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Study of the Stability of $BrClO_3$ Isomers

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The structures, vibrational frequencies, and rotational constants have been determined using ab initio methods of isomers of $BrClO_3$. The BrOCl(O)O structural form is found to be the most stable. This species could be formed from the three-body reactions involving BrO + OClO + M → BrOCl(O)O + M and Br + ClO_3 + M → BrOCl(O)O + M. The heats of reaction for these processes are estimated to be −8.2 and −24.4 kcal mol^{-1}, respectively.

I. Introduction

The role played by halogen oxides in stratospheric ozone chemistry has been intensely investigated.[1−4] Halogen oxide chemistry has been found to be important in the Antarctica polar vortex.[5−8] In particular, the in situ measurements of Anderson and co-workers[9] demonstrated the anticorrelation between chlorine oxide radical (ClO) and ozone abundances in the polar stratosphere. Field measurements have also reported the presence of the OClO radical,[10−12] which is known to result from the coupling reaction between ClO and BrO radicals.[13−17] A reaction between ClO and OClO to produce Cl_2O_3 was first suggested by Lipscomb et al.[18] Sander et al.[19] and Anderson et al.[9] later suggested that Cl_2O_3 could act as a reservoir for atmospheric ClO radicals. A number of experimental studies[20−23] have confirmed the formation of Cl_2O_3. The ClO−BrO coupling chemistry that leads to the formation of OClO, which is critical to the formation of Cl_2O_3, was first pointed out by Clyne and Watson[24] and Yung et al.[25] McElroy et al.[26] later suggested that this coupling chemistry could play an important role in polar ozone chemistry. In the case of Cl_2O_3, this species has been found to be very stable at low temperatures, because the equilibrium constant for the ClO + OClO reaction is extremely temperature dependent.[20,21] A similar behavior might be expected of $BrClO_3$ but would depend on the thermal stability of $BrClO_3$. There are no reports of the existence or stability of $BrClO_3$ in the literature. Consequently, we have employed ab initio molecular orbital theory to examine the structural, spectroscopic, and thermodynamic properties of the various isomers of $BrClO_3$ that could assist in the experimental characterization of these species.

II. Computational Methods

All ab initio calculations were performed using the GAUSSIAN 94 series of programs.[27] The geometries of all structures were fully optimized using Schlegel's analytical gradient method[28] with the Becke three-parameter functional where the nonlocal correlation is provided by the Lee−Yang−Parr method (B3LYP).[29,30] All bond lengths and bond angles were optimized to better than 0.001 Å and 0.1°, respectively. This was achieved with the SCF convergence on the density matrix of at least 10^{-9} and with root-mean-square (rms) force less than 10^{-4} au. The 6-311+G(3df) basis set was used in all optimization and frequency calculations.[31] Vibrational frequencies and zero-point energies were also calculated at the B3LYP/6-311+G(3df) level of theory using analytical second derivatives. Single-point energies were calculated at the CCSD(T) level of theory[32,33] with the core electrons frozen using the B3LYP/6-311+G(3df) optimized geometries.

TABLE 1: Optimized Geometries for $BrClO_3$ Isomers[a]

species	coordinate	B3LYP	species	coordinate	B3LYP
ClOBr(O)O	ClO	1.663	BrOCl(O)O	BrO	1.818
	BrO	1.984		ClO	1.845
	BrO′	1.613		ClO′	1.440
	BrO″	1.613		ClO″	1.443
	BrOCl	112.9		ClOBr	113.3
	OBrO′	103.8		OClO′	104.3
	OBrO″	101.3		OClO″	103.7
	O’BrO″	111.6		O’ClO″	114.2
	ClOBrO′	−91.9		BrOClO′	−88.3
	ClOBrO″	23.9		BrOClO″	31.5
$ClBrO_3$	ClBr	2.244	$BrClO_3$	BrCl	2.306
	BrO	1.600		ClO	1.424
	ClBrO	103.9		BrClO	104.0
	OBrO	114.5		OClO	114.3
BrOOOCl	BrO	1.887			
	OO′	1.385			
	O′O″	1.407			
	O″Cl	1.725			
	BrOO′	111.8			
	O″O′O	109.5			
	O′O″Cl	111.0			
	BrOO′O″	−78.0			
	OO′O″Cl	−77.0			

[a] Bond distances in units of angstroms and bond angles in units of degrees.

