Density-Functional Study of the Equilibrium Structures, Vibrational Spectra, and Energetics of CH_3OBr and CH_3BrO

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The geometries, vibrational spectra, and relative energetics of CH_3OBr and CH_3BrO have been examined using various ab initio and density-functional methods. The estimated heat of formation of CH_3OBr, at 0 K, is -5.4 kcal mol^{-1}, in good agreement with the estimates of bond additivity. The CH_3BrO isomer is 42.6 kcal mol^{-1} higher in energy than CH_3OBr.

I. Introduction

Bromine chemistry has been recognized, in recent years, to play a significant role in the stratospheric ozone budget[1] and in the Arctic troposphere during ozone-loss events.[2,3] The discovery of massive seasonal depletion of ozone[4] in the Antarctic spring centered attention on the role of biogenic and anthropogenic chlorinated species in the polar regions. Analogous to the interactions of the chlorine species implicated in ozone depletion are the stratospheric bromine species.[5] The potential role of bromine species on ozone depletion in the marine boundary layer, at mid-latitudes, has also been suggested.[6]

Bromine is present in atmospheric aerosol particles, precipitation, seawater, and organisms in seawater. Other sources of bromine that can reach the stratosphere (i.e., those that are not removed from the troposphere by rainout, reaction with OH radicals, or photolysis) are methyl bromide (used as soil fumigant), trifluoromethyl bromide (used as fire-retardant and refrigerant), and tetrabromobisphenol-A (used as fire-retardant in circuit boards). The most abundant of these source gases is methyl bromide (CH_3Br), which is produced naturally, mainly due to oceanic biological processes. Once released into the atmosphere, the bromine species are effective not only in destroying ozone, but in also inhibiting ozone formation by sequestering oxygen atoms in the bromide forms.

The coupling of bromine oxides with HO_x species (such as OH and HO_2 radicals) to destroy ozone has been of particular importance. In different parts of the atmosphere, ozone is partially depleted through cycles involving the reaction of BrO and HO_2 radicals, which have been investigated in the laboratory by Poulet et al.,[7] Larichev et al.,[8] and Elrod et al.[9] Such a process should increase the recycling of bromine radicals and could be efficient in regions where the OH concentration profiles are significant. The first step in this catalytic cycle is the reaction of bromine atoms with ozone. The cycle is represented by the following scheme of reactions:

$$\mathrm{Br} + \mathrm{O_3} \rightarrow \mathrm{BrO} + \mathrm{O_2} \quad (1)$$

$$\mathrm{BrO} + \mathrm{HO_2} \rightarrow \mathrm{HOBr} + \mathrm{O_2} \quad (2)$$

$$\mathrm{HOBr} + h\nu \rightarrow \mathrm{OH} + \mathrm{Br} \quad (3)$$

$$\mathrm{OH} + \mathrm{O_3} \rightarrow \mathrm{HO_2} + \mathrm{O_2} \quad (4)$$

$$\text{Net: } 2\mathrm{O_3} \rightarrow 3\mathrm{O_2} \quad (5)$$

HOBr, produced during this reaction, is rapidly recycled into active bromine species through photodissociation in the stratosphere. It has been suggested that in the marine boundary layer, HOBr could be converted into active bromine species on an aerosol surface and that HOBr would also be converted into photochemically labile BrCl and Br_2 species on sulfuric acid, sea salt, or ice particles.[6,10]

It has been postulated that, similar to the BrO + HO_2 reaction, the BrO + CH_3O_2 reaction is also important and may play a role in the ozone depletion cycle in the stratosphere and in the marine boundary layer at different latitudes.[11] In case of the BrO + CH_3O_2 reaction, the BrO gets converted to HOBr via

$$\mathrm{BrO} + \mathrm{CH_3O_2} \rightarrow \mathrm{HOBr} + \mathrm{CH_2O_2} \quad (6)$$

There can be another possible reaction channel in which BrO gets converted into bromine atoms via the reaction

$$\mathrm{BrO} + \mathrm{CH_3O_2} \rightarrow \mathrm{Br} + \mathrm{CH_3O} + \mathrm{O_2} \quad (7)$$

