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# A Density Functional Study of the Structure, Vibrational Spectra, and Relative Energetics of $XBrO_2$ Isomers (Where X = H, Cl, and Br)

**Sujata Guha and Joseph S. Francisco***

*Department of Chemistry and Department of Earth & Atmospheric Sciences, Purdue University, West Lafayette, Indiana 47907-1393*

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The geometries, vibrational spectra, and relative energies of $HBrO_2$, $ClBrO_2$, and $BrBrO_2$ isomers have been examined using various density functional (BLYP, SVWN, and B3LYP) methods. A comparison of the density functional results for $HBrO_2$ isomers with singles and doubles coupled-cluster theory which incorporates a perturbational estimate of the effects of connected triples excitation [CCSD(T)] shows that B3LYP results are in excellent agreement in predicting the geometries, vibrational spectra, and relative energies and should yield reasonable results for $ClBrO_2$ and $BrBrO_2$ isomers. The results also show interesting trends for $HBrO_2$, $ClBrO_2$, and $BrBrO_2$ isomers. The peroxide form, XOOBr, is found to be the lowest energy structure among the isomers. The heats of formation at 0 K for HOOBr, ClOOBr, and BrOOBr are estimated to be 8.6, 38.9, and 46.1 kcal $mol^{-1}$, respectively. Increase in halogenation tends to destabilize the peroxide thermodynamically. We examine the implication for the formation of $XBrO_2$ isomers from atmospheric cross reactions of $HO_x$, $ClO_x$, and $BrO_x$ species.

## I. Introduction

One of the key reactions in processes leading to the catalytic destruction of stratospheric ozone by halogen oxides is the self-reaction of the halogen oxides via

$$XO + XO \rightarrow 2X + O_2 \qquad (1)$$

or by cross halogen oxide reaction via

$$XO + YO \rightarrow X + Y + O_2 \qquad (2)$$

The key halogens are chlorine and bromine, which not only destroy ozone but also inhibit ozone formation by sequestering oxygen atoms in the halogen oxide forms. 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. Bromine is present in atmospheric aerosol particles, precipitation, seawater, and organisms in seawater. Other sources of bromine are methyl bromide, tetrabromobisphenol A (used as a flame retardant in circuit boards), and trifluoromethyl bromide (used as a fire retardant and refrigerant). Once released into the atmosphere, chlorine and bromine species are very effective in depleting ozone.

The general catalytic process in which the halogen oxides destroy ozone is as follows:

$$X + O_3 \rightarrow XO + O_2 \qquad (3)$$

$$XO + XO \rightarrow 2X + O_2 \qquad (4)$$

$$X + O_3 \rightarrow XO + O_2 \qquad (5)$$

$$\text{Net: } 2O_3 \rightarrow 3O_2 \qquad (6)$$

Studies indicate that the FO + FO reaction does not play a significant role in atmospheric photochemistry, as the concentration of FO is too low.[1] However, the chlorine and bromine oxides have the ability to form weakly bound complexes that could play dominant roles in the atmosphere.

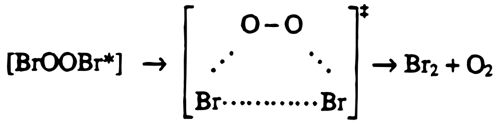
It has been hypothesized that the initial step in reactions of halogen oxides leading to ozone depletion is the probable formation of a transient XOOX or XOXO intermediate which can then decompose to form $X_2$ and $O_2$, i.e.

$$XO + XO \rightarrow [XOOX^*] \rightarrow X_2 + O_2 \qquad (7)$$

$$\rightarrow [XOXO^*] \rightarrow X_2 + O_2 \qquad (8)$$

The rates of these reactions, and thus their importance, are governed by the rates at which the intermediates are formed and by the stabilities and rates of decomposition of these intermediates. For example, the dimer of the ClO radical is stable by less than 19 kcal $mol^{-1}$, yet it is responsible for major ozone loss over Antarctica.

Various experimental studies have been conducted on the BrO + BrO reaction channel by Clyne and Watson,[2] by Clyne and Coxon,[3] and by Basco and Dogra,[4] who have used different techniques to determine the rate constant for the overall rate of removal of BrO. Agreement among these studies for the disappearance of BrO is poor, with values of the rate constant at 298 K ranging from $0.65 \times 10^{-12}$ to $5.2 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. None of these studies have attempted to analyze the stability of the BrOOBr intermediate. Sander and Watson[1] used the flash photolysis−UV absorption technique to measure the rate constant for the BrO + BrO reaction over the temperature range 223−338 K and the pressure range 50−475 Torr of He. They hypothesized that the unstable BrOOBr could form a cyclic four−center BrOOBr complex before decomposing into its products, i.e.



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Mauldin et al.[5] examined the BrO + BrO reaction at 220 K and observed a species that was bounded by at least 5 kcal $mol^{-1}$ which they attribute to BrOOBr.

A theoretical study by Yung et al.[6] has shown that of all the catalytic cycles involving bromine species, the most effective in terms of ozone destruction is the one which involves a synergistic (mixed) disproportionation reaction between BrO and ClO as its rate-determining step:

$$\mathrm{BrO + ClO \rightarrow Br + Cl + O_2} \qquad (10)$$

The kinetics of the ClO + BrO reaction have been studied experimentally by Friedl and Sander,[7-9] Turnipseed et al.,[10] and Poulet et al.[11] Three product channels were observed:

$$\mathrm{ClO + BrO \rightarrow Br + ClOO} \qquad (11)$$

$$\mathrm{\rightarrow Br + OClO} \qquad (12)$$

$$\mathrm{\rightarrow BrCl + O_2} \qquad (13)$$

They hypothesized that the inverse temperature dependences of the observed rate coefficients for each of the reaction channels strongly indicate that the reaction of ClO + BrO proceeds via formation of metastable intermediates:

$$\mathrm{ClO + BrO \rightarrow [ClOOBr^*]} \qquad (14)$$

$$\mathrm{\rightarrow [ClOBrO^*]} \qquad (15)$$

By invoking the existence of short−lived intermediates, the temperature dependences can be rationalized in terms of competition between product formation and reactant re-formation during dissociation of the intermediates. On the basis of the absence of a pressure dependence in the observed rate constants, Sander and Friedl[9] concluded that decomposition of the intermediates is substantially faster than stabilization due to collision of the reactants. Consequently, the formation of a long-lived $ClBrO_2$ molecule in the atmosphere is not likely.

The hydroxyl radical is present in reasonable abundance in the atmosphere, and so the reaction between BrO and OH is possible, i.e.

$$\mathrm{BrO + OH \rightarrow HBr + O_2} \qquad (16)$$

$$\mathrm{\rightarrow Br + HO_2} \qquad (17)$$

It is possible that each of these reactions proceeds through the formation of an unstable HOOBr intermediate. There have been some recent *ab initio* studies performed by Lee[12] on the isomers of $HBrO_2$ which suggest that HOOBr is the lowest energy structure of all the $HBrO_2$ isomers. His study was motivated by the fact that previous studies by Francisco et al.[13] predicted the HOOCl molecule to be stratospherically significant.

It is, thus, important to undertake a study of the $XBrO_2$ isomers (X = H, Cl, Br) in order to understand the reaction mechanism of the halogen oxides, and the pathways through which such oxides react to form their products. The purpose of this paper is to present an in-depth study of the isomers of $HBrO_2$, $ClBrO_2$, and $BrBrO_2$. There are three plausible connectivities for $HBrO_2$ isomers: (1) HOOBr, (2) HOBrO, and (3) $HBrO_2$; six plausible connectivities for $ClBrO_2$ isomers: (1) ClOOBr, (2) ClOBrO, (3) BrOClO, (4) $ClBrO_2$, (5) $BrClO_2$, and (6) OBrClO; and three plausible connectivities for $BrBrO_2$ isomers: (1) BrOOBr, (2) BrOBrO, and (3) $BrBrO_2$. Isolation of these complexes of $XBrO_2$ isomers is a challenge in the laboratory because of the lack of information on where to look for these short-lived species. In this paper we present *ab initio* molecular orbital results of the structure, vibrational spectra, relative energetics, and heats of formation of the $XBrO_2$ isomers (X = H, Cl, Br). That information could be useful in aiding the experimental characterization of these important intermediates. From a review of the energetics and the reaction pathways resulting in the formation and eventual degradation of the $XBrO_2$ isomers, we elucidate the role that such compounds could play and the extent to which they participate in stratospheric chemical processes.

## II. Computational Methods

*Ab initio* molecular orbital calculations are performed using the GAUSSIAN 94 program.[14] All equilibrium geometries are fully optimized to better than 0.001 Å for bond distances and 0.1° for bond angles. The BLYP, SVWN, and B3LYP density functional methods are used with the large 6-311++G(3df,3pd) basis set. The harmonic vibrational frequencies, and intensities of all the species are calculated with the BLYP, SVWN, and B3LYP levels of theory in conjugation with the 6-311++G(3df,3pd) basis set, using the geometries calculated at these levels of theory. The heats of formation of HOOBr, ClOOBr, and BrOOBr are determined using isodesmic reactions and are compared to heats of formation estimated using G2 theory. Details of the G2 method are described elsewhere.[15,16]

## III. Results and Discussion

**A. $HBrO_2$ Isomers.** *1. Geometries and Vibrational Frequencies.* Computations on the isomeric forms, HOOBr, HOBrO, and $HBrO_2$, were previously performed by Lee[12] using the CCSD(T) method in conjunction with a TZ2P one-particle basis set. We have reexamined these structures using the 6-31l++G(3df,3pd) basis set in conjugation with the BLYP, SVWN, and B3LYP levels of theory. Significant structural changes occur when the BLYP and SVWN levels of theory are used. At the B3LYP level, our calculated structures of the $HBrO_2$ isomers agree very well with those reported by Lee.[12] This suggests that the results obtained from the B3LYP/6-31l++G(3df,3pd) geometry are quite reasonable.

