Study of the Stability of Cl_2O_3 Using ab Initio Methods

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The structure, vibrational frequencies, and rotational constants have been determined using ab initio methods of all stable conformers of Cl_2O_3. Contrary to previous studies, only four structures remained stable at higher levels of theory. The most stable structure, ClOCl(O)O, could be formed from the three-body reactions ClO + OClO + M → ClOCl(O)O + M and Cl + ClO_3 + M → ClOCl(O)O + M. The heat of reaction for these processes was determined to be -10.9 and −37.7 kcal mol^{-1}, respectively. The internal rotation barrier for this structure is found to be 2.4 kcal mol^{-1}, with a shallow minimum in the Cl′OClO′ dihedral angle. The results are compared with experimental measurements and other theoretical calculations.

I. Introduction

As higher concentrations of ClO and OClO were being measured during the Antarctic springtime, Sander et al.[1] and Anderson et al.[2] suggested that higher chlorine oxides may be formed. These higher chlorine oxides are suggested to have atmospheric importance if they are produced in abundance as either a temporary or long-term reservoir. One such higher order chlorine oxide, Cl_2O_3, can be produced through a three-body reaction involving ClO and OClO. A number of experimental studies have been conducted to confirm the formation of Cl_2O_3. Hayman and Cox[3] and Burkholder et al.[4] have examined the equilibrium constant for the formation of Cl_2O_3. Zabel,[5] using discharge flow-UV + IR absorption studies, reported infrared bands for Cl_2O_3. Discharge flow-submillimeter wave spectroscopic studies of Friedl et al.[6] have also yielded an effective r_0 structure determined in the ground vibration state for Cl_2O_3. Recent experimental evidence[7] has suggested that, while Cl_2O_3 may be stable, its overall concentration in the stratosphere is expected to be minor. While there is general agreement on this, discrepancies exist as to the physical properties of Cl_2O_3.

The results of previous theoretical studies of possible Cl_2O_3 structures have been inconsistent with the published experimental work. Part of this discrepancy can be explained by the poor choice of methods and/or basis sets used to handle this chemical system during these investigations. The earliest theoretical results[8] were performed using only the Hartree−Fock method of theory with a 6-31G(d) basis set. A shortcoming of this earlier work is that it failed to include effects of electron correlation on the Cl_2O_3 structure. A study by Flesch et al.[9] investigated the photodissociation of OClO and its derivatives. This study included theoretical calculations of the stability of various chlorine oxides, including conformers of Cl_2O_3. The structures were optimized using MP2 and CISD levels of theory, while single-point energy calculations were performed using the QCISD(T) level. These calculations utilized only the 6-31G(d) basis set, and the internal geometries were restricted during the optimization process. As a result, the structures obtained were not fully optimized. Moreover, various vibrational frequencies were calculated to be imaginary. This equates to structures that have not been fully optimized, as they were restricted in at least one degree of freedom. Consequently, there is uncertainty in what constitutes the stable structures of Cl_2O_3.

Also at issue is what is the thermal stability of Cl_2O_3. Determining this is critical before addressing the issue (raised by Sander et al.[1] and Anderson et al.[2]) of whether Cl_2O_3 could be produced in sufficient abundance as a chlorine reservoir. Experiments of Hayman and Cox,[3] have shown that from the reaction of ClO and OClO in equilibrium with Cl_2O_3, the enthaply of reaction, $\Delta H°$, is -14.8 ± 2.9 kcal mol^{-1}. This suggested a heat of formation for Cl_2O_3 of 34 ± 3 kcal mol^{-1}. An entropy value of 79.6 ± 11.9 cal mol^{-1} K^{-1} was also derived. Experiments from Burkholder et al.[4] estimate a $\Delta H°$ for the reaction of -11.1 ± 1.2 kcal mol^{-1} and an entropy value of 95 ± 19 cal mol^{-1} K^{-1}. The entropy value derived by Burkholder et al.[4] is in discrepancy with the experimental value of Hayman and Cox.[3]

In this study, we have used a variety of ab initio methods to examine the existence of all stable conformers of Cl_2O_3 and their thermodynamic properties. The lowest energy structure, a product of the reaction involving ClO and OClO, has been investigated further. The potential surface for the internal rotational of this molecule has been examined and revealed information that may assist in understanding experimental results.

