Structures, Vibrational Spectra, and Relative Energetics of $HBrO_3$ Isomers

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Received: November 21, 1997; In Final Form: January 12, 1998

The geometries, vibrational spectra, and relative energetics of $HBrO_3$ isomers have been examined using various ab initio and density functional [MP2, CISD, CCSD(T), and B3LYP] methods. The results show interesting trends for the $HBrO_3$ isomers. The $HOBrO_2$ isomer is found to be the lowest energy structure among the isomers, with an estimated heat of formation of 12.6 kcal mol^{-1} at 0 K. We have examined the implication of the formation of the $HBrO_3$ isomers from the atmospheric cross-reactions of the HO_2 and BrO species.

I. Introduction

The importance of chlorine in the destruction of ozone has been well established for many years, since 1970. Chlorine is primarily introduced in the stratosphere by means of CFCs (chlorofluorocarbons) which are used in refrigerants for space cooling, in fire extinguishers, in foam applications, and in aerosols. In 1975, Watson et al. first recognized that bromine could perturb stratospheric ozone in a manner similar to chlorine. Bromine is present in atmospheric aerosol particles, precipitation, seawater, and organisms in seawater. Other gaseous sources of bromine that can reach the stratosphere (i.e., are not removed from the troposphere by rainout, reaction with OH radicals, or photolysis) are methyl bromide (used as soil fumigant), tetrabromobisphenol A (used as fire retardant in circuit boards), and trifluoromethyl bromide (used as fire retardant and refrigerant). The most abundant of these source gases is methyl bromide (CH_3Br) whose natural source is mainly due to oceanic biological processes.

Once released into the atmosphere, the chlorine and bromine species are effective not only in destroying ozone but also in inhibiting ozone formation by sequestering oxygen atoms in the halogen forms. Yung et al.[1] found that there can be a synergistic effect due to the coupling reaction of chlorine and bromine oxides, which can be a potent ozone destroyer. This synergistic reaction greatly enhances the power of bromine compounds to destroy ozone.

$$\mathrm{BrO} + \mathrm{ClO} \rightarrow \mathrm{Br} + \mathrm{Cl} + \mathrm{O_2} \qquad (1)$$

Despite the fact that bromine compounds are more than 2 orders of magnitude less abundant than chlorine compounds in the stratosphere, it has been estimated that such chemistry involving bromine species is responsible for ∼25% of the ozone loss observed during the Antarctic ozone hole event[2] and up to 40% of the loss over the Arctic in winter.[3] In 1975 Wofsy et al.[4] suggested that bromine atoms could be more effective than chlorine atoms in destroying stratospheric ozone. When atmospheric bromine chemistry is compared to chlorine chemistry, it can be seen that much more bromine is present in the active forms Br and BrO (due to the long length of bromine's free radical chain termination) than chlorine is present in its active Cl and ClO forms. Consequently, bromine concentrations as small as 1 part in 10^{11} (v/v) have a greater potential to destroy stratospheric ozone than does chlorine. Wennberg et al.[5] also arrived at such a conclusion and presented a detailed analysis of the current understanding of the destruction of stratospheric ozone by OH, HO_2, NO, NO_2, ClO, and BrO radicals during the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE). Their conclusion has motivated several studies during the past two years to obtain a better understanding of bromine and bromine oxide compounds and their reactivity, photodissociation rates, and reaction pathways in atmospheric chemical processes that perturb ozone profiles.

The reaction of bromine atoms with ozone yields bromine oxide (BrO), as first proposed by Wofsy et al.[4] The reaction of BrO with oxygen atoms is the last step in the catalytic loss mechanism for ozone as the bromine atom is regenerated. The coupling of the bromine oxides with HO_x species (such as OH and HO_2 radicals) to destroy ozone has been of particular importance. There has been recent interest in this catalytic cycle involving bromine that was also originally suggested in 1980 but was dismissed as unimportant because the rate constant for the reaction (based on the first kinetic study of that reaction) was too slow in the atmosphere to contribute significantly to ozone depletion.[1] A critical reaction that couples BrO_x and HO_x species in the above cycle for the destruction of ozone is the reaction between BrO and HO_2. This process should increase the recycling of bromine radicals and could be efficient in regions where the OH concentration profiles are significant.

$$\mathrm{Br} + \mathrm{O_3} \rightarrow \mathrm{BrO} + \mathrm{O_2} \qquad (2)$$

$$\mathrm{BrO} + \mathrm{HO_2} \rightarrow \mathrm{HOBr} + \mathrm{O_2} \qquad (3)$$

$$\mathrm{HOBr} + h\nu \rightarrow \mathrm{OH} + \mathrm{Br} \qquad (4)$$

$$\mathrm{OH} + \mathrm{O_3} \rightarrow \mathrm{HO_2} + \mathrm{O_2} \qquad (5)$$

$$\text{net:} \quad 2\mathrm{O_3} \rightarrow 3\mathrm{O_2} \qquad (6)$$

New experimental results have suggested that the reaction 3 proceeds at a substantially faster rate than had been indicated by previous measurements and may indeed play a major role in ozone-related chemistry of bromine compounds.

The reaction between BrO and HO_2 (reaction 3) has two thermodynamically feasible channels:

$$\mathrm{BrO} + \mathrm{HO_2} \rightarrow \mathrm{HOBr} + \mathrm{O_2} \qquad \Delta H^0_{\mathrm{r},298} = -45.1\ \mathrm{kcal\ mol^{-1}} \quad (7)$$

S1089-5639(98)00299-0 CCC: $15.00 © 1998 American Chemical Society
Published on Web 02/20/1998

$$BrO + HO_2 \rightarrow HBr + O_3 \qquad \Delta H^0_{r,298} = -7.7 \text{ kcal mol}^{-1} \quad (8)$$