The ground-state geometry for HOOBr is given in Table 1. From computations, the minimum-energy structure for HOOBr appears to be skewed (Figure 1a). The HOOBr dihedral angle at the B3LYP/6-311++G(3df,3pd) level of theory is predicted to be 90.1°. Lee[12] obtained a similar result (90.8°) at the CCSD(T)/TZ2P level of theory. Using the B3LYP method, the HOO and BrOO angles are predicted to be 102.6° and 111.2°, respectively. These values are in close agreement with the HOO angle (100.6°) and the BrOO angle (109.3°) values obtained by Lee using the CCSD(T) method. The computed HOO angle is smaller than the BrOO angle. This can be explained by the fact that the HOO angle is a result of the repulsion between two lone pairs of electrons on the oxygen that is attached to the hydrogen, and the bond pairs surrounding the oxygen atom. The hydrogen atom does not have any lone pairs of electrons on it which can repel the lone pairs of electrons on oxygen. The formation of the BrOO angle is influenced not only by the repulsions between the two lone pairs of electrons on the oxygen atom (attached to bromine) and its surrounding bond pairs but also those between the three lone pairs of electrons on bromine and the bonding electron pairs surrounding them, which tend to widen the bond angle. It is interesting to compare the O−O bond length of HOOBr with that of the stratospherically important molecule HOOCl and its precursor, HOOH. Our calculations using the B3LYP method yield an O−O bond length of 1.405 Å, which is smaller than the O−O bond length in HOOCl (1.423 Å) calculated by Francisco et al.[13] using the

**TABLE 1: Computed Geometries (Å and deg) and Energies (hartrees) Using the 6-311++G(3df,3pd) Basis Set for $HBrO_2$ Isomers**

| species | coordinate/energy | BLYP | SVWN | B3LYP | CCSD(T)/ TZ2P[a] |
|---|---|---|---|---|---|
| HOOBr | BrO | 1.954 | 1.883 | 1.887 | 1.884 |
| | OO | 1.425 | 1.374 | 1.405 | 1.446 |
| | HO | 0.982 | 0.982 | 0.970 | 0.967 |
| | BrOO | 112.0 | 111.6 | 111.2 | 109.3 |
| | HOO | 102.2 | 103.2 | 102.6 | 100.6 |
| | BrOOH | 89.2 | 88.0 | 90.1 | 90.8 |
| | energy | −2 725.116 56 | −2 721.567 76 | −2 725.115 25 | −2 723.235 55 |
| HOBrO | BrO | 1.918 | 1.834 | 1.851 | 1.868 |
| | BrO′ | 1.695 | 1.652 | 1.665 | 1.676 |
| | HO | 0.979 | 0.978 | 0.968 | 0.967 |
| | HOBr | 103.9 | 104.6 | 105.3 | 103.5 |
| | OBrO′ | 110.9 | 109.5 | 109.3 | 110.0 |
| | HOBrO′ | 79.2 | 81.0 | 79.0 | 79.0 |
| | energy | −2 725.110 14 | −2 721.565 22 | −2 725.104 98 | −2 723.219 81 |
| $HBrO_2$ | HBr | 1.555 | 1.543 | 1.515 | 1.503 |
| | BrO | 1.669 | 1.629 | 1.640 | 1.645 |
| | HBrO | 100.1 | 110.0 | 100.0 | 100.2 |
| | OBrO | 114.4 | 113.8 | 113.7 | 114.4 |
| | $HBrO_2$ | −106.1 | −105.7 | −105.7 | |
| | energy | −2 725.027 11 | −2 721.488 52 | −2 725.019 68 | −2 723.131 89 |
| HOOH | HO | 0.977 | 0.975 | 0.965 | |
| | OO | 1.487 | 1.425 | 1.446 | |
| | HOO | 99.6 | 101.0 | 100.8 | |
| | HOOH | 113.7 | 110.8 | 112.4 | |
| | energy | −151.597 41 | −150.886 36 | −151.613 19 | |
| HOBr | HO | 0.977 | 0.975 | 0.966 | |
| | BrO | 1.880 | 1.819 | 1.843 | |
| | HOBr | 102.5 | 103.2 | 103.7 | |
| | energy | −2 649.952 97 | −2 646.763 74 | −2 649.956 29 | |
| HOH | HO | 0.970 | 0.968 | 0.961 | |
| | HOH | 104.3 | 104.9 | 105.1 | |
| | energy | −76.447 70 | −76.097 81 | −76.464 51 | |

[a] Reference 12.

MP2/6-311G(2d,2p) level of theory, and the O−O bond length in HOOH (1.446 Å) predicted by our B3LYP/6-31l++G(3df,3pd) calculations. The dihedral angles of the three species are comparable, with values of 90.1° for HOOBr, 88.2° for HOOCl, and 112.4° for HOOH. The skewed structure of HOOBr was verified to be the minimum-energy structure (see Table 2).

The second isomeric form we considered is HOBrO. This is a straight-chain structure with oxygen as the terminal atom. The minimum-energy structure for HOBrO is the structure shown in Figure 1b. The dihedral angle between HOBrO′ atoms is 79.0° at the B3LYP level of theory. The OBrO′ angle (109.3°) is a little larger than the HOBr angle (105.3°). This can be explained by considering the repulsions between the lone pairs and bond pairs of electrons, the repulsive effect being greater between the lone pairs on bromine, the bond pairs surrounding bromine, and the lone pairs on the two oxygens attached to bromine, that lead to the production of the OBrO′ angle, as compared to the repulsive effect between the lone pairs on the oxygen atom attached to the hydrogen, the bond pairs surrounding the oxygen, and the lone pairs on bromine, resulting in the formation of the HOBr angle. The hydrogen atom (in the HOBr angle) does not play a significant part in the repulsive effect due to the lack of lone electron pair(s) on the hydrogen. At the B3LYP level the Br−O bond distance is 1.851 Å. When other levels of theory (BLYP and SVWN) are used, the values for the Br−O bond length either overestimate or underestimate the bond distances (Table 1). The Br−O and Br−O′ bond lengths show similar trends, since, at the SVWN level of theory the value of each is a little lower than the corresponding values at the BLYP, B3LYP, and CCSD(T) levels. 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 bromine atoms. Thus, the Br−O′ bond (with its partial double-bond character) is smaller than the Br−O single bond [Br−O (1.868 Å) versus Br−O′ (1.676 Å)]. Overall, the B3LYP/6-311++G(3df,3pd) values for the geometry of HOBrO′ agree well with the CCSD(T)/TZ2P values obtained by Lee.[12]

The third isomeric form is $HBrO_2$, having $C_s$ symmetry. It has an H−Br bond length of 1.515 Å and a Br−O bond length of 1.640 Å, as predicted at the B3LYP/6-311++G(3df,3pd) level of theory. The Br−O bond in $HBrO_2$ appears to be the shortest of the isomeric forms. This is because of the Br═O multiple bonding characteristics that occur in $HBrO_2$ due to one of the three lone pairs of electrons on an oxygen atom entering into resonance with the Br−O bonding electrons. Such an effect does not occur for HOOBr and occurs only for the terminal oxygen atom of HOBrO. Resonance plays a much stronger role in $HBrO_2$ than it does in HOBrO, making the Br═O double-bonded character more pronounced in $HBrO_2$ than in HOBrO. Thus, the Br−O bond distance of 1.640 Å in $HBrO_2$ is smaller than the terminal Br−O′ bond distance of 1.665 Å in HOBrO′. There is greater repulsion between the $\pi$-electrons of the Br═O bond in $HBrO_2$ and the lone pairs of electrons on bromine, those on the oxygen atoms, and the electrons of the Br−O bond, which results in the wider OBrO angle (113.7°). The HBrO angle (100.0°) is relatively smaller, since there the repulsion occurs primarily between the lone pairs of electrons on bromine and its surrounding bond pairs. The hydrogen atom does not have any lone pairs of electrons, so it does not contribute much to the resonance effect. Here again, the overall structural values for $HBrO_2$, obtained by our B3LYP calculations, are in good agreement with the CCSD(T) values.

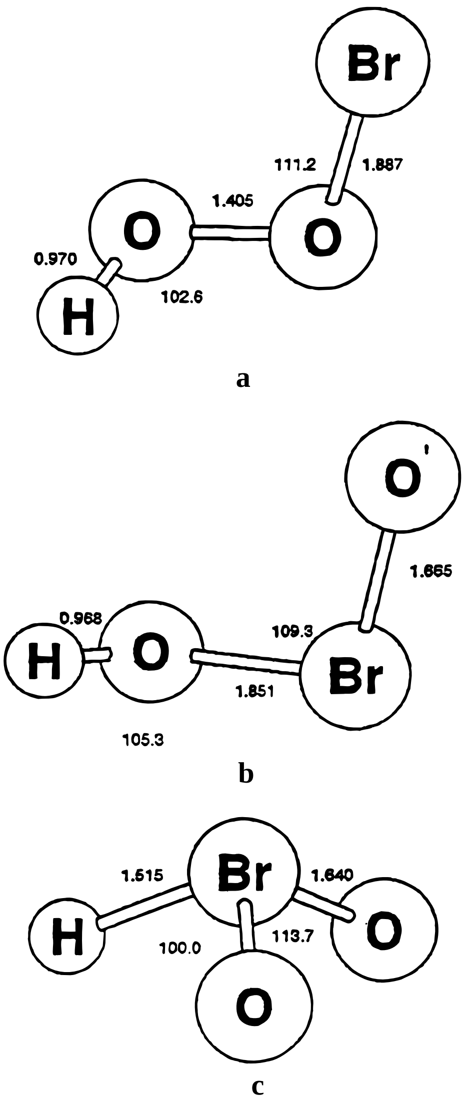

**Figure 1.** Minimum energy structures for $HBrO_2$ isomers (a) HOOBr, (b) HOBrO′, and (c) $HBrO_2$. The values given are at the B3LYP/6-311+G(3df,3d) level of theory. See Table 1 for the complete list of geometrical parameters.

The calculated vibrational frequencies of the three isomers of $HBrO_2$ are provided in Table 2. All vibrational frequencies noted in the table are calculated at the BLYP, SVWN, and B3LYP levels of theory using the 6-311++G(3df,3pd) basis set. To establish a degree of confidence in the various levels of calculation, we have compared our calculated values of vibrational frequencies and intensities with the CCSD(T)/TZ2P values obtained by Lee.[12] The B3LYP values appear to agree very well with the CCSD(T) values.

In the prediction of the vibrational frequencies of HOOBr, the most intense bands are predicted to be $\nu_3$ (903 $cm^{-1}$) and $\nu_5$ (422 $cm^{-1}$), and the least intense band is $\nu_6$ (305 $cm^{-1}$). The Br−O stretch 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 H−O and O−O bond lengths. The harmonic frequencies of HOOBr are very similar to those obtained by Francisco et al.[13] and by Lee and Rendell[17] for HOOCl, 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 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 HOOBr are smaller in their IR intensities compared to the analogous modes involving chlorine. The $\nu_2$ mode (HOO bend) is similar to the bend in HOOH.[13] The torsion mode, $\nu_6$, calculated by the B3LYP level of theory, agrees reasonably well with the torsional frequency of HOOH.[13] This information should be useful in the assignment of the experimental spectrum of HOOBr. However, it also points to some potential experimental problems that could block the assignment of the HOOBr spectrum. If HOOH is used as a precursor for the production of HOOBr, the absorption bands, $\nu_3$ and $\nu_5$, of HOOH could overlap the most intense bands of HOOBr, thus obscuring its identification. In this case, the band which would allow the two species to be clearly distinguished is the $\nu_4$ (580 $cm^{-1}$) mode, which is the Br−O stretch of HOOBr.