II. Computational Methods

All ab initio calculations were performed using the Gaussian 94 series of programs.[10] The geometries of all structures were fully optimized using Schlegel's analytical gradient method[11] at the second-order Møller−Plesset (MP2) levels of theory[12] and two types of density functional theory (BLYP and B3LYP) models.[13,14] 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 the rms force less than 10^{-4} au. The following basis sets were used at all levels of correlations: 6-31G(d), 6-311G(d), 6-311+G(2d), 6-311+G(2df), and 6-311+G(3df). Vibrational frequencies and zero-point energies were also calculated at all levels of theory using analytical second derivatives. Single-point energies were calculated at the CCSD(T) level of theory using the B3LYP/6-311+G(3df) optimized geometries. All structures were also optimized using the configuration interaction with all single and double substitutions (CISD) from the Hartree−Fock reference determinant.[15] The CISD calculations were performed only for comparison with previously published calculations.

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TABLE 1: Optimized Geometries for Cl_2O_3 Isomers

		6-31G(d)					6-311+G(3df)		
species	coordinate	HF	MP2	CISD	BLYP	B3LYP	BLYP	B3LYP	expt.
ClOCl(O)O [A]	ClO	1.689	2.321	1.734	2.130	1.966	2.098	1.934	1.825
	OCl′	1.667	1.651	1.680	1.679	1.671	1.652	1.647	1.705
	ClO′	1.429	1.484	1.445	1.525	1.483	1.478	1.440	1.427
	ClO″	1.429	1.511	1.445	1.529	1.486	1.481	1.443	
	ClOCl′	113.5	96.3	112.7	107.0	110.1	108.0	110.9	108.6
	OClO′	98.3	104.8	104.4	104.4	103.3	102.9	102.3	96.5
	OClO″	104.8	90.5	104.4	98.4	101.3	116.8	101.7	104.3
	O′ClO″	114.8	117.7	113.7	117.6	116.2	99.2	115.6	114.3
	Cl′OClO′	179.3	107.0	59.8	108.9	104.7	111.8	108.1	
	Cl′OClO″	60.9	−11.9	59.8	−12.5	−15.9	−8.5	−11.8	49.7
ClOCl(O)O [B]	ClO	1.689	2.322	1.734	2.123	1.967	2.094	1.933	
	OCl′	1.667	1.651	1.680	1.681	1.671	1.654	1.647	
	ClO′	1.429	1.511	1.445	1.528	1.486	1.481	1.443	
	ClO″	1.429	1.484	1.445	1.524	1.483	1.478	1.440	
	ClOCl′	113.5	96.2	112.7	107.2	110.1	108.0	111.0	
	OClO′	104.8	90.4	104.4	98.5	101.3	99.1	101.7	
	OClO″	98.3	104.8	104.4	104.2	103.3	102.9	102.1	
	O′ClO″	114.7	117.8	113.7	117.7	116.2	116.8	115.7	
	Cl′OClO′	−60.9	11.8	59.8	11.2	15.6	8.3	11.2	
	Cl′OClO″	−179.3	−107.2	59.8	−110.2	−105.0	−112.0	−108.7	
ClOOOCl	ClO	1.678	1.735	1.700	2.073	1.761	2.093	1.727	
	OO′	1.359	1.428	1.385	1.247	1.400	1.228	1.399	
	O′O″	1.359	1.428	1.385	1.789	1.401	1.856	1.399	
	O″Cl′	1.678	1.735	1.700	1.670	1.671	1.625	1.727	
	ClOO′	110.0	108.7	109.4	115.5	110.7	115.9	111.0	
	OO′O″	108.1	107.8	107.8	111.6	109.7	109.5	109.7	
	O′O″Cl′	110.0	108.7	109.4	106.4	111.0	104.3	111.0	
	ClOO′O″	−82.4	−77.4	−80.3	92.2	−78.0	94.2	−78.0	
	OO′O″Cl′	−82.5	−77.4	−80.3	10.0	−78.0	10.0	−78.0	
$ClClO_3$	Cl′Cl	2.041	2.207	2.081	2.316	2.208	2.214	2.131	
	ClO	1.414	1.448	1.428	1.498	1.464	1.449	1.419	
	Cl′ClO	104.3	103.0	104.0	103.2	103.5	103.4	103.5	
	OClO′	114.1	115.1	114.4	115.0	114.8	114.9	114.7	