The first study of this reaction was performed by Cox and Sheppard using the molecular-modulation UV absorption technique.[6] BrO and HO_2 were produced by photolysis of O_3 in the presence of Br_2, H_2, and O_2 and analyzed directly by UV absorption. The rate constant was obtained indirectly by computer modeling of the experimental data and was determined as 5×10^{-12} cm^3 molecule^{-1} s^{-1} at 303 K and 760 Torr total pressure. A similar value of the rate constant was suggested by Baulch et al.[7] for use in atmospheric modeling. This was based on analogy with the reaction of ClO with HO_2 which had been fairly extensively studied over a wide range of pressure and temperature and had a room-temperature value of 6×10^{-12} cm^3 molecule^{-1} s^{-1}. A more direct study was performed by Poulet et al.[8] by means of the discharge flow-mass spectrometric method. The rate constant was determined under pseudo-first-order conditions monitoring BrO by mass spectrometry as a function of reaction time in the presence of excess HO_2. The only product they observed at 298 K was HOBr. The rate constant measured for this reaction was much higher (by a factor of 6) than that given by Cox and Sheppard.[6] The higher value of the rate constant has been confirmed by flash photolysis and UV absorption studies of $Br_2/O_3/Cl_2/CH_3OH/O_2/He$ mixtures carried out by Hayman, Danis, and Thomas[9] and Bridier, Veyret, and Lesclaux[10] at 298 K and 760 Torr total pressure. The fair agreement between these three recent determinations suggests a value around $k = 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at $T = 298$ K for the BrO + HO_2 reaction. Larichev et al.[11] used the discharge flow-mass spectrometric technique to investigate the kinetics and mechanism of the HO_2 + BrO reaction in the temperature range 233−344 K and observed that HOBr was the major product. They obtained a rate constant value of $(4.77 \pm 0.32) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and observed a negative temperature dependence suggesting the presence of an $HBrO_3$ complex, since previous studies conducted on the ClO + HO_2 reaction by Poulet et al.[12] showed negative temperature dependence and concluded the formation of an $HClO_3$ complex. Other experiments performed by Elrod et al.[13] reported a much smaller value of the rate constant $(1.4 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K. Elrod et al.[13] did not find any evidence for non-Arrhenius behavior below 243 K, as suggested in the previous temperature dependence study.

Mellouki, Talukdar, and Howard[14] tried to measure the yield of the HBr-forming channel. They determined an upper limit on the yield of HBr from the reaction HO_2 + BrO → products by measuring an upper limit for the rate coefficient of the reverse reaction HBr + O_3 → HO_2 + BrO. They employed a discharge flow reactor with laser magnetic resonance (LMR) for the measurements of the HO_2 radical concentration. The limits measured at 300 and 441 K were extrapolated to low temperatures to determine that the yield of HBr from the HO_2 + BrO reaction was negligible throughout the stratosphere (<0.01%). An upper limit for the rate coefficient of the reaction of HO_2 with HBr was also determined to be very low, $\leq 3 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 300 K, and low, $\leq 3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 400 K. Mellouki et al.[14] observed a negative temperature dependence for the BrO + HO_2 reaction, suggesting the presence of an $HBrO_3$ complex. It was postulated that if a stable complex was to be formed, it would be one with the oxygen on the HO_2 bound to the Br or O atoms on BrO. Garcia and Solomon[15] have reported a theoretical analysis of the BrO atmospheric measurements database using a two-dimensional photochemical model. From their study of the latitudinal variation of the BrO concentration, Garcia and Solomon[15] concluded that the HO_2 + BrO reaction could not have a significant yield of HBr. Recently, Li et al.[16] performed experimental studies of the reaction of BrO with HO_2 over the temperature range 233−348 K using discharge flow/mass spectroscopy. They found that, at 298 K, the rate coefficient was $(1.73 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} with excess HO_2 and $(2.05 \pm 0.64) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} with BrO in excess.

In this paper we raise the question of the possibility of stable $HBrO_3$ adducts that could be formed from the reaction of HO_2 with BrO radicals. There have been no experimental studies that have isolated an $HBrO_3$ intermediate, although it has been suggested to exist.[13] It is important to consider the possible existence of such an intermediate (and its isomers) because the $HBrO_3$ intermediate, if present in a stable form, could act as a long-term or temporary reservoir of inorganic bromine. There are four types of plausible connectivities for $HBrO_3$ isomers: (1) HOOOBr, (2) HOOBrO, (3) $HOBrO_2$, and (4) $HBrO_3$. In the present work we examine the structure, vibrational spectra, and energetics of the $HBrO_3$ isomers, to determine the relative order of stability among the isomers. Such a study should shed new light on the intimate details of the chemistry of the BrO + HO_2 reaction.

II. Computational Methods

Ab initio molecular orbital calculations are performed using the GAUSSIAN 92[17] and GAUSSIAN 94 programs.[18] All equilibrium geometries are fully optimized to better than 0.001 Å for bond distances and 0.1° for bond angles. The MP2 (second-order Møller−Plesset perturbation),[19] CISD (configuration interaction theory using single and doubles excitations),[20] CCSD(T) (singles and doubles coupled-cluster theory including a perturbational estimate of the effects of connected triple excitations),[21] and B3LYP (Becke's nonlocal three-parameter exchange with Lee−Yang−Parr correlation functional)[22] density functional methods are used with the 962(d)/6-311G(d), TZ2P (triple-ζ double polarized), and the large 6-311++G(3df,3pd) basis sets. The harmonic vibrational frequencies and intensities of all species are calculated at the B3LYP level of theory in conjugation with the 6-311++G(3df,3pd) basis set, using the geometry calculated at the B3LYP level of theory with the same basis set. For estimating the vertical energies of low-lying excited electronic states, the configuration interaction singles method (CIS)[23] is used with the 6-311++G(3df,3pd) basis set using the B3LYP/6-311++G(3df,3pd) geometries. The heats of formation of HOOOBr are determined using isodesmic reactions and are compared to the heats of formation estimated using G1 and G2 theories. Details of the methods are described elsewhere.[24,25]

III. Results and Discussion

A. Structural and Energetic Properties of $HBrO_3$ Species. *1. Equilibrium Geometries of $HBrO_3$ Isomers.* There has been no previous computational work on the isomeric forms of $HBrO_3$. To identify the lowest energy isomer on the hypersurface of the $HBrO_3$ potential energy, we performed calculations at various levels of theory. Four local minimum-energy structures were located. The optimized structural parameters are given in Table 1 and illustrated in Figure 1.