The harmonic frequencies of the HOBrO and $HBrO_2$ isomers are somewhat lower relative to their chlorine counterparts. This is probably due to the fact that the chlorine or bromine atom is involved in most of the normal modes due to its central, multibonded position in these isomers. Intense bands for HOBrO predicted at the B3LYP level of theory, are the H−O stretch mode, $\nu_1$ (3761 $cm^{-1}$), and the OBrO′ bend mode, $\nu_5$ (362 $cm^{-1}$). The H−O stretch has a much larger frequency than the Br−O′ and Br−O stretches, since the H−O bond is

**TABLE 2: Vibrational Frequencies for $HBrO_2$ Isomers Using the 6-311++G(3df,3pd) Basis Set**

| basis set | | | | frequencies ($cm^{-1}$) | | | | intensities (km $mol^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| species | symmetry | mode no. | mode description | BLYP | SWVN | B3LYP | CCSD(T)[a] | BLYP | SWVN | B3LYP | CCSD(T)[a] |
| HOOBr | a | 1 | HO stretch | 3538 | 3568 | 3706 | 3745 | 35 | 39 | 44 | 41 |
| | | 2 | HOO bend | 1344 | 1372 | 1410 | 1391 | 38 | 39 | 43 | 46 |
| | | 3 | OO stretch | 826 | 937 | 903 | 828 | 110 | 113 | 80 | 42 |
| | | 4 | BrO stretch | 512 | 575 | 580 | 568 | 52 | 41 | 19 | 10 |
| | | 5 | BrOO bend | 441 | 458 | 422 | 379 | 61 | 79 | 88 | 92 |
| | | 6 | torsion | 275 | 300 | 305 | 298 | 10 | 13 | 5 | 2 |
| HOBrO | a | 1 | HO stretch | 3614 | 3665 | 3761 | 3772 | 68 | 98 | 89 | 77 |
| | | 2 | HOBr bend | 1040 | 1063 | 1119 | 1127 | 47 | 54 | 49 | 42 |
| | | 3 | BrO′ stretch | 787 | 881 | 838 | 818 | 43 | 52 | 50 | 40 |
| | | 4 | BrO stretch | 475 | 587 | 563 | 517 | 62 | 78 | 73 | 67 |
| | | 5 | OBrO′ bend | 365 | 394 | 362 | 377 | 91 | 98 | 103 | 104 |
| | | 6 | torsion | 222 | 251 | 253 | 235 | 4 | 4 | 4 | 4 |
| $HBrO_2$ | a′ | 1 | HBr stretch | 1733 | 1865 | 2022 | 1977 | 154 | 116 | 94 | 124 |
| | | 2 | BrO stretch, sym | 782 | 869 | 841 | 834 | 21 | 31 | 19 | 4 |
| | | 3 | OBrO bend | 753 | 794 | 822 | 810 | 9 | 1 | 14 | 28 |
| | | 4 | $HBrO_2$ umbrella | 296 | 316 | 320 | 307 | 12 | 13 | 16 | 18 |
| | a″ | 5 | BrO stretch, asym | 849 | 933 | 921 | 920 | 80 | 125 | 66 | 34 |
| | | 6 | HBrO bend | 806 | 825 | 854 | 855 | 48 | 13 | 64 | 85 |

[a] Reference 12, the CCSD(T) frequencies are calculated with the TZ2P basis set.

**TABLE 3: G2 and CCSD(T) Energies for $HBrO_2$ Isomers**

| species | G2 energy (hartrees) | CCSD(T)/6-311++G(3df,3pd)[a] |
|---|---|---|
| HOOBr | −2 723.304 32 | −2 723.271 23 |
| HOBrO | −2 723.299 74 | −2 723.262 76 |
| $HBrO_2$ | −2 723.220 48 | −2 723.179 86 |
| HOBr | −2 648.258 55 | −2 648.238 07 |
| HOOH | −151.365 78 | −151.361 11 |
| HOH | −76.332 05 | −76.337 42 |

[a] Calculated using B3LYP/6-311++G(3df,3pd) geometry.

**TABLE 4: Relative Energies for $HBrO_2$ Isomers**

| | method[a] | | | | | |
|---|---|---|---|---|---|---|
| relative energy | BLYP | SVWN | B3LYP | CCSD(T)/ B3LYP | G2 | CCSD(T)/ ANO4[b] |
| HOOBr−HOBrO | 3.4 | 1.1 | 5.7 | 4.6 | 2.9 | 4.2 |
| HOOBr−$HBrO_2$ | 49.7 | 47.1 | 57.2 | 55.1 | 52.6 | 53.8 |
| $\Delta H°_{f,o}$(HOOBr) | 5.2 | 4.6 | 8.1 | 8.6 | 7.8 | 10.5 ±1.0 |

[a] All methods used the 6-311++G(3df,3pd) basis set. [b] Reference 12.

much shorter than the Br−O′ and Br−O bonds (see Table 1). For $HBrO_2$, the most intense bands are the H−Br stretch mode, $\nu_1$ (2022 $cm^{-1}$) and the Br−O asymmetric stretch, $\nu_5$ (921 $cm^{-1}$), and the least intense band is $\nu_3$ (822 $cm^{-1}$). The modes that are most useful in experimentally distinguishing HOBrO′ from HOOBr are $\nu_2$, $\nu_3$, and $\nu_5$.

*2. Energetics.* Calculated G2 and CCSD(T) energies for $HBrO_2$ isomers, given in Table 3, and calculated relative energies (see Table 4) for the three stable isomers of $HBrO_2$, show that the lowest energy is possessed by the HOOBr skew structure. The next lowest energy structure is that of the HOBrO isomer, which is consistent with the fact that the H−O bond energy is usually quite high. The highest energy isomer is $HBrO_2$, and it is thus the least stable. The relative stability of the $HBrO_2$ isomers depends on the type of arrangement of atoms in the molecule. When the two oxygen atoms lie next to each other in the interior of the molecule, the stability is maximum. As bromine atoms begin replacing the oxygen atoms, the higher 3d orbitals of bromine start playing significant roles in the bonding pattern, and thus the stability of the molecule decreases. With the B3LYP/6-31l++G(3df,3pd) basis set, the HOBrO isomer appears to be 5.7 kcal $mol^{-1}$ higher in energy than the HOOBr isomer, but this energy difference decreases to 3.4 kcal $mol^{-1}$ using the BLYP method, and further decreases to 1.1 kcal $mol^{-1}$ when the SVWN method is used. Using the B3LYP/6-311++G(3df,3pd) geometries to calculate single-point energies at the CCSD(T)/6-311++G(3df,3pd) level of theory, we find that the HOBrO isomer appears to be 4.6 kcal $mol^{-1}$ higher in energy than the HOOBr isomer.

At the B3LYP level the HOOBr−HOBrO relative energy, at 0 K, is 5.7 kcal $mol^{-1}$. This energy difference is significantly smaller than that found for the analogous chlorine compounds[13,17] (8.3 kcal $mol^{-1}$, 0 K), which is consistent with an earlier observation that bromine hypervalent oxide compounds are more stable relative to their chlorinated counterparts.[18] On the other hand, the $HBrO_2$ isomer is predicted to be 57.2 kcal $mol^{-1}$ (0 K) less stable than HOOBr, which is a slightly larger energy difference than that found[6] for HOOCl−$HClO_2$, (51.0 kcal $mol^{-1}$, 0 K). The much higher energy for the $HBrO_2$ isomer is due to the loss of the very strong H−O bond.

There are two methods that provide reasonable estimates of the heat of formation of HOOBr that are not computationally prohibitive. The first method employs isodesmic reactions, and the second method uses G2 theory to estimate the heat of formation. Isodesmic reactions which have been used to obtain heats of formation for many molecules are those in which the reactants and products contain the same types of bonds (i.e., the number of bonds broken and formed are conserved) and require 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 HOOBr + HOH → HOBr + HOOH. In the calculation of the heat of formation of HOOBr from the isodesmic scheme, literature values for the heats of formation of HOH,[19] HOOH,[19] and HOBr[20] are used. The heat of formation of HOOBr at the B3LYP/6-311++G(3df,3pd) level of theory is 8.1 kcal $mol^{-1}$, which is in reasonable agreement with the value calculated by Lee (10.5 kcal $mol^{-1}$) using the CCSD(T)/ANO4 method. At the CCSD(T)/6-311++G-(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory the estimated heat of formation of HOOBr is 8.6 kcal $mol^{-1}$. The G2 heats of formation for HOOBr, at 0 K, are also listed in Table 4. Using the G2 approach, the heat of formation of HOOBr is predicted to be 7.8 kcal $mol^{-1}$. This value agrees well with the results obtained by using the B3LYP/6-31l++G-(3df,3pd) method and is consistent with the results predicted by the CCSD(T)/ANO4 method. Combination of the heat of formation of HOOBr with the best values for HOOBr−HOBrO relative energy and HOOBr−$HBrO_2$ relative energy leads to 13.2 and 63.7 kcal $mol^{-1}$ as our best estimates of heat of formation for HOBrO and $HBrO_2$, respectively, as determined at the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,-3pd) level of theory. These values are in very good agreement with Lee's values.[12]

In fact, a comparison of the rms (root-mean-square) errors in the B3LYP, G2, and CCSD(T) predictions show that the rms errors are 3.1, 2.3, and 1.7 kcal $mol^{-1}$, respectively, for the methods relative to Lee's results.[12] The CCSD(T) results have better uncertainties in the estimated heats of formation over the B3LYP and G2 methods.

**B. $ClBrO_2$ Isomers.** *1. Geometries and Vibrational Frequencies.* We have examined the isomeric forms ClOOBr, ClOBrO, BrOClO, $ClBrO_2$, $BrClO_2$, and OBrClO using the 6-31l++G(3df,3pd) basis set in conjugation with the BLYP, SVWN, and B3LYP levels of theory. Because the B3LYP/6-31l++G(3df,3pd) method yielded reasonable results for the $HBrO_2$ isomers and were consistent with the CCSD(T)/TZ2P results obtained by Lee,[12] we use the B3LYP/6-311++G(3df,-3pd) method for predicting the properties of the uncharacterized $ClBrO_2$ isomers.

The ground-state geometry of ClOOBr is given in Table 5. Computations indicate that the minimum-energy structure for ClOOBr is skewed (Figure 2a). The ClOOBr dihedral angle at the B3LYP/6-311++G(3df,3pd) level of theory is predicted to be 86.0°, and this agrees reasonably well with the values of the ClOOBr dihedral angle obtained by using the BLYP (85.4°) and SVWN (81.6°) methods. The values for the other structural parameters calculated by the B3LYP method agree quite well with those calculated by the SVWN and BLYP methods. The BrOO angle (112.8°) is a bit larger than the ClOO angle (111.8°). There are two lone pairs of electrons on each oxygen atom which enter into similar modes of repulsive effects with their neighboring bond pairs. However, bromine (being larger than chlorine) repels the lone electron pair on oxygen more than chlorine does, resulting in a larger BrOO angle.