The photolysis of HOBr, or the reaction of Br atoms with ozone, could lead to rapid ozone depletion. Reaction 7 may be oversimplified and may yield CH_3OBr via

$$\mathrm{BrO} + \mathrm{CH_3O_2} \rightarrow \mathrm{CH_3OBr} + \mathrm{O_2} \qquad \Delta H^\circ_{r,0} = ?$$

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TABLE 1: Computed Equilibrium Geometries (Å and deg) for CH_3OBr and CH_3BrO

		6-311++G(3df,3pd)			6-311++G(3d2f,3pd)		
species	coordinates	B3LYP	B3PW86	B3PW91	B3LYP	B3PW86	B3PW91
CH_3OBr	CO	1.423	1.414	1.416	1.424	1.415	1.417
	BrO	1.848	1.830	1.833	1.848	1.829	1.834
	CH	1.091	1.091	1.092	1.091	1.091	1.092
	CH′	1.091	1.092	1.093	1.091	1.092	1.093
	COBr	112.5	112.0	112.1	112.4	111.9	112.0
	HCO	104.0	104.2	104.2	104.0	104.3	104.3
	H′CO	111.8	111.9	111.9	111.8	111.8	111.9
	H′COBr	180.0	180.0	180.0	180.0	180.0	180.0
CH_3BrO	CBr	1.974	1.950	1.953	1.975	1.951	1.954
	BrO	1.712	1.694	1.697	1.711	1.693	1.696
	CH	1.087	1.087	1.088	1.086	1.087	1.087
	CH′	1.084	1.084	1.085	1.084	1.084	1.085
	CBrO	104.4	104.5	104.7	104.5	104.6	104.7
	HCBr	106.6	106.8	106.6	106.6	106.7	106.6
	H′CBr	106.1	106.4	106.5	106.1	106.5	106.5
	H′CBrO	180.0	180.0	180.0	180.0	180.0	180.0

It has been determined that oxybromides absorb light at longer wavelengths than the corresponding bromides, and therefore, the photolysis of the BrO species, and their participation in chain reactions, will contribute to ozone consumption. Benter et al.[12] reported the gas-phase UV−vis absorption spectrum of CH_3OBr in the wavelength range $230 < \lambda < 400$ nm and compared their data with the available data from recent literature.[13] The heat of the $BrO + CH_3O_2$ reaction process is unknown because the heat of formation of CH_3OBr has not been determined. However, Helleis et al.[14] found evidence for the formation of CH_3OCl from the analogous $ClO + CH_3O_2$ reaction.

Aranda et al.[11] used the discharge flow-mass spectrometric method (DF-MS) with laser-induced fluorescence (LIF) to study the kinetics of the $BrO + CH_3O_2$ reaction at 298 K and obtained a rate constant of $(5.7 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. It was found that the $BrO + CH_3O_2$ reaction is likely to be negligible in the stratosphere but is potentially significant in the marine boundary layer and can affect the flora and fauna of that region. The reaction may also significantly contribute to the ozone loss observed in the Arctic troposphere during spring.

There have been no ab initio molecular orbital studies conducted on CH_3OBr thus far. It is important to consider the possible existence of such an intermediate (and its isomeric forms) in order to evaluate its stability. Knowledge of the heat of formation of CH_3OBr is required in order to understand and assess its potential role in stratospheric chemistry. There are two plausible connectivities for CH_3OBr isomers, namely CH_3OBr and CH_3BrO. In the present work, we examine the structures, vibrational spectra, and relative energetics of CH_3OBr and CH_3BrO to gain sufficient knowledge about the participation of the isomers in the $BrO + CH_3O_2$ reaction scheme.