From computations, the straight-chain structure for HOOOBr is skewed (Figure 1a). The HOOO′ dihedral angle at the B3LYP/6-311++G(3df,3pd) level of theory is 75.8°, and the OOO′Br dihedral angle is predicted to be 80.9°. The skewed

TABLE 1: Computed Equilibrium Geometries (Å and deg) for $HBrO_3$ Isomers

		TZ2P				6-311++G(3df,3pd)
species	coordinate	MP2	CISD	B3LYP	CCSD(T)	B3LYP
HOOOBr	OO′	1.425	1.381	1.385	1.420	1.378
	O′Br	1.867	1.822	1.909	1.888	1.897
	OO	1.430	1.389	1.434	1.445	1.425
	HO	0.967	0.953	0.970	0.968	0.970
	OO′Br	109.4	110.5	111.7	110.1	111.7
	OOO	107.5	107.8	109.2	107.7	109.0
	HOO	100.7	102.7	101.9	100.7	102.0
	OOO′Br	79.4	81.8	80.8	81.5	80.9
	HOOO′	77.7	79.3	74.7	77.5	75.8
HOOBrO	BrO	1.919	1.804	1.945	1.923	1.916
	BrO′	1.635	1.634	1.674	1.673	1.663
	OO	1.453	1.408	1.418	1.453	1.415
	HO	0.966	0.952	0.969	0.966	0.969
	OBrO′	112.4	109.0	111.8	111.1	110.5
	OOBr	108.7	110.1	112.0	109.6	112.0
	HOO	100.1	102.0	102.4	100.6	102.4
	OOBrO′	78.1	77.9	77.7	77.8	78.1
	HOOBr	97.3	101.9	93.7	96.4	95.6
$HOBrO_2$	OBr	1.844	1.759	1.844	1.842	1.844
	HO	0.972	0.957	0.973	0.971	0.973
	BrO	1.601	1.579	1.611	1.615	1.611
	BrO′	1.593	1.586	1.619	1.622	1.619
	HOBr	102.4	106.0	104.5	102.5	104.5
	OBrO	100.9	101.3	104.2	104.0	104.2
	OBrO′	103.9	103.7	101.7	101.3	101.7
	HOBrO	−90.5	−79.6	−90.2	−89.7	−89.5
	HOBrO′	25.1	35.0	25.8	26.1	25.8
$HBrO_3$	HBr	1.471	1.447	1.497	1.475	1.497
	BrO	1.587	1.570	1.604	1.605	1.604
	HBrO	103.5	104.0	103.4	103.5	103.4

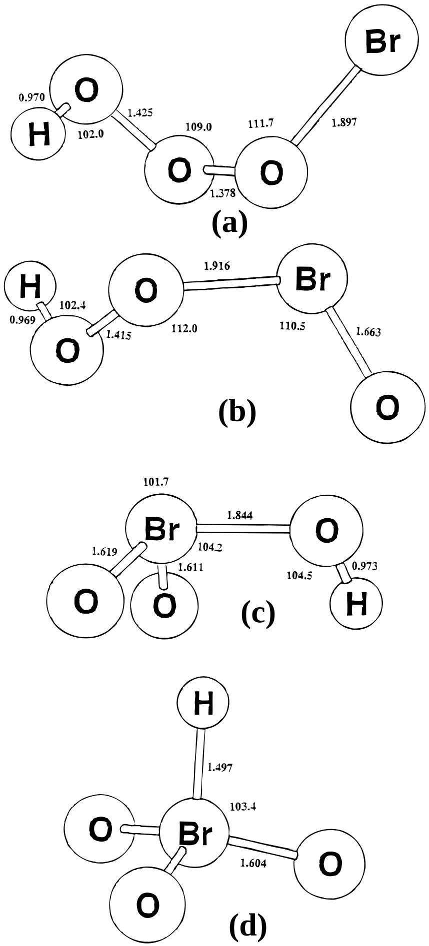

Figure 1. Minimum-energy structures for $HBrO_3$ isomers (a) HOOOBr, (b) HOOBrO, (c) $HOBrO_2$, and (d) $HBrO_3$. The values given are at the B3LYP/6-311++G(3df,3pd) level of theory. See Table 1 for the complete list of geometrical parameters.

structure was verified to be the minimum-energy structure with no imaginary vibrational frequencies. It is interesting to compare the O−O and O−O′ bond lengths in HOOOBr of 1.425 and 1.378 Å, respectively, with the O−O bond in HOOBr of 1.405 Å.[26] The bonding between the two species is quite similar. Using the B3LYP method, the HOO and OO′Br angles are predicted to be 102.0° and 111.7°, respectively. The OOO angle (109.0°) is smaller than the OO′Br angle (111.7°) due to the greater amount of repulsion between the lone pairs of electrons on bromine with those on oxygen, compared to the repulsion occurring between the lone pairs of electrons on the two oxygen atoms. The H−O bond length (0.970 Å) is much smaller than the O−O and O−O′ bond lengths, because there is a larger overlap between the 1s orbital of the small hydrogen atom and the 2p orbital of oxygen, compared to the overlap between the 2p orbitals of the two oxygen atoms. On the other hand, there is poorer overlap between the 3d orbitals of the large bromine atom with the 2p orbital of the oxygen atom, compared to the overlap between the 2p orbitals of two oxygen atoms, making the O′−Br bond length larger than the O−O and O−O′ lengths. It is interesting to compare the O−O bond length of HOOOBr with that of the stratospherically important molecule HOOOCl.[27,28] Our calculations using the B3LYP method yielded an O−O′ bond length of 1.378 Å, which is smaller than the O−O′ bond length in HOOOCl (1.404 Å) calculated by Francisco and Sander[29] using the MP2/6-311G(2df,2p) level of theory.