The second isomeric structure we considered is ClOBrO, which is a straight-chain structure having oxygen as the terminal atom. The minimum-energy structure of ClOBrO is shown in Figure 2b. The dihedral angle between the ClOBrO′ atoms is

**TABLE 5: Computed Geometries (Å and deg) and Energies (hartrees) Using the 6-311++G(3df,3pd) Basis Set for ClBrO$_2$ Isomers**

| species | coordinate/ energy | BLYP | SVWN | B3LYP |
|---|---|---|---|---|
| ClOOBr | ClO | 1.939 | 1.809 | 1.757 |
| | OO | 1.278 | 1.272 | 1.347 |
| | BrO | 2.070 | 1.958 | 1.914 |
| | BrOO | 115.4 | 113.7 | 112.8 |
| | ClOO | 114.4 | 112.8 | 111.8 |
| | BrOOCl | 85.4 | 81.6 | 86.0 |
| | energy | −3 184.691 35 | −3 180.004 29 | −3 184.685 61 |
| ClOBrO | BrO | 1.983 | 1.863 | 1.892 |
| | BrO′ | 1.694 | 1.649 | 1.659 |
| | ClO | 1.724 | 1.685 | 1.699 |
| | ClOBr | 117.0 | 115.9 | 115.7 |
| | OBrO′ | 112.4 | 110.8 | 110.4 |
| | ClOBrO′ | 81.2 | 80.0 | 80.0 |
| | energy | −3 184.671 34 | −3 179.987 11 | −3 184.667 02 |
| BrOClO | ClO | 1.618 | 1.558 | 1.679 |
| | ClO′ | 1.516 | 1.476 | 1.498 |
| | BrO | 2.097 | 2.027 | 1.895 |
| | BrOCl | 118.2 | 117.1 | 116.2 |
| | OClO′ | 116.6 | 115.7 | 113.6 |
| | BrOClO′ | 83.6 | 81.9 | 79.2 |
| | energy | −3 184.673 03 | −3 179.997 24 | −3 184.669 08 |
| OBrClO | OBr | 1.720 | 1.666 | 1.684 |
| | BrCl | 2.729 | 2.379 | 2.570 |
| | OCl | 1.574 | 1.516 | 1.537 |
| | ClBrO | 110.4 | 115.1 | 107.3 |
| | OClBr | 111.8 | 118.4 | 111.6 |
| | OBrClO | −180.0 | −87.6 | −180.0 |
| | energy | −3 184.647 09 | −3 179.964 01 | −3 184.633 43 |
| ClBrO$_2$ | ClBr | 2.393 | 2.274 | 2.315 |
| | BrO | 1.648 | 1.609 | 1.613 |
| | ClBrO | 104.6 | 103.5 | 103.7 |
| | OBrO | 111.9 | 111.5 | 111.3 |
| | ClBrO$_2$ | −112.7 | −110.7 | −111.0 |
| | energy | −3 184.684 59 | −3 180.008 13 | −3 184.677 26 |
| BrClO$_2$ | BrCl | 2.499 | 2.352 | 2.416 |
| | ClO | 1.477 | 1.442 | 1.445 |
| | BrClO | 115.1 | 114.7 | 114.7 |
| | OClO | 105.3 | 104.4 | 104.7 |
| | BrClO$_2$ | −115.6 | −113.7 | −114.2 |
| | energy | −3 184.683 41 | −3 180.017 93 | −3 184.680 04 |
| HOCl | HO | 0.977 | 0.976 | 0.966 |
| | ClO | 1.737 | 1.675 | 1.699 |
| | HOCl | 102.3 | 103.5 | 103.6 |
| | energy | −536.000 06 | −534.511 82 | −536.022 04 |

predicted to be 80.0° at the B3LYP level of theory. Similar to the case of HOBrO′, there are lone pairs of electrons on the terminal oxygen atom which tend to enter into resonance with the Br−O′ bonding electrons, imparting a partial double-bond character to the Br−O′ bond. This effect results in the Br−O′ bond (1.659 Å) being much smaller than the Br−O bond (1.892 Å), since, in the case of the Br−O bond, the oxygen atom lies between chlorine and bromine, and the lone pairs on the oxygen do not resonate with their surrounding bond pairs. The Br−O bond length (1.892 Å) is much greater than the Cl−O bond length (1.699 Å) because of valence shell expansion that occurs on going from chlorine to bromine. The ClOBr angle (115.7°) is greater than the OBrO′ angle (110.4°) because not only does pronounced repulsion occur between the lone pairs of electrons on the large chlorine and bromine atoms, but also there is repulsion between the two lone electron pairs on oxygen and those on chlorine and bromine, leading to the formation of the ClOBr angle. In comparison, the repulsion that occurs between the lone pairs of electrons on the two smaller oxygen atoms and the bromine atom, leading to the formation of the OBrO′ angle, is much smaller. The repulsion is further reduced in OBrO′, because one of the lone pairs of electrons on oxygen enters into resonance with the bonding electrons of Br−O′, and the repulsion between lone pairs and bond pairs is lesser compared to that between lone pairs alone.

The third isomeric structure is BrOClO. Similar to ClOBrO, BrOClO is a straight-chain isomer having oxygen as the terminal atom. The minimum-energy structure of BrOClO is shown in Figure 2c. The dihedral angle between BrOClO′ atoms obtained by the B3LYP level of theory is 79.2°, which is slightly less than the dihedral angle in ClOBrO′ of 80.0°. The terminal oxygen atom in BrOClO′ has lone pairs of electrons which tend to resonate with the electrons of the Cl−O′ bond, making the Cl−O′ bond attain a partial double-bond character. Thus, the Cl−O′ bond (1.498 Å) with its multiple bond character is much shorter than the Cl−O bond (1.679 Å) where there is no multiple bonding. The OClO′ angle (113.6°) is smaller than the BrOCl angle (116.2°) because there is greater repulsion between the lone pairs of electrons on the large bromine and chlorine atoms, compared to the amount of repulsion between the relatively smaller oxygen atoms. The smaller OClO′ angle is also due to the fact that the Cl−O′ is partly double bonded, and the lone pair/bond pair repulsions that occur between the reduced amount of lone electrons on oxygen and those of the Cl−O′ bond are less profound than those between the free lone pairs on chlorine and bromine (in case of BrOCl).

The fourth isomeric form, ClBrO$_2$, is of $C_s$ symmetry. It has a Cl−Br bond length of 2.315 Å, which is much larger than the Br−O bond length of 1.613 Å. This is due to the fact that, similar to the case of HBrO$_2$, the terminal oxygen atoms have electron pairs on them, and one of the electron pairs on oxygen enters into resonance with the electrons of the Br−O bond, giving the Br−O bond the characteristics of a double bond. Such multiple bonding does not exist for the Cl−Br bond. Due to its multiple bonding characteristics, the Br−O bond in ClBrO$_2$ is much smaller than the Br−O bonds in ClOOBr, ClOBrO, and BrOClO. The Br−O bond distance (1.613 Å) in ClBrO$_2$ is shorter than the terminal Br−O′ bond distance (1.659 Å) in ClOBrO because of resonance effects that occur between the lone pairs of electrons on the terminal oxygen atom and the Br−O bonding pairs in ClBrO$_2$, which are much more pronounced than the resonance that takes place between the lone electrons on the terminal oxygen of ClOBrO′ and the Br−O′ bond pairs. The OBrO angle (111.3°) in ClBrO$_2$ is larger than the ClBrO angle (103.7°) because there is greater repulsion between the lone pairs of electrons on the large bromine atom and those on oxygen, compared to the repulsion between the reduced number of electron pairs on the smaller double-bonded oxygen and the other oxygen atom.

The fifth isomeric form that we considered is BrClO$_2$, also having $C_s$ symmetry. The BrClO$_2$ isomer shows similar trends with those observed in the ClBrO$_2$ isomer. The Br−Cl bond length of 2.416 Å in BrClO$_2$ closely resembles the Cl−Br bond length of 2.315 Å in ClBrO$_2$, due to similar type of overlap between the orbitals of the chlorine and bromine atoms. The Cl−O bond length in BrClO$_2$ (1.445 Å) is much shorter than the Cl−O bond lengths in ClOOBr, ClOBrO, and BrOClO isomers, due to the Cl═O multiple bonding characteristics of BrClO$_2$ which do not occur for ClOOBr and only slightly occur for the terminal oxygen atoms of BrOClO and ClOBrO. The Cl−O bond distance in BrClO$_2$ is shorter than the Cl−O distance in BrOClO, due to the fact that resonance effects in BrClO$_2$ are more pronounced than resonance in BrOClO.

The sixth structural isomer is OBrClO, which has oxygen atoms at both terminals. At the B3LYP level of theory the dihedral angle between the OBrClO atoms is predicted to be 180.0°. There are three lone pairs of electrons on each of the terminal oxygen atoms which enter into resonance effects, due

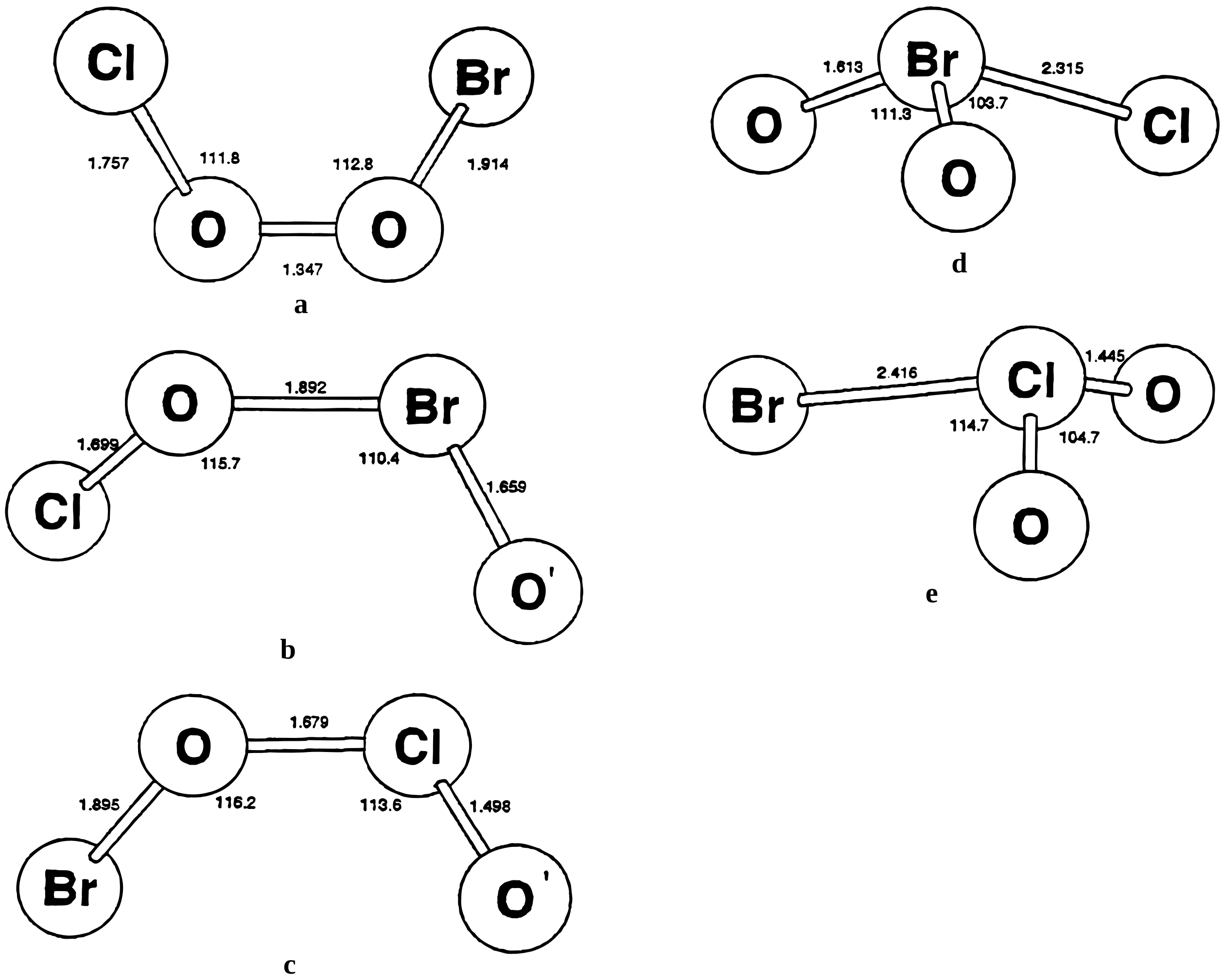

**Figure 2.** Minimum energy structures for $ClBrO_2$ isomers (a) ClOOBr, (b) ClOBrO′, (c) BrOClO′, (d) $ClBrO_2$, and (e) $BrClO_2$. The values given are at the B3LYP/6-311+G(3df,3pd) level of theory. See Table 5 for the complete list of geometrical parameters.

to which both the O−Br and the Cl−O bonds have a partial double-bond character. Thus, the O−Br bond length in OBrClO (1.684 Å) is smaller than the Br−O lengths in ClOOBr, ClOBrO, and BrOClO. Due to the same reason the O−Cl bond in OBrClO (1.537 Å) is noticeably shorter than the Cl−O bonds in ClOOBr, ClOBrO, and BrOClO. The O−Br bond in OBrClO is larger than the Cl−O bond because bromine has an expanded valence shell. The OClBr angle (111.6°) is greater than the ClBrO angle (107.3°) due to the pronounced repulsion between the lone pairs of electrons on oxygen and bromine.