III. Results and Discussion

A. Equilibrium Geometries of $BrClO_3$ Isomers. For $BrClO_3$ we considered eight isomers: (a) ClOBr(O)O, (b) BrOCl(O)O, (c) OBrOClO, (d) O_2ClOBr, (e) O_2BrOCl, (f) $ClBrO_3$, (g) $BrClO_3$, and (h) BrOOOCl. At the B3LYP/6-311+G(3df) level of theory we found that five of the eight structures were bound. The equilibrium geometries for the five $BrClO_3$ conformers are presented in Table 1. The first structure, the ClOBr(O)O isomer (Figure 1a), is very similar to the ClOCl(O)O structure, often referred to as the Hehre structure, though

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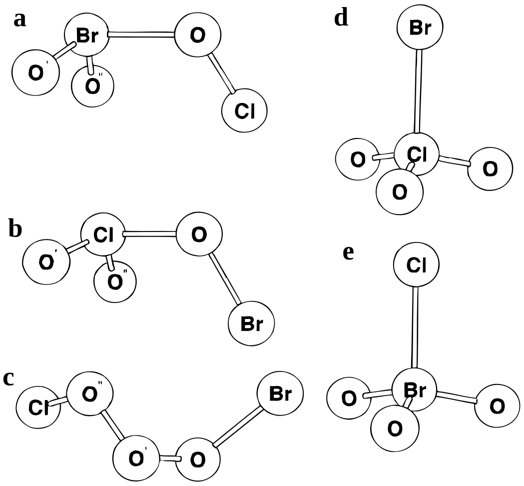

Figure 1. Minimum energy structures of (a) ClOBr(O)O, (b) BrOCl(O)O, (c) BrOOOCl, (d) $BrClO_3$, and (e) $ClBrO_3$.

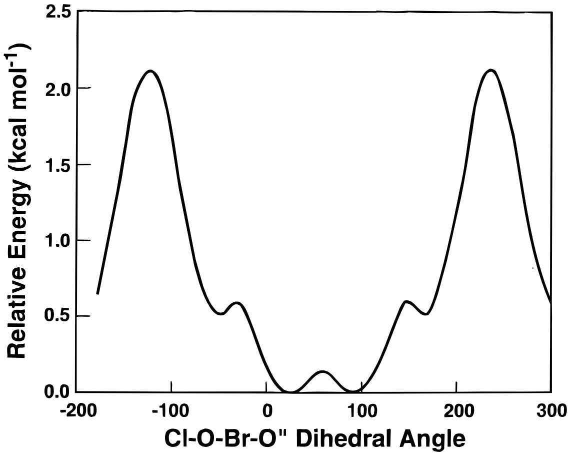

Figure 2. Potential energy surface for internal rotation in ClOBr(O)O.

TABLE 2: Rotational Constants for $BrClO_3$ Isomers

	rotational constants (MHz)[a]		
species	*A*	*B*	*C*
BrOOOCl	8791	929	906
BrOCl(O)O	6919	1373	1290
ClOBr(O)O	5855	1699	1549
$BrClO_3$	5517	1673	1673
$ClBrO_3$	4368	2309	2309

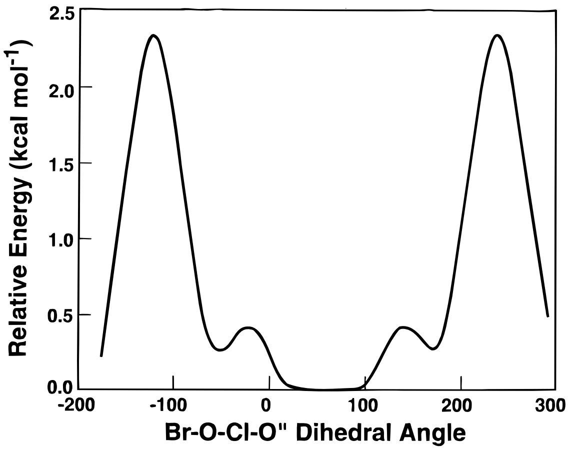

Figure 3. Potential energy surface for internal rotation in BrOCl(O)O.