The second isomeric form we considered is HOOBrO. This, too, is a straight-chain structure but with the oxygen as the terminal atom. Like in the HOOOBr structure, we found the planar conformers to be rotational transition states. The minimum-energy structure for HOOBrO is a nonplanar skew structure (Figure 1b). The dihedral angle between the HOOBr atoms is 95.6° while that between the OOBrO′ is 78.1°. The OBrO′ angle (110.5°) is a little smaller than the OOBr angle (112.0°). As in the case of HOOOBr, the HOO angle (102.4°) is much smaller than the OOBr angle (112.0°), due to the greater degree of replusion between the two lone pairs of electrons on bromine with those on the oxygen. The Br−O bond distance predicted at the B3LYP/6-311++G(3df,3pd) level is 1.916 Å,

TABLE 2: Total and Relative Energies for HBrO$_3$ Species

level of theory	HOOOBr	HOOBrO	HOBrO$_2$	HBrO$_3$
		total energies (hartrees)		
MP2/TZ2P	−2798.44486	−2798.42092	−2798.45519	−2798.34685
CISD/TZ2P	−2798.17805	−2798.13741	−2798.16038	−2798.05110
CCSD(T)/TZ2P	−2798.36006	−2798.32961	−2798.35215	−2798.24375
B3LYP/TZ2P	−2800.32389	−2800.29338	−2800.31065	−2800.19632
B3LYP/6-311++G(3df,3pd)	−2800.28705	−2800.26254	−2800.28768	−2800.17572
CCSD(T)/6-311++G(3df,3pd)// B3LYP/6-311++G(3df,3pd)	−2798.31875	−2798.29460	−2798.32687	−2798.22118
CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/TZ2P	−2798.31861	−2798.29443	−2798.32687	−2798.22126
		relative energies (kcal mol^{-1})[a]		
MP2/TZ2P	0.0	14.5	−7.0	60.2
CISD/TZ2P	0.0	25.0	10.6	81.0
CCSD(T)TZ2P	0.0	18.6	4.5	74.3
B3LYP/TZ2P	0.0	18.5	7.8	78.8
B3LYP/6-311++G(3df,3pd)	0.0	14.9	−0.9	68.6
CCSD(T)/6-311++G(3df,3pd)// B3LYP/6-311++G(3df,3pd)	0.0	14.6	−5.6	59.9
CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/TZ2P	0.0	14.6	−5.7	59.8

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

while at the B3LYP/TZ2P level it is a little larger (1.945 Å). This bond length is influenced by basis set effects. There is also a similar trend in the Br−O′ bond length with increased size of the basis set. Other structural parameters such as the H−O and O−O bond lengths are not vastly influenced by enlargement of basis set. The H−O length (0.969 Å) is smaller than the O−O length (1.415 Å) due to better overlap between the small 1s orbital of the hydrogen atom with the relatively larger 2p orbital of oxygen. For different levels of theory used, the Br−O lengths are greater than the Br−O′ lengths. The lone pairs of electrons on the terminal oxygen atom sometimes tend to enter into resonance with the Br−O′ bond pairs, due to which 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 hydrogen and the bromine atoms. Thus, the Br−O′ bond with its partial double-bond character is smaller (1.663 Å) than the Br−O single bond (1.916 Å).

The third isomeric form is HOBrO$_2$ (Figure 1c). There are noticeable structural changes that occur as a result of increasing basis set size. The OBrO′ angle decreases by 2.0° when going from the TZ2P to the 6-311++G(3df,3pd) basis set. The O−Br bond (1.844 Å) is much larger than the bonds formed between bromine and the terminal oxygen atoms. This is because the lone pairs on the terminal oxygen atoms enter into partial resonance with their immediate bonding electron neighbors, thus rendering a partial double-bond character to the bonds formed between bromine and the terminal oxygen atoms.

The fourth isomeric form is HBrO$_3$, possessing C_{3v} symmetry with the three oxygen atoms forming the base of the pyramid (Figure 1d). The Br−O bond in HBrO$_3$ is the shortest of the isomeric forms. This is due to the resonance associated with the Br═O multiple bonding characteristics of HBrO$_3$. Such an effect does not occur for HOOOBr and occurs only for the terminal oxygen atoms of HOOBrO and HOBrO$_2$. Resonance plays a much stronger role in HBrO$_3$ than it does in HOOBrO or HOBrO$_2$, making the Br═O double-bonded character more pronounced in HBrO$_3$ than in HOOBrO or HOBrO$_2$. The Br−O bond distance of 1.604 Å at the B3LYP/6-311++G(3df,3pd) level of theory is shorter than the terminal Br−O bonds in HOBrO$_2$ of 1.611 and 1.619 Å and that in HOOBrO of 1.663 Å. There is greater repulsion between the π-electrons of the Br═O bond in HBrO$_3$ and the lone pairs of electrons on bromine, those on the oxygen atoms, and the electrons of the Br−O bond. The overall structural values obtained by the B3LYP calculations are in good agreement with those obtained at the MP2, CISD, and CCSD(T) levels of theory.

2. Relative Energetics of HBrO$_3$ Isomers. Calculated relative energies for the four minimum-energy isomers of HBrO$_3$ are presented in Table 2. At the MP2/TZ2P and B3LYP/6-311++G(3df,3pd) levels of theory, the relative stability for HBrO$_3$ isomers from most unstable to most stable is (1) HBrO$_3$, (2) HOOBrO, (3) HOOOBr, and (4) HOBrO$_2$. However, at the CISD/TZ2P and the B3LYP/TZ2P levels of theory the relative energetic stability of the HBrO$_3$ isomers is (1) HBrO$_3$, (2) HOOBrO, (3) HOBrO$_2$, and (4) HOOOBr. The relative stability of the isomers is sensitive to electron correlation and basis set effects. For example, the difference between MP2/TZ2P and CCSD(T)/TZ2P relative energies between the HOOOBr and HBrO$_3$ structures is 14.1 kcal mol^{-1}. The relative energetic stability of HBrO$_3$ isomers is also sensitive to the type of basis set used. For example, comparing the skewed-chain structure of HOOOBr with the hypervalent HBrO$_3$, the B3LYP/TZ2P relative energy between the two structures is 78.8 kcal mol^{-1}. Using the large 6-311++G(3df,3pd) basis set with the B3LYP treatment, the relative energy decreases by ca. 10 kcal mol^{-1}.

The two lowest energy structures on the HBrO$_3$ potential energy surface across all levels of theory are the HOBrO$_2$ and the HOOOBr skewed-chain structure. With both the TZ2P and the 6-311++G(3df,3pd) basis sets the HOBrO$_2$ structure is the lowest energy structure, and it is more stable than HOOOBr by 7.0 and 0.9 kcal mol^{-1}, respectively, at the MP2 and B3LYP levels. At the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level, the HOBrO$_2$ isomer is more stable by only 5.6 kcal mol^{-1}.