The calculated vibrational frequencies for the five isomeric forms of $ClBrO_2$ are provided in Table 6. All vibrational frequencies are calculated at the BLYP, SVWN, and B3LYP levels of theory using the 6-31l++G(3df,3pd) basis set. On the basis of our comparison of frequencies of the BLYP, SVWN, and B3LYP levels with the CCSD(T)/TZ2P results for $HBrO_2$ isomers, the B3LYP calculations of the vibrational frequencies and intensities are the probable best estimates for the $ClBrO_2$ isomers.

In the prediction of the vibrational frequencies for ClOOBr, the most intense bands are predicted to be the O−O stretch (864 $cm^{-1}$) and the Cl−O stretch (602 $cm^{-1}$), and the least intense bands are the BrOO bend (280 $cm^{-1}$) and the torsion (110 $cm^{-1}$). Some of the frequency modes of ClOOBr are comparable with those of HOOBr. The O−O stretch in ClOOBr has a frequency value that is close to the O−O stretch in HOOBr (903 $cm^{-1}$) but slightly lower, due to the participation of the large Cl atom in bonding vibrations. The Br−O stretch in ClOOBr occurs at 533 $cm^{-1}$ and agrees quite well with the Br−O stretch in HOOBr occurring at 580 $cm^{-1}$. The BrOO bend in ClOOBr (280 $cm^{-1}$) is influenced by harmonic vibrations due to the presence of the large chlorine atom and is lower in frequency than the corresponding BrOO bend in HOOBr (422 $cm^{-1}$) which is strongly influenced by the vibrations occurring due to the presence of the small hydrogen atom. The frequency of the ClOO bend (412 $cm^{-1}$) in ClOOBr is close in value to the frequency of the BrOO bend (422 $cm^{-1}$) in HOOBr, due to which the two bends have a tendency of overlapping each other. The torsion mode (110 $cm^{-1}$) in ClOOBr allows ClOOBr to be clearly distinguished from HOOBr. The ClOO bend in ClOOBr is similar to the ClOO bend in HOOCl.[13] The absorption bands, $\nu_1$ and $\nu_5$, of ClOOBr have overlapping frequencies with the absorption bands of HOOCl.

The harmonic frequencies of the ClOBrO and BrOClO isomers are much lower than those of HOBrO, perhaps due to the fact that in ClOBrO and BrOClO the Cl/Br is partially double bonded to the terminal oxygen atom, and is involved in most of the normal modes. The Br−O′ stretch (859 $cm^{-1}$) in ClOBrO′ is comparable to the Br−O′ stretch (838 $cm^{-1}$) in HOBrO′. The Br−O stretch modes in ClOBrO′ (449 $cm^{-1}$) and in BrOClO′ (428 $cm^{-1}$) are comparable to the Br−O stretch in HOBrO′ (563 $cm^{-1}$). The larger Br−O frequency in HOBrO′ is influenced by the vibrational contribution of the small hydrogen atom, compared to the vibrations of the much larger chlorine and bromine atoms attached to the central oxygens in ClOBrO and BrOClO. The OBrO′ bend in ClOBrO′ (261 $cm^{-1}$) occurs at a lower frequency than the OBrO′ bend in HOBrO′

**TABLE 6: Vibrational Frequencies for $ClBrO_2$ Isomers Using the 6-311++G(3df,3pd) Basis Set**

| | | | | frequencies (cm$^{-1}$) | | | intensities (km mol$^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| species | symmetry | mode no. | mode description | BLYP | SWVN | B3LYP | BLYP | SWVN | B3LYP |
| ClOOBr | a | 1 | OO stretch | 1041 | 1064 | 864 | 109 | 91 | 40 |
| | | 2 | ClO stretch | 508 | 575 | 602 | 57 | 77 | 45 |
| | | 3 | BrO stretch | 481 | 523 | 533 | 23 | 20 | 14 |
| | | 4 | ClOO bend | 320 | 394 | 412 | 74 | 67 | 18 |
| | | 5 | BrOO bend | 242 | 280 | 280 | 7 | 7 | 1 |
| | | 6 | torsion | 89 | 106 | 110 | 0 | 0 | 0 |
| ClOBrO | a | 1 | BrO′ stretch | 791 | 888 | 859 | 48 | 57 | 59 |
| | | 2 | ClO stretch | 575 | 620 | 647 | 37 | 34 | 7 |
| | | 3 | BrO stretch | 332 | 441 | 449 | 7 | 8 | 19 |
| | | 4 | OBrO′ bend | 226 | 261 | 261 | 5 | 7 | 8 |
| | | 5 | ClOBr bend | 166 | 200 | 195 | 4 | 3 | 4 |
| | | 6 | torsion | 88 | 95 | 88 | 3 | 3 | 4 |
| BrOClO | a | 1 | ClO′ stretch | 962 | 1092 | 1013 | 112 | 123 | 125 |
| | | 2 | ClO stretch | 578 | 704 | 546 | 30 | 45 | 20 |
| | | 3 | BrO stretch | 377 | 417 | 428 | 7 | 9 | 5 |
| | | 4 | OClO′ bend | 296 | 355 | 348 | 39 | 63 | 12 |
| | | 5 | BrOCl bend | 183 | 224 | 235 | 67 | 55 | 8 |
| | | 6 | torsion | 112 | 115 | 104 | 3 | 1 | 2 |
| $ClBrO_2$ | a′ | 1 | BrO st, sym | 830 | 911 | 900 | 44 | 46 | 59 |
| | | 2 | OBrO bend | 336 | 357 | 367 | 12 | 14 | 15 |
| | | 3 | BrCl stretch | 297 | 346 | 333 | 62 | 79 | 82 |
| | | 4 | umbrella | 211 | 236 | 238 | 2 | 2 | 2 |
| | a″ | 5 | BrO st, asym | 881 | 965 | 955 | 87 | 101 | 104 |
| | | 6 | ClBrO bend | 170 | 186 | 193 | 1 | 1 | 2 |
| $BrClO_2$ | a′ | 1 | ClO st, sym | 944 | 1064 | 1043 | 127 | 132 | 179 |
| | | 2 | OClO bend | 465 | 501 | 512 | 10 | 10 | 13 |
| | | 3 | BrCl stretch | 362 | 415 | 407 | 45 | 68 | 64 |
| | | 4 | umbrella | 175 | 217 | 201 | 8 | 9 | 11 |
| | a″ | 5 | ClO st, asym | 1100 | 1230 | 1213 | 127 | 146 | 156 |
| | | 6 | BrClO bend | 186 | 214 | 213 | 0 | 0 | 1 |

(362 cm$^{-1}$). For ClOBrO, the most intense bands are predicted to be $\nu_1$ (859 cm$^{-1}$) and $\nu_3$ (449 cm$^{-1}$), and the least intense ones are $\nu_5$ (195 cm$^{-1}$) and $\nu_6$ (88 cm$^{-1}$). For BrOClO, the most intense bands are $\nu_1$ (1013 cm$^{-1}$) and $\nu_2$ (546 cm$^{-1}$). The ClOBr bends for both ClOBrO and BrOClO are comparable. The ClOBr bend for ClOBrO is slightly lower in frequency than the BrOCl bend in BrOClO, possibly due to differences in the orientation patterns of the halogens between the two oxygen atoms, and their effect in the bonding vibrations of the molecules. The Br−O symmetric stretch (900 cm$^{-1}$) and the Br−O asymmetric stretch (955 cm$^{-1}$) in $ClBrO_2$ are comparable to the Br−O symmetric and asymmetric stretches in $HBrO_2$. However, the OBrO bend (367 cm$^{-1}$) in $ClBrO_2$ is much lower than the OBrO bend (822 cm$^{-1}$) in $HBrO_2$, which is consistent with the vibrational contribution of the large chlorine atom in $ClBrO_2$, compared to that of the much smaller hydrogen atom in $HBrO_2$. The most intense bands of $ClBrO_2$ are predicted to be the Br−Cl stretch (333 cm$^{-1}$) and the Br−O asymmetric stretch (955 cm$^{-1}$), and those for $BrClO_2$ are predicted to be the Cl−O symmetric stretch (1043 cm$^{-1}$) and the Cl−O asymmetric stretch (1213 cm$^{-1}$). The Br−Cl stretches of $ClBrO_2$ and $BrClO_2$ are comparable, with the Br−Cl stretch of $ClBrO_2$ occurring at a slightly lower frequency than the similar form of stretch in $BrClO_2$. For both $ClBrO_2$ and $BrClO_2$ the $\nu_6$ mode appears to be the weakest IR absorber.

**TABLE 7: G2 and CCSD(T) Energies for $ClBrO_2$ Isomers**

| species | G2 energy (hartrees) | CCSD(T)/6-311++G(3df,3pd)[a] |
|---|---|---|
| ClOOBr | −3 182.396 85 | −3 182.335 20 |
| ClOBrO | −3 182.383 14 | −3 182.319 56 |
| BrOClO | −3 182.388 63 | −3 182.317 79 |
| $ClBrO_2$ | −3 182.392 98 | −3 182.330 96 |
| $BrClO_2$ | −3 182.384 33 | −3 182.326 08 |
| OBrClO | | −3 182.282 54 |

[a] Calculated using B3LYP/6-311++G(3df,3pd) geometry.