TABLE 3: Total and Relative Energies for $BrClO_3$ Isomers

	total energies (hartrees)		relative energies (kcal mol^{-1})[a]	
species	B3LYP	CCSD(T)	B3LYP	CCSD(T)
BrOOOCl	−3259.853 82	−3257.381 21	0.0	0.0
BrOCl(O)O	−3259.860 23	−3257.387 45	−3.1	−3.0
ClOBr(O)O	−3259.849 02	−3257.382 03	3.0	−0.5
$BrClO_3$	−3259.843 02	−3257.372 32	9.3	8.1
$ClBrO_3$	−3259.815 19	−3257.355 02	24.0	16.2

[a] Relative energies include B3LYP/6-311+G(3df) zero-point energy corrections.

the central halogen in ClOBr(O)O is a bromine. The ClO bond length in the ClOBr(O)O structure is predicted to be 1.663 Å. This is quite similar to the ClO bond length in ClOCl(O)O of 1.647 Å calculated using B3LYP/6-311+G(3df) wave functions.[34] In the case of ClOBr(O)O, the calculations suggest that the elongated ClO bond maybe weaker than the ClO bond in ClOCl(O)O. The ClOBr angle is wider in ClOBr(O)O than the ClOCl angle in ClOCl(O)O, i.e., 112.9° versus 110.9°, because of greater repulsion from the central bromine experienced by the terminal chlorine.

The second isomeric structure that we found to have a stable minimum is BrOCl(O)O (Figure 1b). This structure is quite similar to that of ClOCl(O)O structure. The ClO′ and ClO″ bond lengths of 1.440 and 1.443 Å, respectively, at the B3LYP/6-311+G(3df) level of theory are quite similar to the same bond lengths in ClOCl(O)O of 1.440 and 1.442 Å, respectively. The central ClO bond length in BrOCl(O)O is predicted to be 1.845 Å, while in ClOCl(O)O it is predicted to be 1.934 Å at the same level of theory. The BrO terminal bonds in $BrClO_2$ isomers are found to be longer than the ClO bonds. However, in BrOCl(O)O we find the BrO bond length to be significantly shorter than the central ClO bond length, i.e., 1.818 Å (BrO) versus 1.845 Å (ClO).

The third isomeric form found to have a stable minimum is BrOOOCl, shown in Figure 1c. We find that BrOOOCl orients in a skewed straight-chain structure similar to ClOOOCl. The BrOO′O″ dihedral angle at the B3LYP/6-311+G(3df) level of theory is predicted to be −78.0°, and the OO′O″Cl dihedral angle is predicted to be −77.0°. In ClOOOCl the OO bonds were found to be equivalent, i.e., 1.399 Å. In BrOOOCl, the OO′ (the terminal oxygen of the OO group connected to bromine) bond is shorter than the O′O″ (the terminal oxygen of the OO group connected to chlorine) bond, i.e., 1.385 Å for the OO′ bond versus 1.407 Å for the O′O″ bond. The BrO bond is elongated to 1.887 Å in BrOOOCl and is much longer than the BrO bond in BrOCl(O)O of 1.818 Å.

The last two isomers, $BrClO_3$ and $ClBrO_3$, have C_{3v} symmetry. The $BrClO_3$ structure (shown in Figure 1d) is comparable to that of $ClClO_3$. The ClO bonds in $ClClO_3$ have been predicted to be the shortest among those of its isomeric forms. In $BrClO_3$ the ClO bonds are found, similarly, to be shorter than those in BrOCl(O)O and BrOOOCl. In contrast, the BrO bonds in $ClBrO_3$ (shown in Figure 1e) are found to be shorter than those in ClOBr(O)O and BrOOOCl. These effects are attributed to resonances associated with the Cl═O and Br═O multiple bonding in $BrClO_3$ and $ClBrO_3$.

B. Rotational Potential Energy Surface for ClOBr(O)O and BrOCl(O)O. The rotational constants for all the $BrClO_3$ isomers are presented in Table 2. These results should aid in the experimental characterization of these species using microwave or submillimeter spectroscopic methods. Since there are no measurements of the rotational constants for the $BrClO_3$ isomers, it is difficult to access their uncertainties. However, if we use Cl_2O_3 as a model system, we could get some estimate

TABLE 4: Isodesmic Heats of Reaction and Heats of Formation for BrOOOCl at 0 K

	total energies (hartrees)					relative energies (kcal mol^{-1})	
level of theory	H_2O	HOCl	HOBr	HOOH	BrOOOCl	$\Delta H^0_{r,0}$(BrOOOCl + $3H_2O \rightarrow$ HOBr + HOCl + 2HOOH)	$\Delta H^0_{f,0}$(BrOOOCl)
B3LYP/6-311+G(3df,3pd)	−76.464 51	−536.022 04	−2649.956 29	−151.613 19	−3259.853 82	30.3	50.9
CCSD(T)/6-311++G(3df,3pd)	−76.337 42	−535.388 93	−2648.238 07	−151.361 11	−3257.381 21	31.4	49.8