TABLE 2: Total and Relative Energies for Cl_2O_3 Isomers

	total energies (hartrees)				relative energies[a]			
level of theory	ClOCl(O)O [A]	ClOCl(O)O [B]	ClOOOCl	$ClClO_3$	ClOCl(O)O [A]	ClOCl(O)O [B]	ClOOOCl	$ClClO_3$
HF/6-31G(d)	−1143.123 075	−1143.123 075	−1143.194 450	−1143.088 154	41.9	41.9	0.0	65.0
MP2/6-31G(d)	−1144.032 176	−1144.032 176	−1144.049 124	−1143.985 007	11.3	11.3	0.0	42.9
CISD/6-31G(d)	−1143.865 073		−1143.918 488	−1143.826 662	34.1		0.0	60.3
BLYP/6-31G(d)	−1145.704 942	−1145.704 961	−1145.750 005	−1145.659 116	28.2	28.2	0.0	58.3
B3LYP/6-31G(d)	−1145.718 023	−1145.718 023	−1145.762 274	−1145.678 932	28.4	28.4	0.0	54.3
BLYP/6-311+G(3df)	−1145.915 614	−1145.915 718	−1145.916 241	−1145.890 880	0.7	0.7	0.0	19.0
B3LYP/6-311+G(3df)	−1145.927 160	−1145.927 161	−1145.920 142	−1145.914 710	−3.5	−3.5	0.0	6.1
CCSD(T)/6-311+G(3df)	−1144.537 731	−1144.537 739	−1144.532 987	−1143.530 031	−2.1	−2.1	0.0	4.6

[a] Relative energies include zero-point energy correction. CISD energies are corrected using MP2/6-31G(d) zero-point, and CCSD(T) energies are corrected using B3LYP/6-311+G(3df) zero-point energy.