**TABLE 8: Relative Energies for $ClBrO_2$ Isomers Using the 6-311++G(3df,3pd) Basis Set**

| | method | | | | |
|---|---|---|---|---|---|
| relative energy | BLYP | SVWN | B3LYP | G2 | CCSD(T)/B3LYP |
| ClOOBr−ClOBrO | 11.9 | 10.2 | 11.3 | 8.6 | 9.4 |
| ClOOBr−BrOClO | 11.3 | 4.4 | 10.2 | 5.2 | 10.5 |
| ClOOBr−$ClBrO_2$ | 4.3 | −2.3 | 5.6 | 2.4 | 3.0 |
| ClOOBr−$BrClO_2$ | 5.8 | −7.6 | 4.6 | 7.8 | 6.8 |
| $\Delta H^\circ_{f,o}$(ClOOBr) | 29.0 | 28.9 | 38.2 | 36.7 | 38.9 |

*2. Energetics.* Calculated G2 energies for the $ClBrO_2$ isomers are given in Table 7. Calculated relative energies at the BLYP, SVWN, and B3LYP levels are given in Table 8. Relative energy calculations for the six isomers of $ClBrO_2$ show that the structure possessing the lowest energy is that of the ClOOBr isomer. The next lowest energy structure is that of the $BrClO_2$ isomer. The least stable isomer appears to be OBrClO. The order of relative stability of the $ClBrO_2$ isomers at the B3LYP level is ClOOBr > $BrClO_2$ > $ClBrO_2$ > BrOClO > ClOBrO > OBrClO. This is an interesting trend, and could be explained as follows: The ClOOBr isomer is the most stable (with the two oxygens bonded to each other via their 2p orbitals), consistent with the pattern of stability that was observed among the $HBrO_2$ isomers, with HOOBr being the most stable isomer. Looking at the trend of stability among the $HBrO_2$ isomers, it would be expected that the next in stability among the $ClBrO_2$ isomers would be either ClOBrO or BrOClO, with $ClBrO_2$ or $BrClO_2$ being the least stable. But such a trend is not observed. Instead, the second most stable $ClBrO_2$ isomer appears to be $BrClO_2$. Upon using the B3LYP/6-311++G(3df,3pd) basis set, the $BrClO_2$ isomer appears to be 4.6 kcal mol$^{-1}$ higher in energy than the ClOOBr isomer, and the ClOBrO isomer appears to be 11.3 kcal mol$^{-1}$ higher in energy relative to the ClOOBr isomer. At the CCSD(T)/6-311++G(3df,3pd) level the relative energetic ordering of $ClBrO_2$ and $BrClO_2$ changes. At this level the $ClBrO_2$ is more stable than the $BrClO_2$ isomer by 3.8 kcal mol$^{-1}$. The energetic ordering of BrOClO and ClOBrO also changes, with ClOBrO becoming more stable than BrOClO by

**TABLE 9: Computed Geometries (Å and deg) and Energies (hartrees) Using the 6-311++G(3df,3pd) Basis Set for $Br_2O_2$ Isomers**

| species | coordinate/ energy | BLYP | SVWN | B3LYP |
|---|---|---|---|---|
| BrOOBr | BrO | 2.082 | 1.973 | 1.922 |
| | OO | 1.280 | 1.264 | 1.335 |
| | BrOO | 115.6 | 113.9 | 113.3 |
| | BrOOBr | 84.4 | 79.2 | 85.6 |
| | energy | −5 298.644 56 | −5 292.256 72 | −5 298.619 08 |
| BrOBrO | BrO′ | 1.913 | 1.827 | 1.867 |
| | O′Br′ | 1.911 | 1.854 | 1.855 |
| | Br′O | 1.692 | 1.648 | 1.660 |
| | BrO′Br′ | 107.4 | 116.9 | 116.8 |
| | O′Br′O | 112.0 | 110.9 | 110.3 |
| | BrO′Br′O | 87.0 | 79.9 | 79.3 |
| | energy | −5 298.623 11 | −5 292.238 82 | −5 298.600 76 |
| $BrBrO_2$ | BrBr | 2.569 | 2.439 | 2.490 |
| | BrO | 1.653 | 1.613 | 1.618 |
| | BrBrO | 112.0 | 111.5 | 111.4 |
| | OBrO | 105.0 | 104.0 | 104.2 |
| | $BrBrO_2$ | −113.5 | −111.5 | −111.7 |
| | energy | −5 298.631 34 | −5 292.254 66 | −5 298.605 56 |

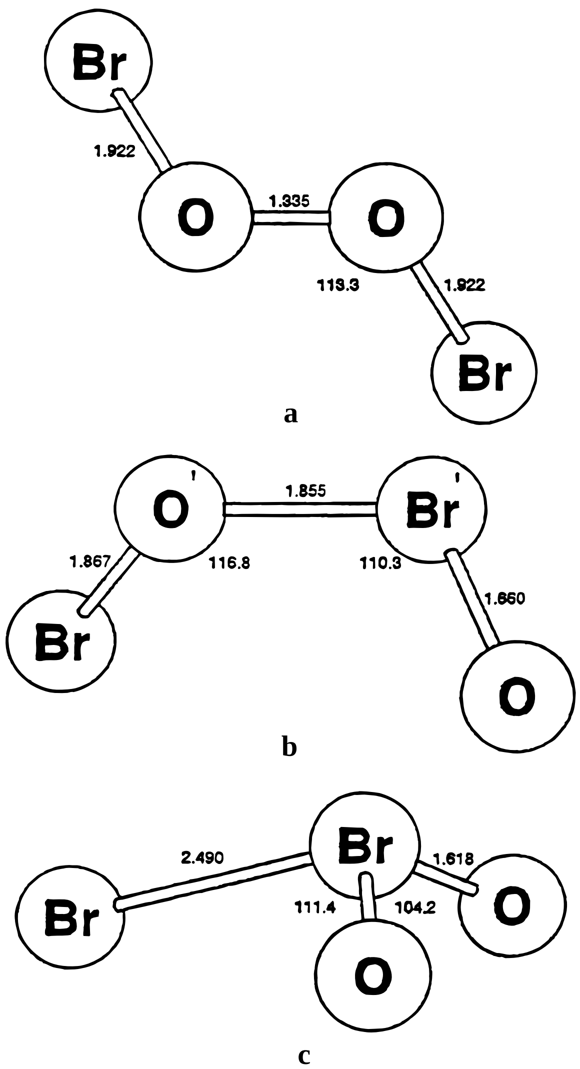

**Figure 3.** Minimum-energy structures for $BrBrO_2$ isomers (a) BrOOBr, (b) BrO′Br′O, and (c) $BrBrO_2$. The values given are at the B3LYP/6-311+G(3df,3pd) level of theory. See Table 9 for the complete list of geometrical parameters.

1.1 kcal mol$^{-1}$. The facts that $ClBrO_2$ is more stable than $BrClO_2$ and ClOBrO is more stable than BrOClO are consistent with earlier observations[18] that ClBrO is more stable than BrClO. We also performed calculations on the OBrClO isomer and found this isomer to be 33 kcal mol$^{-1}$ above the ClOOBr isomer. Consequently, OBrClO may not have atmospheric chemical importance. At the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory the relative stability of the $ClBrO_2$ isomers is ClOOBr > $ClBrO_2$ > $BrClO_2$ > ClOBrO > BrOClO > OBrClO.

An isodesmic scheme can be used to calculate the heats of formation of the $ClBrO_2$ isomers. The reaction employed here is ClOOBr + 2HOH → HOBr + HOCl + HOOH. In the calculation of the heat of formation of ClOOBr from the isodesmic scheme, literature values for the heats of formation of HOH,[19] HOOH,[19] HOCl,[20] and HOBr[20] are used. Our best computed heat of formation of ClOOBr is 38.9 kcal mol$^{-1}$ at the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory. The G2 heats of formation of the isomers of $ClBrO_2$ are also listed in Table 8. Using the G2 approach, the heat of formation of ClOOBr is predicted to be 36.7 kcal mol$^{-1}$, and this value is consistent with the value obtained by the B3LYP method of calculation. We did attempt to do a G2 estimate of the heat of formation for OBrClO. However, we could not calculate an optimized structure for OBrClO at the MP2/6-31G(d) level, which is used in the G2 scheme. Combining the ClOOBr heat of formation with the best values for ClOOBr−$BrClO_2$, ClOOBr−$ClBrO_2$, ClOOBr−BrOClO, and ClOOBr−ClOBrO relative energies leads to our best estimates of the heats of formation for $BrClO_2$ (45.7 kcal mol$^{-1}$), $ClBrO_2$ (41.9 kcal mol$^{-1}$), BrOClO (49.4 kcal mol$^{-1}$), and ClOBrO (48.3 kcal mol$^{-1}$).

**C. $BrBrO_2$ Isomers.** *1. Geometries and Vibrational Frequencies.* The ground-state geometry of BrOOBr is given in Table 9. Computations indicate that the minimum-energy structure for BrOOBr is skewed (Figure 3a). The BrOOBr dihedral angle at the B3LYP/6-31l++G(3df,3pd) level of theory is predicted to be 85.6°. The O−O bond length in BrOOBr (1.335 Å) is smaller than the O−O bond length in ClOOBr (1.347 Å) and in HOOBr (1.405 Å). The decrease in the O−O bond length on going from HOOBr to BrOOBr implies that the length of the centrally positioned O−O bond is influenced by interactions taking place between the oxygen atom and the 1s orbital of hydrogen, and as the hydrogen gets replaced with halogens, between the oxygen and the higher p and d orbitals of the halogens. The Br−O bond length in BrOOBr (1.922 Å) is greater than the Br−O bond length in HOOBr (1.887 Å) and in ClOOBr (1.914 Å). This reiterates the fact that the bond lengths between particular atoms in isomers having similar configurations are largely influenced by the configuration and bonding of the atoms that surround the atoms whose bond lengths are being examined. In particular, the positions of the bonds are of critical importance. In the case of the Br−O bond, it is apparent that the Br−O length in all three isomers is affected not only by the interactions of the bonding orbitals between the two oxygen atoms, but also by the pattern of bonding that occurs between oxygen separately with hydrogen (in HOOBr), chlorine (in ClOOBr), and bromine (in BrOOBr).

The next isomeric structure that we considered is BrOBrO. It is a straight-chain structure having an oxygen as the terminal atom. The minimum-energy structure for BrO′Br′O is shown in Figure 3b. The Br′−O bond distance of 1.660 Å appears to be the shortest of the bond distances in the molecule (among Br−O′, O′−Br′, and Br′−O). This is because of the fact that the Br′−O bond acquires partial double-bond characteristics, due to the lone pairs of electrons on the terminal oxygen atom tending to resonate with the bonding electrons of the Br′−O bond. Such multiple bonding is not observed for the Br−O′ and O′−Br′ bonds where the oxygen atom is not situated at the terminal end of the molecule. Due to its partial double-bond

**TABLE 10: Vibrational Frequencies for $BrBrO_2$ Isomers Using the 6-311++G(3df,3pd) Basis Set**

| | | | | frequencies (cm$^{-1}$) | | | intensities (km mol$^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| species | symmetry | mode no. | mode description | BLYP | SWVN | B3LYP | BLYP | SWVN | B3LYP |
| BrOOBr | a | 1 | OO stretch | 1046 | 1103 | 878 | 123 | 119 | 58 |
| | | 2 | BrO stretch, asym | 480 | 547 | 546 | 61 | 74 | 41 |
| | | 3 | BrO stretch, sym | 475 | 499 | 504 | 10 | 14 | 13 |
| | | 4 | BrOO bend, asym | 301 | 333 | 336 | 56 | 52 | 22 |
| | | 5 | BrOO bend, sym | 220 | 274 | 230 | 4 | 5 | 2 |
| | | 6 | torsion | 74 | 62 | 56 | 0 | 0 | 0 |
| BrOBrO | a | 1 | Br′O stretch | 794 | 886 | 853 | 53 | 63 | 64 |
| | | 2 | O′Br stretch | 454 | 534 | 569 | 21 | 26 | 1 |
| | | 3 | O′Br′ stretch | 348 | 445 | 462 | 6 | 20 | 22 |
| | | 4 | O′Br′O bend | 232 | 259 | 256 | 8 | 10 | 9 |
| | | 5 | BrO′Br′ bend | 165 | 169 | 164 | 3 | 5 | 3 |
| | | 6 | torsion | 57 | 75 | 68 | 5 | 2 | 5 |
| $BrBrO_2$ | a′ | 1 | BrO stretch, sym | 816 | 907 | 893 | 54 | 57 | 76 |
| | | 2 | OBrO bend | 331 | 355 | 364 | 11 | 12 | 15 |
| | | 3 | $BrBrO_2$ umbrella | 254 | 291 | 286 | 37 | 50 | 48 |
| | | 4 | BrBr stretch | 164 | 193 | 186 | 3 | 3 | 5 |
| | a″ | 5 | BrO stretch, asym | 869 | 962 | 950 | 82 | 95 | 97 |
| | | 6 | BrBrO bend | 151 | 172 | 174 | 0 | 0 | 1 |

character, the Br′−O bond in BrO′Br′O (1.660 Å) is smaller than the Br−O bond in BrOOBr (1.922 Å). The O′−Br′ bond length of 1.855 Å is slightly smaller than the Br−O′ bond length of 1.867 Å. The O′−Br′ length in BrO′Br′O is comparable to the O−Br length in HOBrO′ (1.851 Å). The terminal Br′−O length in BrO′Br′O can also be compared to the terminal Br−O′ length in HOBrO′ (1.665 Å). The O′Br′O angle (110.3°) in BrO′Br′O is smaller than the BrO′Br′ angle (116.8°). The BrO′Br′ angle is a result of repulsions between lone pairs of electrons on Br, O′, and Br′ atoms, as well as the repulsions occurring between bonding electrons of the Br−O′ and O′−Br′ single bonds and the lone-electron pairs on the two bromines and oxygen. These repulsions have greater effect than the lone pair/bond pair repulsions which occur between the electron pairs on the two oxygen atoms and the Br′ atom, and the bonding electrons of the O′−Br′ and Br′−O bonds, which make up the O′Br′O angle (since the Br′−O bond has a partial double-bond character, due to which there is one less lone−electron pair on the terminal oxygen).