TABLE 5: Heats of Formation for $BrClO_3$ Isomers at 0 K

	heat of formation (kcal mol^{-1})	
species	B3LYP	CCSD(T)
BrOOOCl	50.9	49.8
BrOCl(O)O	47.8	46.8
ClOBr(O)O	53.9	49.3
$BrClO_3$	60.2	57.9
$ClBrO_3$	74.9	66.0

TABLE 6: Heats of Formation for ClO_x and BrO_x Species of 0 K

species	$\Delta H^0_{f,0}$(kcal mol^{-1})	ref
Cl	28.6 ± 0.0	37
Br	25.2 ± 0.01	37
ClO	24.1 ± 0.05	37
ClOO	24.0 ± 0.4	*a*
OClO	23.2 ± 1.0	*b*
ClO_3	46.0 ± 2	*c*
BrO	31.8 ± 0.5	*d*
OBrO	38.9 ± 6	37

[a] Nicovich, J. M.; Kreutter, K. D.; Shackelford, C. J.; Wine, P. H. *Chem. Phys. Lett*. **1991**, *179*, 367. [b] Nickolaisen, S. L.; Friedl, R. R.; Sander, S. P. *J. Phys. Chem.* **1994**, *98*, 155. [c] Workman, M. A.; Francisco, J. S. *Chem. Phys. Lett*. **1997**, *279*, 158. [d] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halon, I.; Bailey, S. M.; Charney, K. L.; Muttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11* (Suppl. 2).

of the uncertainties for the rotational constants predicted at the B3LYP/6-311+G(3df) level of theory. In a submillimeter spectroscopy study of Cl_2O_3, Friedl et al.[35] determined the experimental rotational constants to be 8629.197, 2106.410, and 1776.122 MHz for *A*, *B*, and *C* parameters, respectively. Clark and Francisco[34] found that at the B3LYP/6-311+G(3df) level of theory, the rotational constants are 7585.8, 2137.8, and 1828.6 MHz for *A*, *B*, and *C* rotational constants, respectively. The differences between experimental and theoretical values are 12.1% (A), 1.5% (B), and 2.9% (C). The largest error that is expected is in the *A* rotational constant because of the underlying subtleties in the internal rotational potential energy surface. This is explored in detail in the next section. Nevertheless, we may expect similar uncertainties in the predicted rotational constants for $BrClO_3$, since the predictions were made at the same level of theory as Cl_2O_3.

We have also mapped out the potential energy surface at the B3LYP/6-311+G(3df) level along the dihedral angle. Stepping along the dihedral angle at intervals of 10°, each structure was fully optimized, and the energy points were calculated. A total of 50 energy points were calculated for the potential surfaces for ClOBr(O)O and BrOCl(O)O. In Figure 2 the resulting potential energy surface for ClOBr(O)O is shown. The rotational potential energy surface about the ClOBrO″ dihedral angle reveals a surface that is quite complex. We also found a double minimum for ClOBr(O)O, the first at 23.9° and the other at 90°, with a 0.1 kcal mol^{-1} barrier separating the two minima. We note that this small barrier is well within the noise limits of the B3LYP calculations. Consequently, its true existence is suscept. When the dihedral angle is 240°, an internal barrier of 2.1 kcal mol^{-1} is found. Our scan of the rotational potential energy surface for ClOBr(O)O clearly shows that the surface is quite complex, and the choice of structure used to analyze the line spectra from microwave or submillimeter experiments is crucial. Moreover, it also suggests that for room-temperature measurements, at which *kT* is ca. 0.6 kcal mol^{-1}, there could be at least four different conformers that could exist. More definitive analysis of the structure from microwave or submillimeter experiments should come from low-temperature studies.