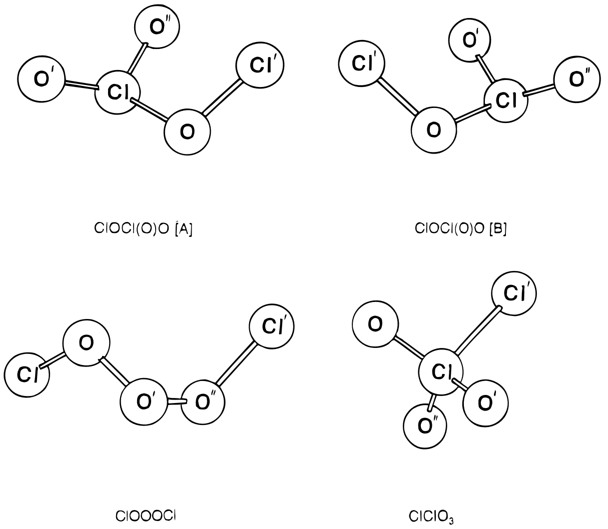
III. Results and Discussion

A. Geometries and Energetics. The various ab initio equilibrium geometries for Cl_2O_3 are presented in Table 1, and their corresponding energies are given in Table 2. We initially attempted to reproduce the theoretical results of previous studies. Burkholder et al.[4] published ab initio parameters for a ClOCl(O)O structure that was obtained by Hehre[8] at the Hartree−Fock level using the medium size 6-31G(d) basis set. At the Hartree−Fock level of theory, we were successful at reproducing the ClOCl(O)O structure of Hehre. Using MP2/6-31G(d) calculations, Flesch et al.[9] optimized five Cl_2O_3 isomers: (a) ClOOClO, (b) O_2ClClO, (c) OClOClO, (d) O_2ClOCl, and (e) ClOOOCl structures. At the MP2/6-31G(d) level the O_2ClClO isomer was found to be unstable, and only three different stable Cl_2O_3 isomers were suggested to form from OClO dimer photolysis, since the ClOOOCl isomer is unlikely to be formed from OClO. However, our re-examination of these structures, using the results from Flesch et al.[9] as our starting geometry, revealed that those structures were not fully optimized structures. We found that they were physically restricted to adhere to certain symmetries during the optimization process. Vibrational frequency calculations for all these structures showed them to have one or more imaginary frequencies, indicating that these structures are not true minimas. With the removal of symmetry restrictions, we found two of the Flesch structures to be unstable when allowed to optimize without constraint, and three distinct structures were found to be bound with all the methods used in this study. These structures have been labeled ClOCl(O)O, ClOOOCl, and $ClClO_3$.

The ClOCl(O)O structure, which we refer to as the Hehre structure, when optimized at the Hartree−Fock level was found to be a true minima. However, when density functional theory was employed, we found two structural changes occurred. Firstly, the internal Cl−O bond initially increased from 1.689 to 1.966 Å from the HF/6-31G(d) to BLYP/6-31G(d) levels. Even when using the MP2/6-31G(d) level the Cl−O bond increases to 2.321 Å, suggesting that the ClOCl(O)O structure is weakly bound. Secondly, the Cl′OClO″ dihedral angle changes from 60.9° to −15.9° from the HF/6-31G(d) to B3LYP/6-31G(d) levels. These results show that the form of correlation is very important for ClOCl(O)O. The geometry results in Table 1 also show a basis set dependence. At the highest level of theory of this study, i.e. B3LYP/6-311+G(3df) level, the internal Cl−O bond length increased to 1.934 Å, while the dihedral angle changes to -11.8°. The results for this structure are significantly different from the HF/6-31G(d) parameters. While both Hehre[8] and Flesch[9] found one conformation of ClOCl(O)O, we found two structures that are rotational conformers. We have also found that the new ClOCl(O)O conformer to which we refer as Cl(O)Cl(O)O [B] is a minimum. It is the mirror image of the Hehre structure (i.e. ClOCl(O)O [A]). The structures differ by an internal rotation of ca. 96.9°. However, at the CISD/6-31G(d) level of theory only one minimum energy structure for this form of Cl_2O_3 is found. Moreover, its dihedral angle was distinctly different from Flesch's structure. At the HF, MP2, and B3LYP levels, the two mirror rotational structures (ClOCl(O)O [A] and [B]) are at the same energies (see Table 2). We have explored the internal rotational potential for ClOCl(O)O. The details of this surface are presented in the next section. It is interesting to compare the structure for ClOCl(O)O at our best level of theory with the experimentally derived structure obtained from the submillimeter spectroscopy study of Friedl et al.[6] These authors found that Cl_2O_3 has no symmetry. The ClO′ and ClO″ bonds were assumed to be of approximately equal length. We find that at the B3LYP/6-311+G(3df) level of theory, the ClO′ and ClO″ bonds are nearly equal, i.e. 1.440 and 1.443 Å, respectively. These bond lengths are in the range expected of Cl═O double bonds, which are in the range 1.42−1.47 Å, if $FClO_2$ is used as a chemical model. The structure has a long inner Cl−O single bond. The submillimeter spectrum measures this bond length to be 1.825 Å. We estimate this bond length to be 1.934 Å at the B3LYP/6-311+G(3df) level. Theory overestimates this bond length by 0.109 Å. Nevertheless, the long Cl−O single bond length is consistent with the experimental results of Friedl et al.[6] and with the fact that the ClOCl(O)O structure is correlated to the dissociation into ClO and OClO. The terminal OCl′ bond length is predicted to be 1.647 Å; in the fit of the spectral data from the submillimeter data this bond was assumed to be 1.705 Å.