At the B3LYP/6-311++G(3df,3pd) level the HOOOBr−HOOBrO relative energy, at 0 K, is 14.9 kcal mol^{-1}. This energy difference is significantly smaller than that found for the analogous chlorine compounds[30] (19.3 kcal mol^{-1}, 0 K), which is consistent with an earlier observation that bromine hypervalent oxide compounds are less stable relative to their chlorinated counterparts.[31] On the other hand, the HBrO$_3$ isomer is predicted to be 68.6 kcal mol^{-1} (0 K) less stable than HOOOBr, which is a much larger energy difference than that found[28,29] for HOOOCl−HClO$_3$ (42.7 kcal mol^{-1}, 0 K). The much higher energy for the HBrO$_3$ isomer is due to the loss of the very strong H−O bond.

The accuracy of the relative energetic data provided in Table 2 can also be assessed by calculating the heats of formation of each of the HBrO$_3$ isomers. There are two methods that provide reasonable estimates of the heats of formation of the isomers that are not computationally prohibitive. The first method employs isodesmic reactions, and the second method uses G1 and G2 theories to estimate the heats of formation. Isodesmic reactions, which have been used to obtain heats of formation for many molecules, are those in which the reactants and

TABLE 3: Isodesmic Heat of Reaction and Heat of Formation of HOOOBr

	total energies (hartrees)				rel energies $\Delta H^0_{r,0}$ (kcal mol^{-1})	
level of theory	HOH	HOBr	HOOH	HOOOBr	HOOOBr + 2HOH → 2HOOH + HOBr	HOOOBr
CCSD(T)/TZ2P	−76.312 00	−2648.318 61	−151.317 51	−2798.360 06	21.2	20.0
B3LYP/6-311++G(3df,3pd)	−76.464 51	−2649.956 29	−151.613 19	−2800.287 05	23.1	18.1
CCSD(T)/6-311++G(3df,3pd)// B3LYP/6-311++G(3df,3pd)	−76.337 42	−2648.238 07	−151.361 11	−2798.318 75	23.0	18.2
CCSD(T)/6-311++G(3df,3pd)// CCSD(T)/TZ2P	−76.337 46	−2648.238 05	−151.360 97	−2798.318 61	23.1	18.1

TABLE 4: Heats of Formation (kcal mol^{-1}) for $HBrO_3$ Species

				CCSD(T)/6-311++G(3df,3pd)//	
species	G1	G2	B3LYP/6-311++G(3df,3pd)	B3LYP/6-311++G(3df,3pd)	CCSD(T)/TZ2P
$HOBrO_2$	6.5	5.7	17.2	12.6	12.4
HOOOBr	13.2	13.6	18.1	18.2	18.1
HOOBrO	25.8	26.2	33.0	32.8	32.7
$HBrO_3$	72.2	71.6	86.7	78.1	77.9

products contain the same types of bonds (i.e., the number of bonds broken and formed is conserved). Such a scheme of reactions requires that the heats of formation of all the molecules involved in the reaction be known, with the exception of the heat of formation of the particular isomer. Because of this property, errors in the energy that might occur due to defects in the basis set and electron correlation cancel to a large extent. The isodesmic scheme used here is HOOOBr + 2HOH → 2HOOH + HOBr. In the calculation of the heat of formation of HOOOBr from the isodesmic scheme, literature values for the heats of formation of HOH (−57.10 ± 0.10 kcal mol^{-1}),[31] HOOH (−31.02 ± 0.05 kcal mol^{-1}),[31] and HOBr (−10.93 ± 1 kcal mol^{-1})[32] are used. Using these results, we are able to calculate the heat of reaction for the isodesmic reaction. The results appear to be insensitive to both basis set and electron correlation effects, as shown in Table 3.

For HOOOBr the heat of formation is predicted to be 18.1 kcal mol^{-1} at the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/TZ2P level, while it is 18.2 kcal mol^{-1} at the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level. Using the relative energies in Table 3 along with the heat of formation of HOOOBr determined using the isodesmic results for the heats of formation of the $HBrO_3$ isomers, we obtain a value of 17.2 kcal mol^{-1} for $HOBrO_2$, 33.0 kcal mol^{-1} for HOOBrO, and 86.7 kcal mol^{-1} for $HBrO_3$. To assess these results further, we have G1 and G2 determinations of the heats of formation for $HBrO_3$ isomers, given in Table 4. The G1 result for the heat of formation of HOOOBr is 13.2 kcal mol^{-1}, and considering the G1 method uncertainties of 3 kcal mol^{-1}, the isodesmic and G1 results deviate by 5 kcal mol^{-1}. To improve the heats of formation, we have determined values using the G2 method. The G2 results show that the heat of formation of HOOOBr is 13.6 kcal mol^{-1}. The deviation is still quite large, being 5 kcal mol^{-1}. The G2 heats of formation for the other isomers are also separately listed in Table 4 along with the heats of formation of the $HBrO_3$ isomers determined by using the B3LYP/6-311++G(3df,3pd), CCSD(T)/6-311++G(3df,3pd)// B3LYP/6-311++G(3df,3pd), and the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/TZ2P methods. A comparison of the values of the heats of formation obtained by the G2 method with the values obtained by the other methods shows that the G2 heats of formation are not reliable estimates. The G2 results proved to be unreliable for the $XBrO_2$ isomers (X = H, Cl, Br),[26] because the geometry is poorly represented at the UMP2/6-31G(d) level of theory. We note that the G2 method values predict the same order of stability for the $HBrO_3$ isomers, as does the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/TZ2P method.