Finally, we considered the isomeric form $BrBrO_2$. This molecule has $C_s$ symmetry. The Br−O bond in $BrBrO_2$ appears to be the shortest of the $BrBrO_2$ isomeric forms. The lone pairs of electrons on the oxygens enter into resonance with the Br−O bond pair, due to which the Br−O bond appears to possess the characteristics of a double bond. This resonance effect is much more pronounced in $BrBrO_2$ than in BrOBrO, and thus the Br−O bond in $BrBrO_2$ (1.618 Å) is smaller than the Br′−O bond in BrO′Br′O (1.660 Å). Due to its double-bond character, the Br═O in $BrBrO_2$ (1.618 Å) is of shorter length than the Br−O single bond in BrOOBr (1.922 Å). The Br═O length in $BrBrO_2$ is comparable to the Br═O length in $HBrO_2$ (1.640 Å) and to that in $ClBrO_2$ (1.613 Å). The OBrO bond angle of 104.2° is smaller than the BrBrO angle of 111.4°, because of the lesser amount of repulsions between the lone-electron pairs on bromine, the two oxygens, and the Br═O bonding electrons (to form the OBrO angle), compared to the repulsive effects of the Br−Br and Br═O bond pairs with the lone-electron pairs on oxygen and the two bromine atoms, leading to the formation of the BrBrO angle.

The calculated vibrational frequencies for the three isomeric forms of $BrBrO_2$ are provided in Table 10. All vibrational frequencies presented in the table are calculated at the BLYP, SVWN, and B3LYP levels of theory using the 6-311++G(3df,3pd) basis set. In the prediction of the vibrational frequencies for BrOOBr, the most intense bands are predicted to be the O−O stretch (878 cm$^{-1}$) and the Br−O asymmetric stretch (546 cm$^{-1}$), and the least intense ones are the BrOO symmetric bend (230 cm$^{-1}$) and the torsion (56 cm$^{-1}$). The harmonic frequencies of BrOOBr are very similar to those obtained earlier for ClOOBr. The O−O stretch in BrOOBr is comparable to the O−O stretches in ClOOBr (864 cm$^{-1}$) and in HOOBr (903 cm$^{-1}$). The frequency of the O−O stretch of HOOBr is greater than the O−O stretches of ClOOBr and BrOOBr, due to the role played by the 1s orbital of the hydrogen atom in bonding of HOOBr which leads to the vibrational motion of the hydrogen atom, and its contribution to the stretch of the O−O bond. The O−O stretches of ClOOBr and BrOOBr have close enough frequency values, with the O−O stretch of BrOOBr being slightly larger than the O−O stretch of ClOOBr, possibly due to the participation of the 3d orbitals of bromine in the bonding of BrOOBr, and their contribution to vibrational motion of the bromine atom attached to the oxygen. The Br−O asymmetric stretch in BrOOBr is comparable to the Br−O stretch in HOOBr (580 cm$^{-1}$) and the Br−O stretch in ClOOBr (533 cm$^{-1}$). A trend is seen, as the Br−O stretch of HOOBr has a higher frequency than when the hydrogen atom is replaced by a chlorine or a bromine.

A comparison of the frequencies of BrOBrO, HOBrO, and ClOBrO reveals that the O′−Br′ stretch in BrO′Br′O (462 cm$^{-1}$) is similar to the O−Br stretch in HOBrO′ (563 cm$^{-1}$) and the O−Br stretch in ClOBrO′ (449 cm$^{-1}$). The Br′−O stretch of BrO′Br′O (853 cm$^{-1}$) is close in value to the Br−O′ stretch of ClOBrO′ (859 cm$^{-1}$) and the Br−O′ stretch of HOBrO′ (838 cm$^{-1}$). The positions of the atoms and the orbitals they possess are important factors that determine the bonding patterns in the isomers and the type of vibrations the atoms in the isomers undergo.

The vibrational modes of the atoms affect the frequencies of the bonds and angles in the molecules. The frequencies of $BrBrO_2$ can be compared to those of $HBrO_2$ and $ClBrO_2$. The Br−O symmetric stretch in $BrBrO_2$, occurring at 893 cm$^{-1}$, is within limits of the Br−O symmetric stretch in $HBrO_2$ (841 cm$^{-1}$) and that in $ClBrO_2$ (900 cm$^{-1}$). The Br−O asymmetric stretches in $BrBrO_2$, (950 cm$^{-1}$), $ClBrO_2$ (955 cm$^{-1}$), and $HBrO_2$ (921 cm$^{-1}$) are also compatible with each other. The OBrO bend in $BrBrO_2$ occurs at 364 cm$^{-1}$ and is comparable to the OBrO bend of $ClBrO_2$ occurring at 367 cm$^{-1}$. However, the OBrO bend of $HBrO_2$ is quite high in comparison. This is possible, due to the large impact of the vibrational motion of the small hydrogen atom which moves around rather flexibly, and can sometimes have a large impact on the vibrations (and thus the frequencies) of the bonds in its vicinity. The most

**TABLE 11: Relative Energies for Br$_2$O$_2$ Isomers Using the 6-311++G(3df,3pd) Basis Set**

| | method | | | |
|---|---|---|---|---|
| relative energy | BLYP | SVWN | B3LYP | CCSD(T)/B3LYP |
| BrOOBr−BrOBrO | 13.0 | 10.6 | 11.3 | 8.7 |
| BrOOBr−BrBrO$_2$ | 8.3 | 1.4 | 8.4 | 6.8 |
| $\Delta H^\circ_{f,o}$(BrOOBr) | 36.5 | 35.3 | 45.5 | 46.1 |

intense bands for BrO′Br′O are predicted to be the Br′−O stretch (853 cm$^{-1}$) and the O′−Br′ stretch (462 cm$^{-1}$), and those for BrBrO$_2$ are predicted to be the Br−O symmetric stretch (893 cm$^{-1}$) and the Br−O asymmetric stretch (950 cm$^{-1}$).

2. *Energetics.* Calculated relative energies (see Table 11) for the three stable isomers of BrBrO$_2$ show that the lowest energy is possessed by the skewed structure of BrOOBr. The next lowest energy structure is that of the BrBrO$_2$ isomer, and the highest energy structure is that of the BrOBrO isomer. With the B3LYP/6-311++G(3df,3pd) basis set, the BrBrO$_2$ isomer appears to be 8.4 kcal mol$^{-1}$ higher in energy than the BrOOBr isomer. The BrOBrO isomer is predicted to be 11.3 kcal mol$^{-1}$ higher in energy relative to the BrOOBr isomer.

As in the case of HBrO$_2$ and ClBrO$_2$ isomers, an isodesmic reaction scheme can be employed to calculate the heats of formation of each of the BrBrO$_2$ isomers. The isodesmic scheme used here is BrOOBr + 2HOH → 2HOBr + HOOH. In the calculation of the heat of formation of BrOOBr from this scheme, literature values for the heats of formation of HOH,[19] HOOH,[19] and HOBr[20] are used. Our best computed value of the heat of formation [CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory] of BrOOBr is 46.1 kcal mol$^{-1}$. Combining the BrOOBr heat of formation with the best values for BrOOBr−BrBrO$_2$ relative energy and BrOOBr−BrOBrO relative energy leads to 52.9 and 54.8 kcal mol$^{-1}$ as our best estimates of the heat of formation for BrBrO$_2$ and BrOBrO isomers, respectively.

**D. Relative Stability of the HBrO$_2$, ClBrO$_2$, and BrBrO$_2$ Isomers.** A comparison of the relative energetic stabilities of the XBrO$_2$ isomers (X = H, Cl, Br), given in Figure 4, indicates that the most stable isomer is HOOBr with an 8.6 kcal mol$^{-1}$ heat of formation, and the least stable isomer is OBrClO with about 81.0 kcal mol$^{-1}$ heat of formation. The next in stability after HOOBr is HOBrO. As the hydrogen atom gets replaced by higher halogens (chlorine and bromine), the stabilities of the isomers decrease. This, however, is not the only factor that contributes to the relative stability or instability of the isomers. It is very important to consider the form of bonding within each isomer and the type of linkages in which each isomer is involved. When hydrogen is one of the terminal atoms and utilizes its 1s orbital to bond with the 2p orbital of an oxygen atom, the stability of the isomer is the greatest. The H−O bond energy is quite high, which makes it very difficult for the H−O bond to be broken easily. As chlorine and bromine atoms start replacing the hydrogen atom, the stabilities of the resulting isomers decrease. In general, when a hydrogen atom is replaced by a bromine, the higher 3d orbitals of bromine play a major part in the process of bonding and impart greater amount of energy to the molecule, thus lowering its stability. Chlorine has no 3d orbitals to affect its bonding with other atoms within the molecule, and thus, when hydrogen is replaced by chlorine, the 3p orbitals of chlorine play a major role in the bonding process. The 3p orbitals of chlorine are much higher in energy than the 1s orbital of hydrogen but have lower energy than the 3d orbitals of bromine; so isomers that form with chlorine are generally more stable than the isomers that are totally brominated with not a single chlorine atom in them.

