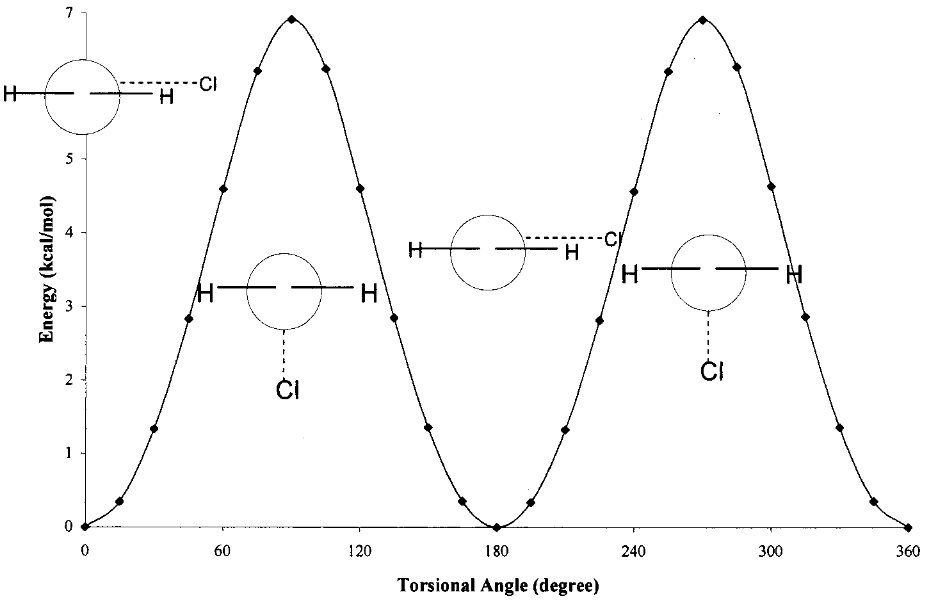

Figure 3. Potential energy for internal rotation about the C~O complex of adduct, ACH_2O~Cl versus torsion angle; calculated in B3LYP/6-31G(d,p).

The B3LYP/6-31G(d,p) determined ΔH°_{f298} for this adduct is −7.68, but the CBS-Q//B3** enthalpy value is 5.8 kcal/mol higher at −1.86 kcal/mol.

3.5. Abstraction Reaction Path on CH_3OCl. The overall exothermicity for OH, Cl and ClO + CH_3OCl reactions undergoing initial abstraction of H is

$$CH_3OCl + OH \rightarrow H_2O + CH_2O + Cl \qquad \Delta H_{rxn\ 298} = -50.42\ \text{kcal/mol} \quad (5)$$

$$CH_3OCl + OH \rightarrow CH_3O + HOCl \qquad \Delta H_{rxn\ 298} = -7.61\ \text{kcal/mol} \quad (6)$$

$$CH_3OCl + Cl \rightarrow HCl + CH_2O + Cl \qquad \Delta H_{rxn\ 298} = -34.35\ \text{kcal/mol} \quad (7)$$

$$CH_3OCl + Cl \rightarrow CH_3O + Cl_2 \qquad \Delta H_{rxn\ 298} = -9.39\ \text{kcal/mol} \quad (8)$$

$$CH_3OCl + ClO \rightarrow HOCl + CH_2O + Cl \qquad \Delta H_{rxn\ 298} = -23.19\ \text{kcal/mol} \quad (9)$$

The overall reaction resulting from abstraction of a hydrogen (vs abstraction of a Cl) is ca. 42.6 kcal/mol more exothermic than abstraction of halogen, but we do not know if the H abstraction transition state structure sees the energy of the final product set. Reactions 5 and 8 are direct chlorine activation pathways, while reactions 6 and 7 are null cycles with respect to chlorine activation. Reaction 9 is likely not important due to kinetic constraints.

3.6. Comparison of CH_3OCl with CH_3OBr and CH_3OOH. The O−Cl, O−Br, and O−OH bond energies in CH_3O-Cl, CH_3O-Br, and CH_3O-OH are 48.50, 39.54, and 45.22 kcal/mol, respectively.[9,10,37] Our calculations on $C{\bullet}H_2OBr$ and $C{\bullet}H_2OOH$ radicals indicate they will thermally dissociate similarly to $C{\bullet}H_2OCl$.

4. Conclusion

Calculations suggest that Cl atom and formaldehyde are generated directly from reactions of active radicals such as CH_3, OH, Cl, O, and H that abstract a H atom from CH_3OCl. The rapid dissociation of the $C{\bullet}H_2OCl$ results in formation of a strong carbonyl π bond and cleavage of the weaker O−Cl bond. $C{\bullet}H_2OCl$ is *not* sufficiently stable to undergo further reactions with O_2 before dissociation. Other similar methyl radical species such as hydroperoxides ($C{\bullet}H_2OOH$) and hypobromates ($C{\bullet}H_2OBr$) will likely behave similarly.

Accuracy of our CBS-Q//MP2/6-31G(d,p) calculation and the working reaction method is supported by the very close agreement between our ΔH°_{f298} value of 32.39 ± 2.21 kcal/mol with that reported by Espinosa-Garcia,[10] 32.0 ± 3.5, using G2 combined with Truhlar's basis set limit method.

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Supporting Information Available: Tables of energies, enthalpies of formation, vibrational frequencies, Fourier coefficients, and thermodynamic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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