II. Computational Methods

Ab initio molecular orbital calculations are performed using the GAUSSIAN 94 program.[15] All equilibrium geometries are fully optimized to better than 0.001 Å for bond distances and 0.1° for bond angles, with an SCF convergence of at least 10^{-9} on the density matrix and a root-mean-square (rms) force of 10^{-4} atomic units. The equilibrium geometries are optimized at various levels of theory using Schlegel's analytical gradient method, first with the B3LYP (Becke's nonlocal three-parameter exchange with the Lee−Yang−Parr correlation functional) method[16] and then with the B3PW86 (Becke's three-parameter functional with the nonlocal correlation provided by the Perdew 86 expression)[17] and B3PW91[18] density functional methods, incorporating the effects of the large 6-311++G(3df,3pd) and 6-311++G(3d2f,3pd) basis sets. The harmonic vibrational frequencies and intensities of all species are calculated at the B3LYP, B3PW86, and B3PW91 levels of theory in conjunction with the 6-311++G(3df,3pd) and 6-311++G(3d2f,3pd) basis sets, using the geometries calculated at the B3LYP, B3PW86, and B3PW91 levels of theory with each of the basis sets. For estimating the vertical energies of low-lying excited electronic states, the configuration interaction singles method (CIS)[19] is used with the 6-311++G(3df,3pd) and 6-311++G(3d2f,3pd) basis sets, using the geometries obtained at the B3LYP, B3PW86, and B3PW91 levels of theory. To improve the energies, single-point calculations are performed with the CCSD(T) (singles and doubles coupled-cluster theory including a perturbational estimate of the effects of connected triple excitations)[20] wave functions, using the 6-311++G(3df,3pd) basis set. The heat of formation of CH_3OBr is determined using an isodesmic reaction scheme and compared to its heat of formation computed at the CCSD(T) level of theory.

III. Results and Discussion

A. Equilibrium Structures and Vibrational Frequencies of CH_3OBr and CH_3BrO. To determine the structures and stability of CH_3OBr and CH_3BrO, computations were performed at the various levels of theory (B3LYP, B3PW86, and B3PW91) using the 6-311++G(3df,3pd) and 6-311++G(3d2f,3pd) basis sets. The optimized structural parameters of the isomers are provided in Table 1.

From computations, CH_3OBr appears to possess a staggered structure with C_s symmetry. At the B3LYP/6-311++G(3df,3pd) level of theory, the COBr angle is predicted to be 112.5°, formed primarily due to the strong repulsion between the lone pairs of electrons residing on the bromine and oxygen atoms. The large Br−O bond length in CH_3OBr (1.848 Å) can be attributed to the poor overlap between the 3d orbitals of the large bromine atom and the 2p orbitals of the comparatively smaller oxygen atom. Our calculated value of the Br−O bond length agrees very well with the Br−O bond length in HOBr (1.853 Å) computed by Lee at the CCSD(T)/TZ2P level of theory.[21] The C−O bond length for CH_3OBr, at the B3LYP/6-311++G(3df,3pd) level of theory, is 1.423 Å. Microwave studies have been performed by Venkateswarha and Gordy,[22] which show the C−O bond length in methanol (CH_3OH) to be 1.427 ± 0.007 Å. Thus, our calculations suggest that the C−O bond lengths in CH_3OBr and methanol are quite similar, the difference being only ca. 0.003 Å.

The other isomeric form is CH_3BrO, where the hypervalent

TABLE 2: Vibrational Frequencies (cm^{-1}) and Intensities (km mol^{-1}) for CH_3OBr and CH_3BrO