The second isomeric structure we found to have a stable minimum is ClOOOCl. Flesch et al.[9] considered it as one of their five isomeric structures. These authors restricted their optimized structure to be of C_{2v} symmetry. A vibrational frequency calculation showed this structure to possess two negative frequencies. An analysis of the frequency components suggested that the structure prefers to orient out-of-plane. With the removal of the symmetry restrictions and the full optimization of all parameters, we find that ClOOOCl orients in a straight-chain skewed structure. The ClOO′O″ dihedral angle at the B3LYP/6-311+G(3df) level of theory is −78.0°, and the OO′O″Cl′ dihedral angle is predicted to be −78.0°. The skewed structure was verified to be the minimum energy structure with no imaginary vibrational frequencies (see Table 4). When the C_{2v} symmetry contraints were lifted from ClOOOCl, the OO bonds contracted from 1.52 to 1.428 Å at the MP2/6-31G(d) level of theory. It is interesting to compare the OO bond lengths in ClOOOCl of 1.399 and 1.399 Å, predicted at the B3LYP/6-311+G(3df) level of theory, with the OO bond in ClOOCl of 1.426 Å. The bonding is remarkably similar.

The third isomeric form, $ClClO_3$, was found in this study to have C_{3v} symmetry. The ClO bond in $ClClO_3$ is predicted to be the shortest of the isomeric forms. This is due to the resonances associated with the Cl═O multiple bonding characteristics of $ClClO_3$. The ClO bond distance of 1.419 Å at the B3LYP/6-311+G(3df) level of theory is shorter than the terminal ClO′ bonds in ClOCl(O)O at 1.440 and 1.443 Å. The optimized structures determined in this study are shown in Figure 1.



ClOCl(O)O [A] ClOCl(O)O [B]

ClOOOCl $ClClO_3$

Figure 1. Stable geometrical structures of Cl_2O_3. The complete parameter list is given in Table 1 for all structures.

The calculated total and relative energies for Cl_2O_3 isomers are given in Table 2. At the HF/6-31G(d) level of theory, the relative stability for Cl_2O_3 isomers are, in decreasing order, (1) $ClClO_3$, (2) ClOCl(O)O, and (3) ClOOOCl. However, we note that the relative energetic stability of Cl_2O_3 isomers is sensitive to basis set and electron correlation effects. For example, comparing ClOOOCl with the ClOCl(O)O, the HF/6-31G(d) relative energy between the two structures is 41.9 kcal mol^{-1}. At the MP2 level, it decreases to 30.6 kcal mol^{-1}. The CISD level shows a decrease of 7.8 kcal mol^{-1}, while both density functional methods show a decrease of ca. 13 kcal mol^{-1}. At the B3LYP/6-311+G(3df) level of theory, the energetic ordering of these structures reverses. The ClOCl(O)O becomes the more stable structure by 3.5 kcal mol^{-1}. The energetic difference between the ClOOOCl and $ClClO_3$ structure at the B3LYP/6-311+G(3df) is also small (ca. 6.1 kcal mol^{-1}). Note that from the HF/6-31G(d) to the B3LYP/6-311+G(3df) level, the relative energy difference drops from 65.0 to 4.6 kcal mol^{-1}, respectively. These dramatic effects are the result of the hypervalent character of the $ClClO_3$. These results show that the energy gap between normal-valent and hypervalent structures, upon both improvement of the treatment of electron correlation and increased size of the basis set, is reduced significantly. Moreover, these calculations also show that the predictions of the energetics of Cl_2O_3 isomers using ab initio methods with the medium size 6-31G(d) basis set are unreliable. Because the energy differences between the structures obtained at the B3LYP/6-311+G(3df) level are small, and because there are multiple factors occurring in these isomers that affect their relative energies, we also performed CCSD(T)/6-311+G(3df) single-point energies for each of the isomers using these B3LYP/6-311+G(3df) geometries. We find the CCSD(T)/6-311+G(3df)//B3LYP/6-311+G(3df) and B3LYP/6-311+G(3df) energetics to be in agreement with the ordering in stabilities of the Cl_2O_3 isomers:

$$\mathrm{ClOCl(O)O} < \mathrm{ClOOOCl} < \mathrm{ClClO_3}$$

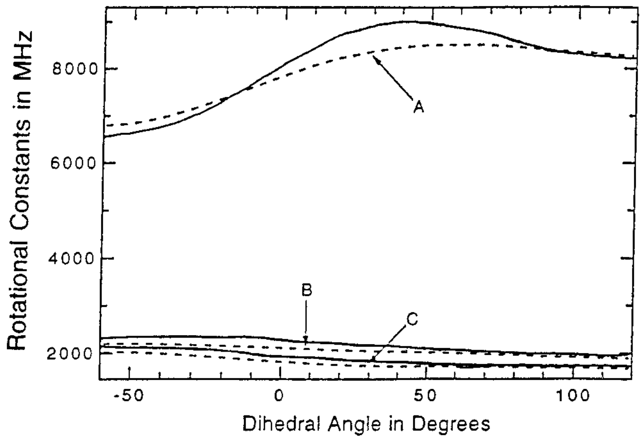


Figure 2. Comparison of calculated and experimental rotational constants for ClOCl(O)O as a function of dihedral angle (solid line, data taken from ref 6; dashed line, calculated from the B3LYP/6-311+G(3df) level of theory).

TABLE 3: Rotational Constants for Cl_2O_3 Isomers

		rotational constants (MHz)		
species	level of theory	*A*	*B*	*C*
ClOCl(O)O [A]	HF/6-31G(d)	9048.3	2154.3	1862.9
	MP2/6-31G(d)	7025.7	2029.8	1773.7
	CISD/6-31G(d)	6823.4	2332.4	2138.7
	BLYP/6-31G(d)	6845.7	1942.6	1689.9
	B3LYP/6-31G(d)	7123.3	2080.7	1819.3
	BLYP/6-311+G(3df)	7263.8	1994.1	1732.1
	B3LYP/6-311+G(3df)	7585.8	2137.8	1865.6
ClOCl(O)O [B]	HF/6-31G(d)	9051.2	2154.1	1828.6
	MP2/6-31G(d)	7030.7	2030.2	1773.6
	CISD/6-31G(d)			
	BLYP/6-31G(d)	6889.7	1942.3	1686.7
	B3LYP/6-31G(d)	7133.8	2079.7	1818.0
	BLYP/6-311+G(3df)	7275.1	1996.8	1734.1
	B3LYP/6-311+G(3df)	7601.6	2137.0	1863.1
ClOOOCl	HF/6-31G(d)	11640.9	1422.7	1407.0
	MP2/6-31G(d)	9467.3	1410.5	1381.0
	CISD/6-31G(d)	10678.1	1423.7	1402.3
	BLYP/6-31G(d)	5565.4	1574.3	1349.1
	B3LYP/6-31G(d)	9560.9	1367.4	1334.2
	BLYP/6-311+G(3df)	5525.9	1612.2	1369.2
	B3LYP/6-311+G(3df)	9872.2	1388.7	1356.0
$ClClO_3$	HF/6-31G(d)	5612.1	2951.1	2951.1
	MP2/6-31G(d)	5292.1	2645.4	2645.4
	CISD/6-31G(d)	5468.1	2859.3	2854.3
	BLYP/6-31G(d)	4946.1	2421.8	2421.2
	B3LYP/6-31G(d)	5192.9	2614.7	2614.5
	BLYP/6-311+G(3df)	5299.3	2626.0	2625.8
	B3LYP/6-311+G(3df)	5530.3	2798.0	2798.0

At the CCSD(T)/6-311+G(3df)//B3LYP/6-311+G(3df) level of theory, the ClOCl(O)O structure is the lowest energy structure and is more stable than the ClOOOCl structure by 2.1 kcal mol^{-1}.