The analysis provided here suggests that the lowest energy $HBrO_3$ isomer is $HOBrO_2$. The skewed-chain HOOOBr structure is higher in energy by 5.6 kcal mol^{-1}. The two species, HOOBrO and $HBrO_3$, are higher in energy by 20.2 and 65.5 kcal mol^{-1}, respectively. The $HBrO_3$ isomer possesses the highest energy and thus has the least stability. The stability of the $HBrO_3$ isomers is consistent with the order of stability for $HClO_3$ isomers determined by Francisco and Sander.[29]

A comparison of the heats of formation of the $HBrO_3$ isomers with the $HBrO_2$ isomeric forms[26] at the CCSD(T)/B3LYP level of theory shows that the heats of formation of the $HBrO_3$ species are, in general, higher than those of the $HBrO_2$ species. The heat of formation of HOOBr at the CCSD(T)/B3LYP level of calculation is 8.6 kcal mol^{-1}, and it increases almost by a factor of 10 kcal mol^{-1} when another oxygen atom is placed in between the oxygen and bromine atoms of HOOBr to give HOOOBr. The same trend in increasing heat of formation is seen when an oxygen in placed in between the oxygen (attached to the hydrogen) and bromine in HOBrO to give HOOBrO. The heat of formation of $HBrO_2$ is the highest among the $HBrO_2$ isomeric forms (63.7 kcal mol^{-1}). If another oxygen atom is attached to the bromine atom of $HBrO_2$, the heat of formation increases by more than 10 kcal mol^{-1} to form $HBrO_3$ with a 78.1 kcal mol^{-1} heat of formation. Thus, the $HBrO_2$ isomers, having lower heats of formation relative to the $HBrO_3$ isomers, are more stable. The addition of another atom of moderate size affects the internal bonding pattern and thus the stability of the species quite remarkably.

B. Spectroscopic Characterization of $HBrO_3$ Isomers. The calculated vibrational frequencies and intensities for the four isomeric forms of $HBrO_3$ are provided in Table 5. All vibrational frequencies noted in the table are calculated at the B3LYP level of theory using the 6-311++G(3df,3pd) basis set.

In the prediction of the vibrational frequencies of HOOOBr, the most intense bands are predicted to be the H−O stretch,ν_1 (3713 cm^{-1}), and the HOOO torsion, ν_7 (395 cm^{-1}), while the least intense bands are ν_5 (584 cm^{-1}) and ν_9 (131 cm^{-1}). The Br−O′ stretch (517 cm^{-1}) occurs at a lower frequency than the H−O and O−O stretches and is consistent with the Br−O′ bond length being larger than the lengths of the H−O and O−O bonds. The harmonic frequencies of HOOOBr are very similar to those obtained by Francisco and Sander[29] for HOOOCl, except that the Br−O stretch is predicted to occur at a lower frequency than the Cl−O stretch and the BrOO bend is predicted

TABLE 5: Vibrational Frequencies (cm^{-1}) and Intensities ($km\ mol^{-1}$) for $HBrO_3$ Isomers

			B3LYP/6-311++G(3df,3pd)	
species	mode no.	mode descriptn	freq	int
HOOOBr	1	HO str	3713	57
	2	HOO bend	1398	43
	3	OO str	914	53
	4	OO′ str	743	34
	5	OOO′ bend	584	4
	6	BrO′ str	517	16
	7	HOOO torsion	395	70
	8	BrOO bend	285	26
	9	BrOOO torsion	131	5
HOOBrO	1	HO str	3724	66
	2	HOO bend	1396	4
	3	OO str	899	44
	4	BrO sym bend	845	95
	5	BrO asym str	481	4
	6	H-wag	405	86
	7	BrOO bend	281	1
	8	OBrO bend	208	14
	9	torsion	105	4
$HOBrO_2$	1	HO str	3708	106
	2	HOBr bend	1086	55
	3	BrO asym str	952	140
	4	BrO sym str	898	38
	5	O′Br str	549	122
	6	OBrO bend	382	27
	7	OBrO′ bend	322	24
	8	OBrO′ bend	278	13
	9	H-wag	121	73
$HBrO_3$	1	HBr str	2154	21
	2	BrO sym str	863	16
	3	umbrella	388	41
	4	BrO asym str	966'	119
	5	HBrO bend	880'	2
	6	OBrO bend	344'	17

[a] A single prime denotes a double degenerate mode.

to occur at a lower frequency than the ClOO bend. Both of these observations are consistent with the larger mass of the bromine atom relative to the chlorine atom. The modes involving bromine in HOOOBr are smaller in their IR intensities compared to the analogous modes involving chlorine. The ν_2 mode (HOO bend) is similar to the HOO bend in HOOH.[33] The BrOO bend, ν_8, agrees quite well with the torsional frequency of HOOH.[33] This information should be useful in the assignment of the experimental spectrum of HOOOBr. However, it also points to some potential experimental problems that could hinder the assignment of the HOOOBr spectrum. If HOOH is used as a precursor to produce HOOOBr, the absorption bands, ν_1 and ν_3, of HOOH could overlap the most intense bands of HOOOBr and, in that process, obscure its identification. The band that would allow HOOH to be clearly distinguished from HOOOBr is ν_9.

The harmonic frequencies of the HOOBrO and $HOBrO_2$ isomers are somewhat lower relative to their chlorinated counterparts (HOOClO and $HOClO_2$). This is probably due to the fact that the chlorine or bromine atom is involved in most of the normal modes due to its almost central, multibonded position in these isomers. For HOOBrO the most intense bands predicted at the B3LYP level of theory are ν_4 (845 cm^{-1}) and ν_6 (405 cm^{-1}), and the least intense band is the BrOO bend at ν_7 (281 cm^{-1}). The H−O stretch (3724 cm^{-1}) has a much larger frequency than the Br−O stretch, since the H−O bond is much shorter than the BrO bond (see Table 1). For $HOBrO_2$ the most intense bands are ν_3 (952 cm^{-1}) and ν_5 (549 cm^{-1}) while the least intense is the ν_8 band (278 cm^{-1}). The modes that are most useful in distinguishing HOOBrO from HOOOBr experimentally are ν_4 and ν_5. HOOOBr can be clearly distinguished from $HOBrO_2$ by the ν_2 mode.