				6-311++G(3df,3pd)						6-311++G(3d2f,3pd)					
				B3LYP		B3PW86		B3PW91		B3LYP		B3PW86		B3PW91	
species	mode no.	mode symmetry	description	freq	int	freq	int	freq	int	freq	int	freq	int	freq	int
CH_3OBr	1	a′	CH_3 asym str	3099	8	3118	7	3112	8	3100	8	3118	7	3112	8
	2		CH_3 sym str	3012	39	3021	39	3016	40	3012	39	3021	39	3016	40
	3		CH_3 asym dfm	1506	13	1500	13	1499	13	1506	13	1500	13	1499	13
	4		CH_3 sym dfm	1457	4	1451	3	1450	3	1456	4	1450	3	1450	3
	5		CH_3 rock	1188	18	1190	21	1189	20	1187	18	1189	21	1188	20
	6		CO str	1010	47	1040	45	1035	45	1009	47	1038	45	1034	45
	7		OBr str	595	6	615	7	612	7	592	6	613	7	609	7
	8		COBr bend	316	2	318	2	317	2	316	2	318	2	316	2
	9	a″	CH_3 asym dfm	3082	29	3097	27	3092	28	3083	28	3097	26	3092	27
	10		CH_3 asym dfm	1463	9	1456	10	1456	10	1463	9	1456	10	1456	10
	11		CH_3 rock	1170	1	1170	1	1169	1	1170	1	1170	1	1168	1
	12		torsion	234	3	236	3	235	3	234	3	237	3	235	3
CH_3BrO	1	a′	CH_3 asym str	3181	0	3194	0	3189	0	3182	0	3195	0	3189	0
	2		CH_3 sym str	3066	4	3075	3	3070	3	3067	4	3075	3	3070	3
	3		CH_3 asym dfm	1465	8	1458	9	1457	9	1464	8	1457	9	1456	9
	4		CH_3 sym dfm	1296	5	1293	3	1293	3	1295	5	1292	3	1291	3
	5		CH_3 rock	932	3	932	3	932	3	931	3	931	3	930	3
	6		BrO str	723	39	765	42	759	42	720	39	761	42	755	42
	7		CBr str	530	2	557	2	554	2	529	2	556	2	553	2
	8		CBrO bend	222	6	227	6	227	6	221	6	225	6	226	6
	9	a″	CH_3 asym str	3197	0	3210	0	3205	7	3199	0	3211	0	3206	0
	10		CH_3 asym dfm	1441	9	1432	10	1431	10	1439	9	1431	10	1430	9
	11		CH_3 rock	938	2	939	2	938	2	936	2	938	2	937	2
	12		torsion	128	0	130	0	131	0	130	0	132	0	132	0

bromine atom lies in place of the oxygen atom of CH_3OBr. The structure of CH_3BrO also appears to possess C_s symmetry. For CH_3BrO, it is important to note that the lone pairs of electrons on the terminal oxygen atom sometimes tend to enter into resonance with the bonding electron pair of the Br−O bond, in which process the Br−O bond attains a partial double-bond character. This resonance effect is not observed with the oxygen atom that is sandwiched between the carbon and bromine atoms in CH_3OBr. Due to this partial double-bond character in CH_3BrO, the repulsion between the lone pairs of electrons on bromine and oxygen atoms is partially offset by the repulsion between the lone electron pairs and the C−Br and Br−O bond pairs. Thus, the CBrO angle gets shrunk (104.4°) and is a little smaller than the HCBr angle (106.6°), which is primarily formed due to the repulsion between the H−C and C−Br bonds (with the added repelling input of the lone electrons on bromine). The partial double-bond character in CH_3BrO manifests its effect on the BrO bond length, which has a smaller value at the B3LYP/6-311++G(3df,3pd) level of theory (1.712 Å), compared to the BrO bond length value in CH_3OBr at the same level of theory. Our computed value of the Br−O bond length in CH_3BrO is comparable to the Br−O bond length in HBrO (1.731 Å), FBrO (1.661 Å), and BrBrO (1.690 Å) computed by Lee at the CCSD(T)/TZ2P level of theory.[21]

The calculated vibrational frequencies and intensities for CH_3OBr and CH_3BrO are provided in Table 2. For CH_3OBr, the most intense bands are the CH_3 symmetric stretch and CO stretch while the least intense bands are the COBr bend and CH_3 rock. The OBr stretch occurs at a lower frequency than the CO stretch, consistent with the larger O−Br bond length than that of the C−O bond. The OBr stretch in CH_3OBr agrees well with the OBr stretches in $HOBr$[23] and Br_2O.[21] This information should be useful in the assignment of the experimental spectra of CH_3OBr. The vibrational frequencies of CH_3OBr also exhibit certain spectral features (CH_3 asymmetric and symmetric stretches and CO stretch) similar to CH_3OH.[24,25]

For CH_3BrO, there is maximum absorption at 723 cm^{-1}. This is the BrO stretch, and it lies between the BrO stretches in HBrO and BrBrO.[21] There appears to be very little absorption at 530 and 938 cm^{-1} and extremely little or no absorption at 3181, 3197, and 128 cm^{-1}. The BrO stretch band of CH_3BrO would allow its clear distinction from CH_3OBr.