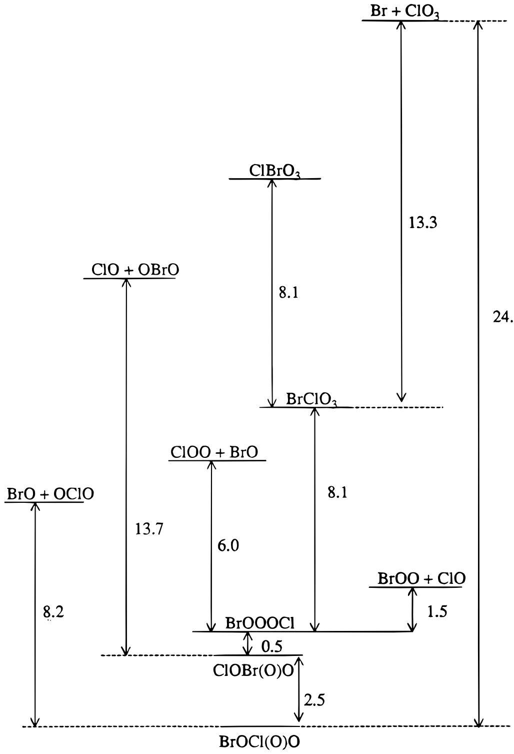

Figure 4. Relative energy diagram for dissociation pathways for $BrClO_3$ isomers. Numbers are in units of kcal mol^{-1}. Heats of formation for BrO_x and ClO_x species are given in Table 6.

The potential energy surface for BrOCl(O)O is quite different from that of the ClOBr(O)O isomer. As shown in Figure 3, the global minimum exists in a very shallow well. As shown in Table 1, we were able to find a global minimum at 31.5° in the BrOClO″ dihedral angle. However, structures could also be found at angles between 30° and 90°. We optimized a structure at 50° and found all positive frequencies, but with small energy differences (i.e., 0.002 kcal mol^{-1}) relative to the minimum at 31.5°. Unlike ClOBr(O)O, there is no small barrier between 30° and 90° rotation. A large barrier of 2.4 kcal mol^{-1} is found at the BrOClO″ dihedral angle of 240°, quite similar to that in BrOCl(O)O.

C. Relative Energetics of $BrClO_3$ Isomers. Calculated relative energies for the five minimum-energy $BrClO_3$ isomers are presented in Table 3. At the B3LYP/6-311+G(3df) level of theory, the order of relative stability for $BrClO_3$ isomers from most stable to most unstable is (1) BrOCl(O)O, (2) BrOOOCl, (3) ClOBr(O)O, (4) $BrClO_3$, and (5) $ClBrO_3$. At the CCSD-

TABLE 7: Vibrational Frequencies and Intensities for $BrClO_3$ Isomers

				intensity	
species	mode no.	tentative mode assign	freq[a]	absolute[b]	relative
BrOOOCl	1	OO′ stretch	871	6	0.4
	2	O″O′ stretch	722	16	1.0
	3	OO bend	628	2	0.1
	4	ClO stretch	550	5	0.3
	5	OOO wag	498	12	0.8
	6	BrO stretch	414	10	0.6
	7	BrOO bend	220	0	0
	8	ClOO bend	144	1	0.1
	9	torsion	51	0	0
BrOCl(O)O	1	ClO′ stretch	1222	186	1.0
	2	ClO′ stretch	1066	122	0.6
	3	BrO stretch	661	12	0.1
	4	O′ClO bend	544	8	0.0
	5	O′ClO″ rock	446	25	0.1
	6	ClO stretch	353	48	0.3
	7	OClO′ bend	296	5	0.0
	8	BrOCl bend	146	1	0.0
	9	OCl(O′)O″ torsion	31	3	0.0
ClOBr(O)O	1	BrO′ stretch	964	110	1.0
	2	BrO′ stretch	910	55	0.5
	3	ClO stretch	739	8	0.1
	4	BrO stretch	411	15	0.1
	5	O′BrO″ bend	364	11	0.1
	6	O′BrO″ rock	315	30	0.3
	7	OBrO′ bend	222	4	0.0
	8	ClOBr bend	155	2	0.0
	9	OBr(O′)O″ torsion	38	3	0.0
$BrClO_3$	1 (a_1)	ClO stretch	1015	123	0.6
	2 (a_1)	ClO_3 deformation	618	191	1.0
	3 (a_1)	BrCl stretch	225	6	0.0
	4 (e)	ClO stretch	1240	174	0.9
	5 (e)	ClO_3 deformation	528	12	0.1
	6 (e)	ClO_3 rocking	249	01	0.0
$ClBrO_3$	1 (a_1)	BrO stretch	871	35	0.3
	2 (a_1)	BrO_3 deformation	403	120	1.0
	3 (a_1)	BrCl stretch	301	2	0.0
	4 (e)	BrO stretch	962	85	0.7
	5 (e)	BrO_3 deformation	361	16	0.1
	6 (e)	BrO_3 rocking	215	1	0.0

[a] In units of cm^{-1}. [b] In units of km mol^{-1}.