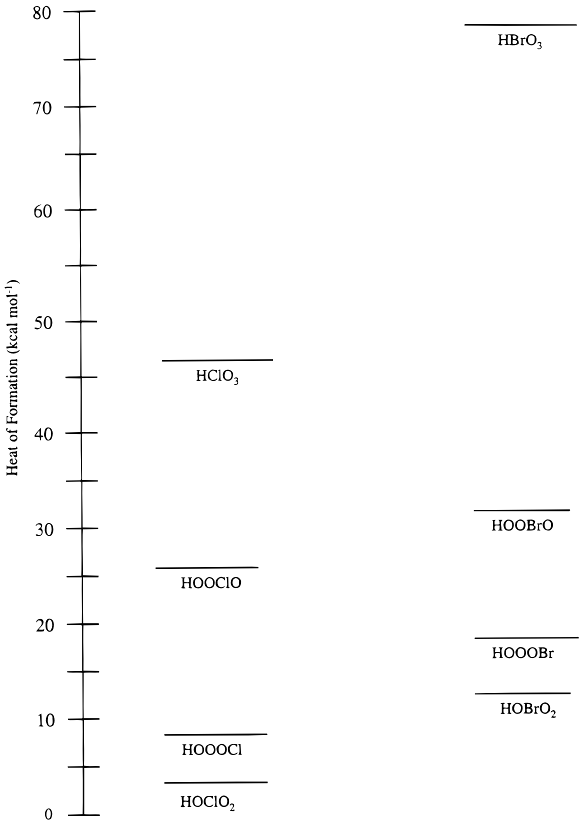

Figure 2. Relative energies of HXO_3 isomers (where X = Cl, Br).

For the $HBrO_3$ isomeric form, the most intense band is the Br−O asymmetric stretch occurring at 966 cm^{-1}. The least intense band is the HBrO bend occurring at 880 cm^{-1}. The H−Br stretch has a much larger frequency (2154 cm^{-1}) than the Br−O symmetric and asymmetric stretches, since the length of the H−Br bond is smaller than the length of the Br−O bond (Table 1). The H−Br stretch in $HBrO_3$ is comparable to the H−Br stretch in the $HBrO_2$ isomer.[26] The BrOOO torsion mode in HOOOBr (131 cm^{-1}) is the mode that can clearly distinguish $HBrO_3$ from HOOOBr.

Another spectroscopic property that is useful and important in the characterization of the electronic spectrum of $HBrO_3$ isomers is the vertical excitation energy for each of the isomers. 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.[23] 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 $HBrO_3$ isomers are provided in Table 6.

Examination of the predicted electronic spectra of the two lowest energy $HBrO_3$ structures, $HOBrO_2$ and HOOOBr, reveals that there are certain features that could allow these two species to be characterized. For HOOOBr the first excited state located at 3.8 eV has a 0.0002 relative oscillator strength and consequently should be quite weak, but the singlet state with the most oscillator strength is the excited state located at 6.7 eV. A

TABLE 6: Calculated Vertical Excitation Energies and Oscillator Strengths[a] for $HBrO_3$ Isomers and a Comparison with $HClO_3$ Isomers[b]

	state 1		state 2		state 3	
species	Δ*E* (eV)	*F*(rel)	Δ*E* (eV)	*F*(rel)	Δ*E* (eV)	*F*(rel)
HOOOCl	5.3	0.0	5.8	1×10^{-4}	7.6	3.94×10^{-2}
HOOOBr	3.8	2×10^{-4}	4.6	5×10^{-4}	6.7	2.2×10^{-1}
HOOClO	4.1	3×10^{-4}	6.2	0.0	6.4	1.86×10^{-2}
HOOBrO	3.6	4×10^{-4}	4.9	2×10^{-4}	5.4	6.3×10^{-3}
$HOClO_2$	7.1	6.59×10^{-2}	7.8	1.99×10^{-2}	8.4	2.2×10^{-3}
$HOBrO_2$	6.2	3.86×10^{-2}	6.9	1.29×10^{-2}	7.1	2.4×10^{-3}
$HClO_3$	9.2	0.0	10.1	0.0	10.3	1.772×10^{-1}
$HBrO_3$	6.9	0.0	7.5	6.2×10^{-3}	7.5	6.2×10^{-3}

[a] Obtained at the CIS level of theory using the B3LYP/6-311++G(3df,3pd) geometries with the 6-311++G(3df,3pd) basis set for $HBrO_3$. [b] Data for $HClO_3$ taken from ref 30.

comparison of the oscillator strengths of HOOOBr with HOOOCl shows that the relative oscillator strengths for HOOOBr are greater than those for HOOOCl. The first excited state of $HOBrO_2$ that should have a strong absorption band is located at 6.2 eV. The first excited state for $HBrO_3$ is located at 6.9 eV; however, this state has zero oscillator strength and thus should be very weak. The second and third excited states of the $HBrO_3$ isomer appear to have the same relative oscillator strengths. For $HBrO_3$ isomers there is a tentative shift toward the red region in the electronic spectrum relative to the $HClO_3$ isomers. It appears that bromination red-shifts the electronic features. This has important atmospheric chemical implications in that photolysis may be an important removal process for these compounds.

C. Comparison of Relative Stability of the HXO_3 Isomers (Where X = Cl, Br). Figure 2 shows a comparison of the relative energetic stability of the $HBrO_3$ isomers with that of $HClO_3$, calculated by Francisco and Sander.[29] Such a comparison clearly indicates that the most stable isomer is $HOClO_2$ with a 4.2 kcal mol^{-1} heat of formation, and the least stable isomer is $HBrO_3$ with a 78.1 kcal mol^{-1} heat of formation. The next in stability after $HOClO_2$ is HOOOCl. It is very important to consider the form of bonding within each isomer and the types of linkages in which each isomer is involved to gain a proper insight into the relative stability and instability among the isomers. In general, when a bromine atom replaces a chlorine atom, the higher 3d orbitals of bromine play a major part in the process of bonding and impart a greater amount of energy to the molecule, thus lowering its stability. Chlorine has no 3d orbitals to affect its bonding process with other atoms lying next to it within the molecule and only uses its 3p orbitals (which possess much lower energy than 3d orbitals). Thus, in general, the $HClO_3$ isomers are more stable than the $HBrO_3$ isomers. The $HOBrO_2$ isomer lies above the $HOClO_2$ isomer on the energy scale, since the isomer becomes less stable as the chlorine atom is replaced by the bromine atom. It is relatively easier to break apart the O−Br bond than it is to break the O−Cl bond, so the HOOBrO isomer (with its 32.8 kcal mol^{-1} heat of formation) is less stable than the HOOClO isomer (25.3 kcal mol^{-1} heat of formation). The overlap between the 2p orbitals of the oxygen atoms is quite strong in HOOOCl, compared to the overlap between the 2p orbitals of oxygen with the 3p orbitals of chlorine in $HOClO_2$, and thus the HOOOCl isomer possesses higher energy than the $HOClO_2$ isomer. In general, the $HBrO_3$ isomers are unstable relative to their chlorine analogues.