B. Excited States of CH_3OBr and CH_3BrO. A spectroscopic property that is particularly useful and important in the characterization of the electronic spectra of CH_3OBr and CH_3BrO is their vertical excitation energies. Configuration interaction with all singlet excited determinations, CIS, has been shown to be an effective method of surveying the excited states of closed-shell molecules with reasonable experience for polyatomic molecules.[19] However, we note that the CIS results are, at best, qualitative, but nevertheless, they provide an avenue for identifying the most distinguishing features among the isomeric forms. The CIS vertical excitation energies and oscillator strengths (F) for CH_3OBr and CH_3BrO, calculated at the B3LYP, B3PW86, and B3PW91 levels of theory, are provided in Table 3 and compared to those of HOBr. Benter et al.[12] reported the UV−vis absorption spectra for CH_3OBr and HOBr, and they are included in Table 3.

Critical examination of the predicted electronic spectra of CH_3OBr and CH_3BrO reveals that there are certain features that would allow these two molecules to be distinctly characterized. For CH_3OBr, the excited states located at 8.1 and 8.2 eV have the most relative oscillator strengths while the excited state located at 4.0 eV has the least relative oscillator strength (0.0003) and consequently should be quite weak. In comparison, for HOBr, the excited state located at 7.6 eV has the maximum relative oscillator strength (0.0065) while the excited state located at 4.1 eV has the least relative oscillator strength (0.0001).

Experiments conducted[12] exploring the CH_3OBr spectrum reveal an excited state ($^1A''$) located at 3.6 eV, which is comparable to the $^1A''$ excited state according to our calculation at the B3LYP/6-311++G(3df,3pd) level of theory located at 4.0 eV. Another excited sate ($^1A'$) that was distinctly revealed by the experiments[12] appeared to be located at 4.4 eV, comparable to our computed excited state at 4.9 eV. Thus, our calculations of the excited states of CH_3OBr agree well with experimental observation. In case of HOBr, experiments[12] were

TABLE 3: Calculated Vertical Excitation Energies and Oscillator Strengths for HOBr, CH_3OBr, and CH_3BrO