(T)/6-311+G(3df)//B3LYP/6-311+G(3df) level of theory the order of stability of the $BrClO_3$ isomers changes:

$$\mathrm{BrOCl(O)O > ClOBr(O)O > BrOOOCl > BrClO_3 > ClBrO_3} \quad (1)$$

The most stable of the $BrClO_3$ isomers is the BrOCl(O)O conformation, while the least stable isomer is the $ClBrO_3$ conformation.

We have used an isodesmic reaction scheme to estimate the heat of formation of BrOOOCl. An isodesmic reaction is one in which the total number of each type of bond is identical in the reactants and products in the reaction scheme. Because the total number and types of bonds are conserved, good estimates of the heat of formation can be obtained as a result of the cancellation of errors or both sides of the isodesmic reaction scheme. Also required are the heats of formation of all the molecules involved in the isodesmic reaction with the exception of the heat of formation of the particular $BrClO_3$ isomer. We have examined the BrOOOCl heat of formation using the following isodesmic reaction scheme:

$$\mathrm{BrOOOCl + 3HOH \rightarrow HOBr + HOCl + 2HOOH} \quad (2)$$

The literature values of the heat of formation of HOH[36] at 0 K is -57.10 ± 0.01 kcal mol^{-1}; for HOOH[36] it is -31.05 ± 0.05 kcal mol^{-1}, and for HOCl[37] it is -17.1 ± 0.5 kcal mol^{-1}. There are several recent determinations for the heat of formation of HOBr;[38−41] however, we use the value reported by Ruscic and Berkowitz[38] of $-10.93 \pm$ kcal mol^{-1}. Using these results, we are able to calculate the heat of reaction for the isodesmic reaction. For BrOOOCl the estimated heat of formation is given in Table 4. At the B3LYP/6-311+G(3df) level of theory, the heat of formation is estimated as 50.9 kcal mol^{-1}. Using CCSD(T) wave functions to improve the energies, it is revealed that the heat of formation value decreases by 1.1 kcal mol^{-1} to yield an estimate of 49.8 kcal mol^{-1}. If we use the relative energies in Table 3 along with the heat of formation of BrOOOCl determined using the isodesmic results, we obtain values of 46.8, 49.3, 57.9, and 66.0 kcal mol^{-1}, respectively, for the heats of formation of BrOCl(O)O, ClOBr(O)O, $BrClO_3$, and $ClBrO_3$. These results are summarized in Table 5. We note that there are significant energy differences between B3LYP and CCSD(T) results for the heats of formation for $BrClO_3$ and $ClBrO_3$ isomers. Such dramatic energy changes have been seen in $ClClO_3$.[34] Similar effects have been noted for $ClBrO_2$ and $BrClO_2$ isomers.[42] In this study we have used basis sets that are quite large, yet there are still dramatic energy differences. Clearly, smaller basis sets would be inappropriate to describe the energetics of $BrClO_3$ isomers.

To assess the uncertainty limits of the calculated heats of formation for $BrClO_3$ isomers at the CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311+G(3df) level of theory, we have examined the heat of formation of ClOBr with the same level of theory, which gives an estimate of probable errors in the BrOOOCl value. At the CCSD(T)/6-311+G(3df)//B3LYP/6-311+G(3df) level of theory, the estimated heats for ClOBr are within 0.7 kcal mol^{-1}, respectively of the experimental determination.[37,43] Using Cl_2O_3 as an additional model, the $ClOClO_2$ heat of formation has been estimated to within 2 kcal mol^{-1} of the experimental determination using similar levels of theory, depending on the experimental heat of formation of OClO used.[34]

Virtually nothing is known about the chemistry of higher oxides of bromine.[44] The present ab initio calculations on the energetics of $BrClO_3$ isomers, which are summarized in Figure 4, suggest the possibility of new pathways leading to the formation of $BrClO_3$ isomers. Moreover, from Figure 4, we see that BrOCl(O)O is stable with respect dissociation into Br + ClO_3 by 24.4 kcal mol^{-1}, and BrO + OClO by 8.2 kcal mol^{-1}.

D. Spectroscopic Characterization of $BrClO_3$ Isomers. The calculated vibrational frequencies and intensities for the five isomeric forms of $BrClO_3$ are represented in Table 7. For the $BrClO_3$ isomers there are nine fundamental vibrational modes. In the cases of $BrClO_3$ and $ClBrO_3$ some of the modes are degenerate. This is because these isomers assume a different point group symmetry than the symmetry of the other isomers. $BrClO_3$ and $ClBrO_3$ are under the C_{3v} point group, for which there are six distinct fundamental vibrations: three total symmetric vibrations and three doubly degenerate vibrations. All the vibrational modes are infrared-active. The other isomers, namely BrOOOCl, BrOCl(O)O, and ClOBr(O)O, assume C_1 symmetry. Under this representation all nine vibrational are infrared-active.