B. Rotational Potential Energy Surface for ClOCl(O)O. Friedl et al.,[6] in their submillimeter spectroscopy study of Cl_2O_3, determined the experimental rotational constants for the Cl_2O_3 isomer to be 8629.197 MHz (*A*), 2106.410 MHz (*B*), and 1776.122 MHz (*C*). Our calculated rotational constants for all the different conformers are listed in Table 3. When the rotational constants for ClOCl(O)O are compared to the results of Friedl et al.,[6] we find good agreement with the *B* and *C* rotational constants. A comparison of the rotational constants calculated with changing dihedral angle and those determined by Friedl (Figure 2) illustrates the good agreement in the *B* and *C* rotational constants with the dihedral angle rotation, though there is a difference with the A rotational constant when the dihedral angle is between −20° and 85°. This difference suggests there are underlying subtleties with the internal rotational potential surface.

With the changes in the rotational constants with dihedral angle and the prediction of two minimum energy structures for ClOCl(O)O, we decided to explore the ClOCl(O)O internal rotational potential energy surface in detail. In mapping out the potential energy surface at the B3LYP/6-311+G(3df) level, step sizes in the dihedral angle of 0.5° were taken and the energy points calculated for each structure. The resulting potential energy surface is shown in Figure 3. When the dihedral angle of Cl′OClO″ was 120.5°, an internal barrier of 2.5 kcal mol^{-1} was found at the B3LYP/6-311+G(3df) level. A barrier of 0.50 kcal mol^{-1} was also found when the dihedral angle was −59.5°. This barrier is located between the two minima ClOCl(O)O rotational structures. At a dihedral angle of 43.5° and −163.0° a very shallow local minimum with a well depth of only 0.2 kcal mol^{-1} was also found. The barrier height 0.5 kcal mol^{-1} between the two ClOCl(O)O mimimas (i.e. structure A and B) is smaller than the expected error range for the B3LYP calculation. Consequently, its existence is questionable. Nevertheless, these calculations suggest that the internal rotational potential energy surface for ClOCl(O)O is quite complex and care should be taken in the choice of structure even for the analysis of the experimental submillimeter spectrum. We performed CCSD(T)/6-311+G(3df) single-point calculations for the two maxima using the B3LYP/6-311+G(3df) geometry. The barrier at 120.5° decreased to 2.4 kcal mol^{-1}, while the barrier at −59.5° decreased to 0.1 kcal mol^{-1}.

C. Vibrational Spectra of Cl_2O_3 Isomers. The point group for the ClOCl(O)O isomer is C_1. Under C_1 point group symmetry, there are nine fundamental vibrational modes of ClOCl(O)O, all of which are both infrared and Raman active. We have calculated the vibrational frequencies at various levels of theory, ranging from the Hartree−Fock, MP2, BLYP, and B3LYP levels, using the 6-31G(d) basis set firstly to reproduce previous published and unpublished results. These are given in Table 4. The Hartree−Fock frequencies reproduce the results calculated by Hehre which were included in the experimental paper by Burkholder et al.[4] However, we find the incorporation of electron correlation, such as MP2, has the effect of lowering all the vibrational frequencies except the ν_9 torsion mode. The rms percentage difference is 31.7%, with the maximum percentage difference as much as ca. 45% in the ν_7. The percent difference between MP2 and B3LYP results is smaller, i.e. 19.8% (rms). These results suggest that post-Hartree−Fock treatments are needed to describe the vibrational frequencies for Cl_2O_3. We extended the basis set size for these calculations utilizing the large 6-311+G(3df) basis set with the B3LYP method. These results are included in Table 4. In this table we have also included results from the experimental reports of Cheng and Lee,[16] Zabel,[5] and Burkholder.[4] These researchers reported vibrations in the ranges 1226−1224 cm^{-1}, 1058−1057 cm^{-1}, 740−731 cm^{-1}, and 565−560 cm^{-1}, which they attribute to Cl_2O_3. These modes are consistent with ν_1 (ClO′ asymmetric stretch mode), ν_2 (ClO symmetric stretch), ν_3 (Cl′O stretch), and ν_4 (O′Cl bend) modes for ClOCl(O)O. The vibration mode vectors for the mode assignments are shown in Figure 4. The rms error between the reported experimental frequencies for Cl_2O_3 and the B3LYP/6-311+G(3df) frequencies is 3.2%. The relative intensities show good qualitative agreement with that predicted for Cl_2O_3. To our knowledge there is no report of the full vibrational spectrum for Cl_2O_3. The present B3LYP/6-311+G(3df) vibrational frequencies and intensities should aid the experimental interpretation and assignment of the infrared and/or Raman spectrum of Cl_2O_3.