		CIS/6-311++G(3df,3pd)//						CIS/6-311++G(3d2f,3pd)//						
		B3LYP		B3PW86		B3PW91		B3LYP		B3PW86		B3PW91		expt[a]
species	states	ΔE (ev)	F (rel)	ΔE (ev)	F (rel)	ΔE (ev)	F (rel)	ΔE (ev)	F (rel)	ΔE (ev)	F (rel)	ΔE (ev)	F (rel)	ΔE (ev)
HOBr	$^1A''$	4.1	0.0001	4.2	0.0001	4.2	0.0001	4.1	0.0001	4.2	0.0001	4.2	0.0001	3.66
	$^1A'$	4.9	0.0034	5.0	0.0034	5.0	0.0034	4.9	0.0034	5.0	0.0034	5.0	0.0034	4.69
	$^1A''$	7.6	0.0065	7.8	0.0199	7.8	0.0135	7.6	0.0067	7.9	0.0223	7.8	0.0145	
CH_3OBr	$^1A''$	4.0	0.0003	4.2	0.0004	4.1	0.0004	4.1	0.0003	4.2	0.0004	4.1	0.0004	3.6
	$^1A'$	4.9	0.0033	5.0	0.0033	5.0	0.0033	4.9	0.0033	5.0	0.0033	5.0	0.0033	4.4
	$^1A''$	7.0	0.0014	7.2	0.0015	7.1	0.0014	7.0	0.0015	7.2	0.0015	7.1	0.0015	
	$^1A'$	8.1	0.2981	8.2	0.1187	8.2	0.1187	8.1	0.2981	8.2	0.1181	8.2	0.1181	
	$^1A''$	8.2	0.1184	8.3	0.2936	8.2	0.2947	8.2	0.1178	8.3	0.2934	8.3	0.2946	
	$^1A''$	8.6	0.1015	8.6	0.1008	8.6	0.1009	8.6	0.1008	8.6	0.1000	8.6	0.1002	
CH_3BrO	$^1A''$	4.1	0.0006	4.3	0.0005	4.2	0.0005	4.1	0.0006	4.3	0.0005	4.3	0.0005	
	$^1A'$	4.9	0.0057	5.2	0.0062	5.1	0.0063	4.9	0.0057	5.2	0.0063	5.1	0.0063	
	$^1A''$	6.2	0.0001	6.3	0.0001	6.3	0.0001	6.2	0.0001	6.3	0.0001	6.3	0.0001	
	$^1A''$	7.3	0.0146	7.2	0.0147	7.3	0.0146	7.3	0.0146	7.2	0.0147	7.2	0.0146	
	$^1A'$	8.1	0.1887	8.2	0.1808	8.1	0.1812	8.1	0.1893	8.2	0.1808	8.1	0.1819	
	$^1A'$	8.4	0.0412	8.3	0.0402	8.3	0.0393	8.4	0.0409	8.3	0.0400	8.3	0.0391	

[a] Benter, T.; Feldman, C.; Kirchner, U.; Schmidt, M.; Schmidt, S.; Schindler, R. N. *Ber. Bunsenges. Phys. Chem.* **1995**, *99*, 1144.

TABLE 4: Total Energies (hartrees) of Species in the Isodesmic Scheme

	6-311++G(3df,3pd)				6-311++G(3d2f,3pd)		
species	B3LYP	B3PW86	B3PW91	CCSD(T)	B3LYP	B3PW86	B3PW91
H_2O	−76.46451	−76.64039	−76.43416	−76.33743	−76.46446	−76.64034	−76.43411
HOBr	−2649.95629	−2650.92147	−2649.90784	−2648.23807	−2649.95659	−2650.92174	−2649.90810
CH_3OH	−115.77432	−116.09436	−115.72763	−115.55497	−115.77423	−116.09429	−115.72757
CH_3OBr	−2689.27248	−2690.38192	−2689.20744	−2687.46387	−2689.27254	−2690.38198	−2689.20750
CH_3BrO	−2689.20360	−2690.31464	−2689.14084	−2687.39377	−2689.20401	−2690.31508	−2689.14129

TABLE 5: Heats of Formation (kcal mol^{-1}) for CH_3OBr

	isodesmic reaction	
	$CH_3OBr + HOH \rightarrow CH_3OH + HOBr$	
levels of theory	$\Delta H_{r,0}^\circ$	$\Delta H_{f,0}^\circ$
B3LYP/6-311++G(3df,3pd)	4.8	−4.2
B3PW86/6-311++G(3df,3pd)	4.9	−4.3
B3PW91/6-311++G(3df,3pd)	4.6	−4.0
B3LYP/6-311++G(3d2f,3pd)	4.7	−4.1
B3PW86/6-311++G(3d2f,3pd)	4.7	−4.1
B3PW91/6-311++G(3d2f,3pd)	4.5	−3.9
CCSD(T)/6-311++G(3df,3pd)	6.0	−5.4

able to distinctly identify excited states at 3.66 ($^1A''$) and 4.69 eV ($^1A'$) compared to our computed excited states at 4.1 and 4.9 eV, respectively. For CH_3BrO, our calculations indicate that, similar to the spectrum of CH_3OBr, the excited state located at 8.1 eV possesses the maximum relative oscillator strength (0.1887) while that located at 6.2 eV possesses the least relative oscillator strength (0.0001).