D. Comparison with Experiments. There have not been many experiments conducted on the $HBrO_3$ isomers to determine their reaction pathways. Mellouki et al.[14] in their analysis of the HO_2 + BrO reaction assumed that the forward and reverse processes occurred as elementary reactions. Their studies showed a negative temperature dependence for the HO_2 + BrO reaction and suggested the possibility that the process may be a complex reaction. For example, if the HO_2 and BrO reactants formed a long-lived [O_2H.BrO] complex that reacted with O_2 to form HBr + O_2 + O_3 products, the overall processes would be a sequence of two elementary steps. However, this scheme seemed unlikely, as it was doubtful that the HO_2 and BrO radicals would form a long-lived complex. They then concluded that a complex with the oxygen on the HO_2 bound to the Br or O atoms on BrO, [HO_2·BrO], would seem to be the most stable arrangements. Larichev et al.[11] also considered the formation of a complex with different possible structures for the BrO + HO_2 reaction:

$$BrO + HO_2 \rightarrow BrOHOO \text{ or } HOOBrO \text{ or } HOOOBr \quad (9)$$

Mellouki et al.[14] suggested that HOBr may be produced either from the BrOHOO adduct via a simple hydrogen atom transfer mechanism or from the HOOBrO adduct after a five-membered ring formation. The cyclization of the HOOOBr complex would have to be necessary to produce HBr. It is clear from the observed negative temperature dependence of the HOBr channel that the potential energy surfaces are qualitatively similar to the chlorine system. In this study of the reaction pathways on the $HBrO_3$ potential energy surface, we found a new channel. The new channel

$$HO_2 + BrO \rightarrow [HOOBrO]^* \rightarrow HO + BrOO \rightarrow HO + O_2 + Br \quad (10)$$

may be a direct source of bromine atoms. The pathway to produce HO + BrOO is exothermic by 3.7 kcal mol^{-1}. The BrOO radical is bound by about 2.0 kcal mol^{-1}. Assuming that the excess energy goes into BrOO, the heavier fragment, it is enough to break the weak Br−O bond to produce Br atoms and O_2. Thus, the HOBr formation channel (reaction 3) may not be the only channel for the formation of bromine atoms. The bromine atoms produced by reaction 10 can reenter into the catalytic ozone destruction cycle.

$$HO_2 + BrO \rightarrow HO + O_2 + Br \qquad \Delta H^0_{r,298} = -1.7 \text{ kcal mol}^{-1} \quad (11)$$

To our knowledge there is no experimental evidence that this

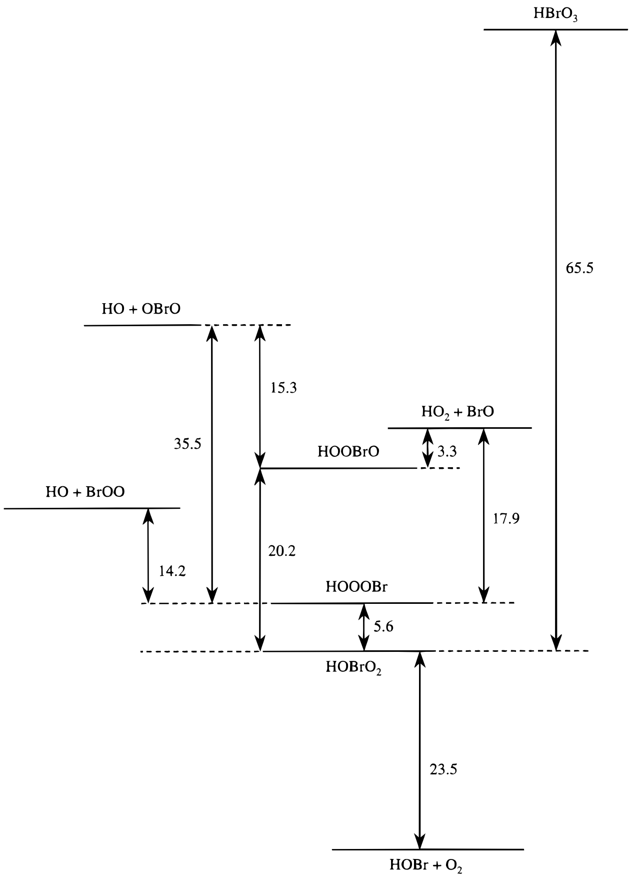

Figure 3. Relative energy diagram for $HBrO_3$ reaction pathways, as calculated at the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/TZ2P level of theory.

pathway occurs. We note that this pathway is unlikely in the HO_2 + ClO system, because it is endothermic by 9.4 kcal mol^{-1}.

The relative energy diagram for the $HBrO_3$ isomer reaction pathways is shown in Figure 3. The most likely dissociation products for the $HOBrO_2$ isomer are the HO and OBrO radicals. The HOOOBr isomeric form is quite stable, and its process of dissociation would require 14.2 kcal mol^{-1} energy. The dissociation products for the HOOOBr isomer would most likely be HO + BrOO rather than HO_2 + BrO, since the formation of the HO + BrOO radicals requires less energy than the formation of the HO_2 + BrO radicals. If the HOOBrO isomer was to dissociate, it would most likely produce HO_2 + BrO rather than HO + OBrO radicals, since it is energetically unfavorable to break the strong O−O bond. The $HBrO_3$ isomer is the least stable of all the isomers with a 65.5 kcal mol^{-1} energy relative to $HOBrO_2$.

IV. Summary

The equilibrium structures, vibrational and electronic spectra, relative energetics, and heats of formation of the $HBrO_3$ isomers have been investigated with the MP2, CISD, CCSD(T), and B3LYP ab initio electronic structure methods in conjugation with the TZ2P and 6-311++G(3df,3pd) basis sets. The $HOBrO_2$ structure is found to be the most stable among the isomers, while the $HBrO_3$ isomeric form is found to be the least stable. Due to the thermal stability of $HOBrO_2$ and HOOOBr, it is possible that these isomers may play roles in the atmospheric cross-reactions of HO_x and BrO_x species. A comparison of the relative stability of the $HBrO_3$ isomers with the isomers of $HClO_3$[29] shows that the $HBrO_3$ isomers follow the same pattern of stability among themselves, as do the $HClO_3$ isomers.

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