For BrOOOCl, the most intense modes predicted are the O″O′ stretch (ν_2), the OOO wag (ν_5), and the BrO stretch (ν_6) modes. The calculations also predict moderately intense modes: the OO′ stretch (ν_1), the ClO stretch (ν_4), and the OOO bend (ν_3). For BrOCl(O)O and ClOBr(O)O, the most intense modes predicted for the infrared spectra result from the stretches involving the central halogen. For BrOCl(O)O the most intense modes that could be observed in the infrared spectra are the ClO′ stretch (ν_1) at 1222 cm^{-1} and the ClO′ stretch (ν_2) at 1066 cm^{-1}. A moderate peak should be observed at 353 cm^{-1} for the ClO stretch mode (ν_6) as well as a couple of weak modes at 661 cm^{-1} (for the BrO stretch) and 446 cm^{-1} (the O′ClO″ rock). For ClOBr(O)O the most intense modes are the BrO′ stretch (ν_1) at 964 cm^{-1} and the BrO′ stretch (ν_2) of 910 cm^{-1}.

For $BrClO_3$ and $ClBrO_3$, the most intense modes result from both deformation and stretching motions. For $BrClO_3$, the ClO_3 deformation mode is at 618 cm^{-1}, and the ClO stretch ν_1 (a_1) mode is at 1015 cm^{-1} and the ν_4 (e) ClO stretch mode is at 1240 cm^{-1}. However, for $ClBrO_3$ the most intense modes are the BrO_3 deformation mode at 403 cm^{-1}, the totally symmetric a_1 BrO stretch mode at 871 cm^{-1} (ν_1), and doubly degenerate BrO stretch at 962 cm^{-1} (ν_4) modes.

If the B3LYP/6-311+G(3df) vibrational frequencies and intensities are to be used to aid the experimental interpretation and assignment of the infrared spectrum of $BrClO_3$ isomers, the results at that level of theory should be well predicted. A good model to judge the uncertainty, for comparison, is Cl_2O_3. The rms error found between the reported experimental[22] and calculated frequencies, determined at the B3LYP/6-311+G(3df) level of theory, is 3.2%. Assuming that these uncertainties are transferable to the $BrClO_3$ isomers, this should provide spectral uncertainty brackets for experimental searches and characterization of peaks in the infrared spectra of $BrClO_3$ isomers.

IV. Summary

The equilibrium structures, vibrational spectra, relative energetics, and heats of formation for $BrClO_3$ isomers have been investigated. The lowest energy isomer is the BrOCl(O)O structure. Its heat of formation is estimated as 46.8 kcal mol^{-1}, while those for ClOBr(O)O, BrOOOCl, $BrClO_3$, and $ClBrO_3$ are 49.3, 49.8, 57.9, and 66.0 kcal mol^{-1}, respectively.

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References and Notes

(1) Waters, J. W.; Froidevaux, L.; Read, W. G.; Manney, G. L.; Elson, L. S.; Flowers, D. A.; Jarnot, R. F.; Harwood, R. S. *Nature* **1993**, *362*, 597.

(2) Wofsy, S. C.; Moina, M. J.; Salawitch, R. J.; Fox, L. E.; McElroy, M. B. *J. Geophys. Res., A* **1988**, *93*, 2442.

(3) Salawitch, R. J.; Wofsy, S. C.; McElroy, M. B. *Planet. Space Sci.* **1988**, *36*, 213.

(4) Brune, W. H.; Anderson, J. G.; Chan, R. R. *J. Geophys. Res.* **1989**, *94*, 16649.

(5) Solomon, S.; Garcia, R. R.; Rowland, F. S.; Wuebbles, D. J. *Nature* **1986**, *321*, 755.

(6) Molina, L. T.; Molina, M. J. *J. Phys. Chem.* **1987**, *91*, 433.

(7) Farman, J. C.; Gardiner, B. G.; Shanklin, J. D. *Nature* **1985**, *315*, 207.

(8) Prather, M. J.; Jaffe, A. H. *J. Geophys. Res.* **1990**, *95*, 3473.