C. Energetics of CH_3OBr and CH_3BrO. For calculation of the heats of formation of CH_3OBr at various levels of theory, an isodesmic reaction scheme, namely $CH_3OBr + HOH \rightarrow CH_3OH + HOBr$, is employed. Isodesmic reactions are those in which the reactants and products contain the same types of bonds (i.e., the number of bonds broken and formed is conserved) and requires the heats of formation of all the molecules involved in the reaction (except that of the isomer in question) to be known. Because of this property, errors in the energy due to defects in the basis set and electron correlation cancel to a large extent. Table 4 contains values of the absolute energies for species involved in the isodesmic scheme, and Table 7 contains literature values for the heats of formation of HOH, HOBr, and CH_3OH. The results do not appear to vary much with basis set and electron correlation effects, as shown in Table 5. For CH_3OBr, the heat of formation is predicted to be −5.4 kcal mol^{-1} at the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory, which is its best estimate.

TABLE 6: Relative Energy Differences (kcal mol^{-1})[a] between CH_3OBr and CH_3BrO

levels of theory	ΔE ($CH_3OBr - CH_3BrO$)
B3LYP/6-311++G(3df,3pd)	41.8
B3PW86/6-311++G(3df,3pd)	40.8
B3PW91/6-311++G(3df,3pd)	40.4
B3LYP/6-311++G(3d2f,3pd)	41.6
B3PW86/6-311++G(3d2f,3pd)	40.6
B3PW91/6-311++G(3d2f,3pd)	40.1
CCSD(T)/6-311++G(3df,3pd)	42.6

[a] Relative energies are corrected for zero-point energy using B3LYP/6-311++G(3df,3pd) frequencies.

TABLE 7: Heats of Formation (kcal mol^{-1}) of Species in the Isodesmic Scheme

species	$\Delta H_{f,0}^\circ$	ref
H_2O	−57.10 ± 0.0	*a*
HOBr	−10.93 ± 1.0	*b*
CH_3OH	−45.60 ± 0.1	*c*

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The relative stability between CH_3OBr and CH_3BrO has been examined by computing the relative energy differences between them and correcting for zero-point energies, as presented in Table 6. To assess the accuracy of the relative energetic data, a calculation has been performed at the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory, which generates a value of 42.6 kcal mol^{-1}. CH_3OBr appears to be lower in energy (and thus more stable) than CH_3BrO.

D. Implication for the BrO and CH_3O_2 Cross-Reaction. It has been recently postulated that the atmospheric cross-reaction between the BrO and CH_3O_2 species could play a role in stratospheric chemistry, particularly in the marine boundary layers.[11] For CH_3OBr to be made in the atmosphere by a

homogeneous gas-phase mechanism, the most likely pathway is the $BrO + CH_3O_2$ reaction.

$$BrO + CH_3O_2 \rightarrow \text{products} \quad (8)$$

There are two possible intermediates that could be formed during this reaction, namely CH_3OBr and CH_3BrO, via the channels

$$BrO + CH_3O_2 \rightarrow CH_3OBr + O_2 \quad (9a)$$

$$BrO + CH_3O_2 \rightarrow CH_3BrO + O_2 \quad (9b)$$

According to our calculations, the CH_3OBr-forming reaction channel (eq 9a) is exothermic by -39.6 kcal mol^{-1} whereas the channel for the formation of CH_3BrO (eq 9b) is endothermic by 3.0 kcal mol^{-1}, implying that channel 9a is thermodynamically favored.

IV. Summary

The equilibrium structures, vibrational and electronic spectra, and relative energetics of CH_3OBr and CH_3BrO have been investigated, along with the heat of formation of CH_3OBr, by the B3LYP, B3PW86, B3PW91, and CCSD(T) ab initio electronic structure methods, in conjugation with the large 6-311++G(3df,3pd) and 6-311++G(3d2f,3pd) basis sets. The CH_3OBr structural form is found to be more stable than CH_3BrO. Due to its thermal stability, it is possible that CH_3OBr may play an important role in the atmospheric cross-reactions of the BrO and CH_3O_2 species.

References and Notes

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