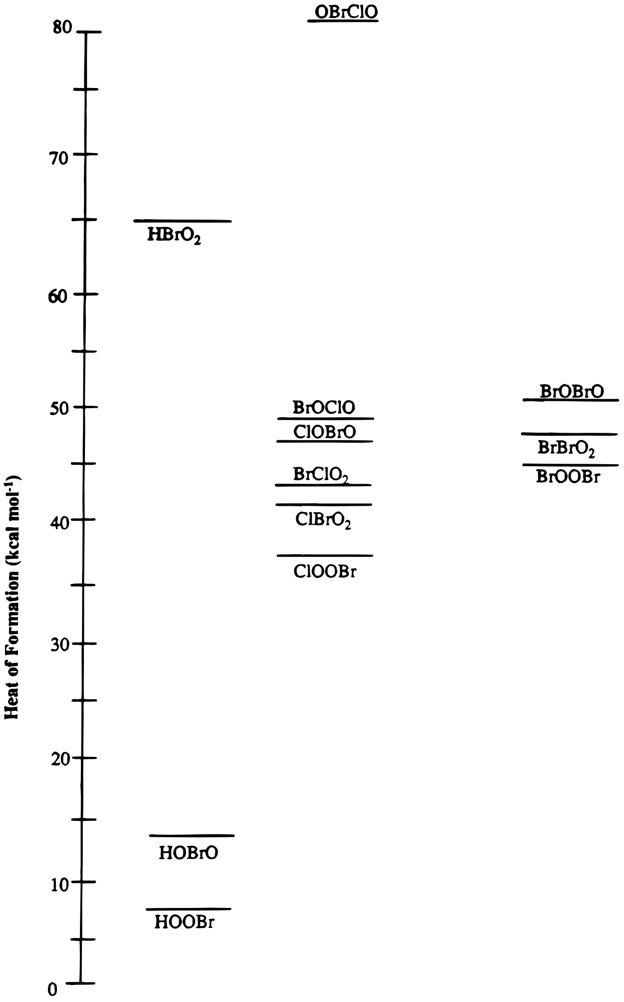

**Figure 4.** Relative energies of XBrO$_2$ (where X = H, Cl, Br) isomers as calculated at the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G-(3df,3pd) level of theory.

Among ClBrO$_2$ and BrBrO$_2$ isomers, the ClOOBr and BrOOBr structures are the most stable. In these cases, the two oxygen atoms are positioned next to each other and interact by bonding with their 2p orbitals. There is a decrease in relative stability when the two halogen atoms lie next to each other, and the oxygen atoms lie toward the terminal end of the molecules. The chlorine and bromine atoms form a strong single bond with each other, but the Br−Cl bond strength is lesser than that of the Cl−O bond, due to which the BrClO$_2$ isomer lies above the ClOOBr isomer on the energy scale. A difference in the bonding pattern occurs when the bromine atom is linked to the two oxygens (in ClBrO$_2$), in comparison to when the chlorine atom is linked to the two oxygen atoms (in BrClO$_2$). Not only is the chlorine atom devoid of any high-energy d orbitals that it can utilize for its bond formation with oxygen, but the Cl−O bond possesses higher energy than the Br−O bond, and thus the ClBrO$_2$ isomer is less stable than the BrClO$_2$ isomer. The least stable among the ClBrO$_2$ and BrBrO$_2$ isomers are the isomers in which the oxygen atoms lie alternately between the halogen atoms. When the oxygen and the bromine atoms lie next to each other within the center of the molecule, the single bond that is formed by the interaction of the high energy and larger 3d orbitals of bromine and the 2p orbitals of oxygen is relatively weaker than the single bond that is formed by interaction of the relatively smaller and lower in energy (relative to bromine) 3p orbitals of chlorine and the 2p orbitals of oxygen. Thus, the ClOBrO isomer lies above the BrOClO

**TABLE 12: Heat of Formation for $HO_x$, $ClO_x$, and $BrO_x$ Species at 0 K[a]**

| species | $\Delta H^\circ_{f,o}$ | species | $\Delta H^\circ_{f,o}$ |
|---|---|---|---|
| Cl | 28.6 ±0.00 | $H_2O$ | −57.1 ± 0.0 |
| Br | 25.2 ±0.01 | HOCl | −17.1 ± 0.5 |
| O | 58.98 ± 0.02 | HOBr | −10.93 ± 1 |
| H | 51.63 ± 0.001 | BrO | 31.8 ± 0.5 |
| HO | 9.17 ± 0.29 | OBrO | 38.9 ± 6 |
| $HO_2$ | 4.3 ± 1.2 | ClOBr | 26.7 |
| ClO | 24.1 ± 0.5 | ClBrO | 38.0 |
| ClOO | 24.0 ± 0.4 | BrClO | 44.7 |
| OClO | 27.9 ± 2 | | |

[a] Data taken from refs 18 and 19.

isomer on the relative energy scale and is the least stable of the $ClBrO_2$ isomers, as predicted by the B3LYP method.

**E. Comparison with Experiments.** There have not been many experiments conducted on the isomers of $HBrO_2$, thus far, to determine their reaction pathways. However, there has been a recent experimental study[21] which examined the reaction of HO + BrO. In this work, the authors suggested that the reaction of HO radicals with BrO radicals proceeds through an HOOBr complex which is believed to be a short-lived vibrationally excited addition complex. From the heats of formation determined for the $HBrO_2$ species and the product species, as given in Table 12, we can explore what the important pathways are that may result in the formation of the $HBrO_2$ species. The HOOBr isomer can, most likely, be formed by either of the two reactions

$$\mathrm{Br} + \mathrm{HO_2} \rightarrow \mathrm{HOOBr} \tag{18}$$

or

$$\mathrm{BrO} + \mathrm{OH} \rightarrow \mathrm{HOOBr} \tag{19}$$

Both of these reactions are exothermic by 20.9 and 32.4 kcal mol$^{-1}$, respectively. It is interesting to note that Bogan et al.[21] estimated the O−O bond dissociation energy for HOOBr to be about 35 kcal mol$^{-1}$. This compares well with our estimate of 32.4 kcal mol$^{-1}$. The HOBrO isomer would probably be formed by the reaction

$$\mathrm{BrO} + \mathrm{OH} \rightarrow \mathrm{HOBrO} \tag{20}$$

which is exothermic by 27.1 kcal mol$^{-1}$. However, if HOOBr is formed by reaction 19, about 11.5 kcal mol$^{-1}$ internal energy would have to be lost to make dissociation via reaction 18 inaccessible. Bogan et al.[21] found that the predominant products from the reaction of HO radicals with BrO radicals are Br + $HO_2$. Their observations are consistent with the calculated results of this study.

A relative energy diagram for the reaction pathways of the $ClBrO_2$ isomers is provided in Figure 5. It is evident that the most likely dissociation products for the ClOOBr isomer would be the Br and ClOO radicals, rather than ClO + BrO, since the energy of formation of Br + ClOO (relative to ClOOBr) is much lower (10.3 kcal mol$^{-1}$) than the energy of formation of ClO + BrO, implying that it is much easier to break the Br−Cl bond than it is to break a Br−O bond. The dissociation products for the BrOClO isomer would, most likely, be Br and OClO. These observations are consistent with the experimental observations of Sander et al.,[8] from where they concluded that BrOClO would indeed dissociate to produce Br and OClO radicals. If the $BrClO_2$ isomer was to dissociate, it would produce Br and OClO radicals, but the process would take 7.4 kcal mol$^{-1}$ energy. The $ClBrO_2$ isomer is quite stable, and if it dissociated, it would produce Cl and OBrO radicals, using up 25.6 kcal mol$^{-1}$ energy.

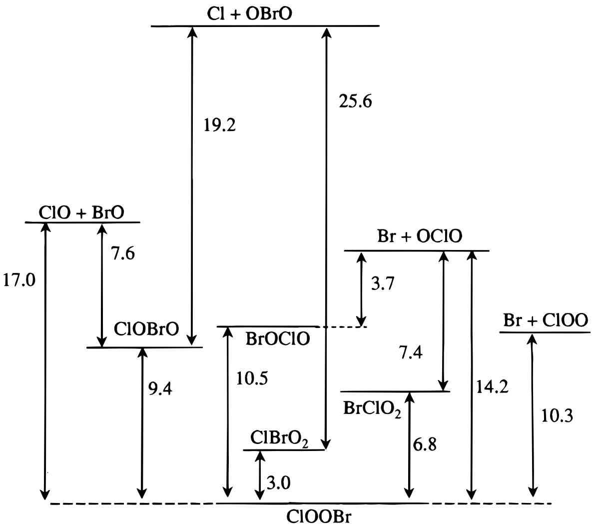

**Figure 5.** Relative energy diagram for $ClBrO_2$ isomer reaction pathways as calculated at the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory.

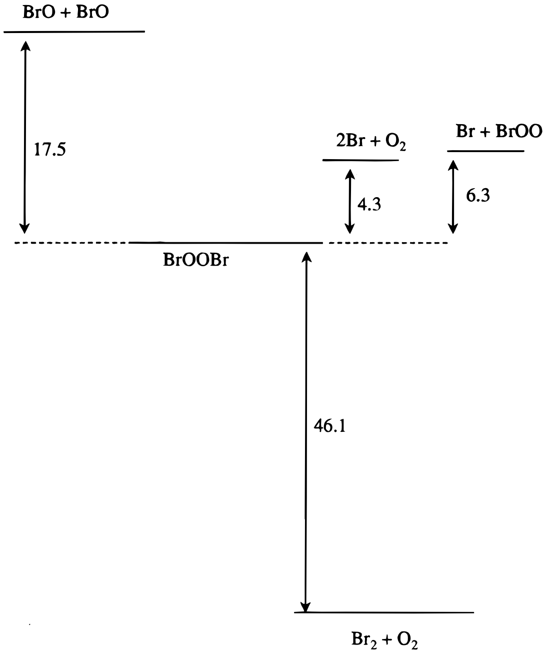

**Figure 6.** Thermochemistry of the BrO + BrO reaction as calculated at the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory.

It is interesting to note that breaking the Br−Cl bond in $BrClO_2$ is easier than in $ClBrO_2$. The formation of the Br and OClO radicals is more likely to be facilitated by the dissociation of the BrOClO isomer, which is higher in energy than $BrClO_2$ and thus more unstable. The ClOBrO isomer upon dissociation would be more likely to produce ClO + BrO, rather than Cl + OBrO, since the energy of dissociation of the Cl−O bond is much greater than that needed to dissociate the O−Br bond.

The relative energy diagram for the thermochemistry of BrOOBr is depicted in Figure 6. From Figure 6 it is evident that from the reaction of BrO + BrO, the BrOOBr species could be involved. Because it is bounded by 6.3 kcal mol$^{-1}$ energy, and since the reaction of BrO + BrO is 17.5 kcal mol$^{-1}$ above BrOOBr on the energy scale, the 11.2 kcal mol$^{-1}$ remaining in the BrOO species from the dissociation of BrOOBr exceeds its −2 kcal mol$^{-1}$ bond energy for the Br−O bond in BrOO, due to which the resulting products of the BrO + BrO reaction are 2Br and $O_2$. These observations are consistent with the experimental observations of Mauldin et al.,[5] who have observed the formation of $2Br + O_2$. At low temperatures, Mauldin et al.[5] observed a species which they attributed to BrOOBr and suggested that it is probably bound by 5 kcal $mol^{-1}$. The present calculations suggest that, with respect to the products ($2Br + O_2$), the BrOOBr is bounded by 4.3 kcal $mol^{-1}$, in good agreement with the observations of Mauldin et al.[5]

## IV. Summary

The equilibrium structures, vibrational and electronic spectra, relative energies, and heats of formation of the $XBrO_2$ isomers ($X = H$, Cl, Br) have been investigated with the BLYP, SVWN, and B3LYP *ab initio* electronic−structure methods with the 6-311++G(3df,3pd) basis set. In general, the XOOBr peroxide form (where $X = H$, Cl, Br) is found to be the most stable among the isomers. As the hydrogen atom is replaced by chlorine and bromine atoms, the peroxide form becomes increasingly destabilized. Due to the thermal stability of HOOBr and ClOOBr, it is very likely that these isomers may play a role in the $HO_x/BrO_x$ and $ClO_x/BrO_x$ cross reactions. The BrOOBr peroxide form is found to be the least stable, and its role in the BrO + BrO reaction may be that of a transient species.

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