(9) Anderson, J. G.; Brune, W. H.; Lloyd, S. A.; Toohey, D. W.; Sander, S. P.; Starr, W. L.; Loewenstein, M.; Podolske, J. R. *J. Geophys. Res.* **1989**, *94*, 11480.

(10) Solomon, S.; Sander, R. W.; Jakoubek, R. O.; Arpag, K.; Stephens, S. L.; Keys, J. G.; Garcia, R. R. *J. Geophys. Res.* **1994**, *99*, 3509.

(11) Brandtjen, R.; Klupfel, T.; Perner, D.; Knudsen, B. M. *Geophys. Res. Lett.* **1994**, *21*, 1363.

(12) Sessler, J.; Chipperfield, M. P.; Pyle-JA; Toumi, R. *Geophys. Res. Lett.* **1995**, *22*, 687.

(13) Friedl, R. R.; Sander, S. P. *J. Phys. Chem.* **1989**, *93*, 4756.

(14) Sander, S. P.; Friedl, R. R. *J. Phys. Chem.* **1989**, *93*, 4764.

(15) Sander, S. P.; Friedl, R. R. *Geophys. Res. Lett.* **1988**, *15*, 887.

(16) Turnipseed, A. A.; Birks, J. W.; Calvert, J. G. *J. Phys. Chem.* **1991**, *95*, 4356.

(17) Poulet, G.; Lancar, I. T.; Laverdet, G.; LeBras, G. *J. Phys. Chem.* **1990**, *94*, 278.

(18) Lipscomb, F. J.; Norrish, R. G. W.; Thrush, B. A. *Proc. R. Soc. London, A* **1956**, *233*, 455.

(19) Sander, S. P.; Friedl, R. R.; Yung, Y. L. *Science* **1989**, *254*, 1095.

(20) Hayman, G. D.; Cox, R. A. *Chem. Phys. Lett.* **1989**, *155*, 1.

(21) Burkholder, J. B.; Mauldin, R. L. III; Yokelson, R. J.; Solomon, S.; Ravishandara, A. R. *J. Phys. Chem.* **1997**, *97*, 99597.

(22) Zabel, F. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 893.

(23) Friedl, R. R.; Birk, M.; Oh, J. J.; Cohen, E. A. *J. Mol. Spectrosc.* **1995**, *170*, 383.

(24) Clyne, M. A. A.; Watson, R. A. *J. Chem. Soc., Faraday Trans.* **1977**, *73*, 1169.

(25) Yung, Y. L.; Pinto, J. P.; Watson, R. T. *J. Atmos. Sci.* **1980**, *37*, 339.

(26) McElroy, M. B.; Salawitch, R. J.; Wofsy, S. C.; Logan, J. A. *Nature* **1986**, *321*, 759.

(27) Gaussian94, Revision B.3: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(28) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(29) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(30) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(31) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J.-P.; Davis, N. E.; Binning Jr., R. C.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104.

(32) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(33) Lee, T. J.; Rendell, A. P. *J. Chem. Phys.* **1991**, *69*, 399.

(34) Clark, J.; Francisco, J. S. *J. Phys. Chem. A* **1997**, *101*, 7145.

(35) Friedl, R. R.; Birk, M.; Oh, J. J.; Cohen, E. A. *J. Mol. Spectrosc.* **1995**, *170*, 383.

(36) Giguere, P. A.; Liu, I. D. *J. Am. Chem. Soc.* **1955**, *77*, 6477.

(37) *JANAF Thermochemical Tables*, 3rd ed.; Chase, M. W., Jr., Davies, C. A., Downey, J. R., Fruip, D. J., McDonald, R. A., Syverud, A. N., Eds. *J. Phys. Chem. Ref. Data Suppl.* **1985**, *14*.

(38) Ruscic, R.; Berkowitz, J. *J. Chem. Phys.* **1994**, *101*, 7795.

(39) Hassanzadeh, P.; Irikura, K. K. *J. Phys. Chem. A* **1997**, *101*, 1580.

(40) Lock, M.; Barnes, R. J.; Sinha, A. *J. Phys. Chem.* **1996**, *100*, 7972.

(41) Kukui, A.; Kirchner, U.; Benter, T.; Schindler, R. N. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 455.

(42) Guha, S.; Francisco, J. S. *J. Phys. Chem. A* **1997**, *101*, 5347.

(43) Lee, T. J. *J. Phys. Chem.* **1995**, *99*, 15074.

(44) Chase, M. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1069.