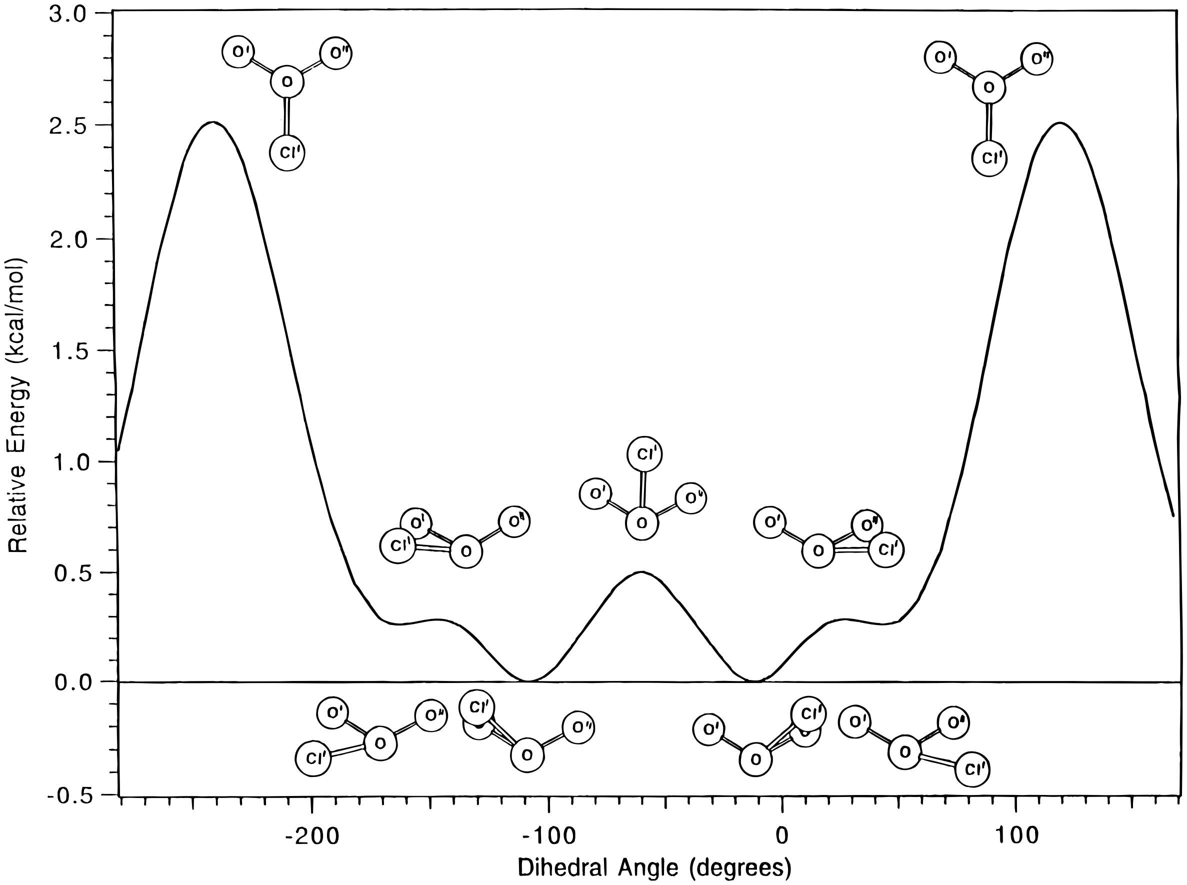
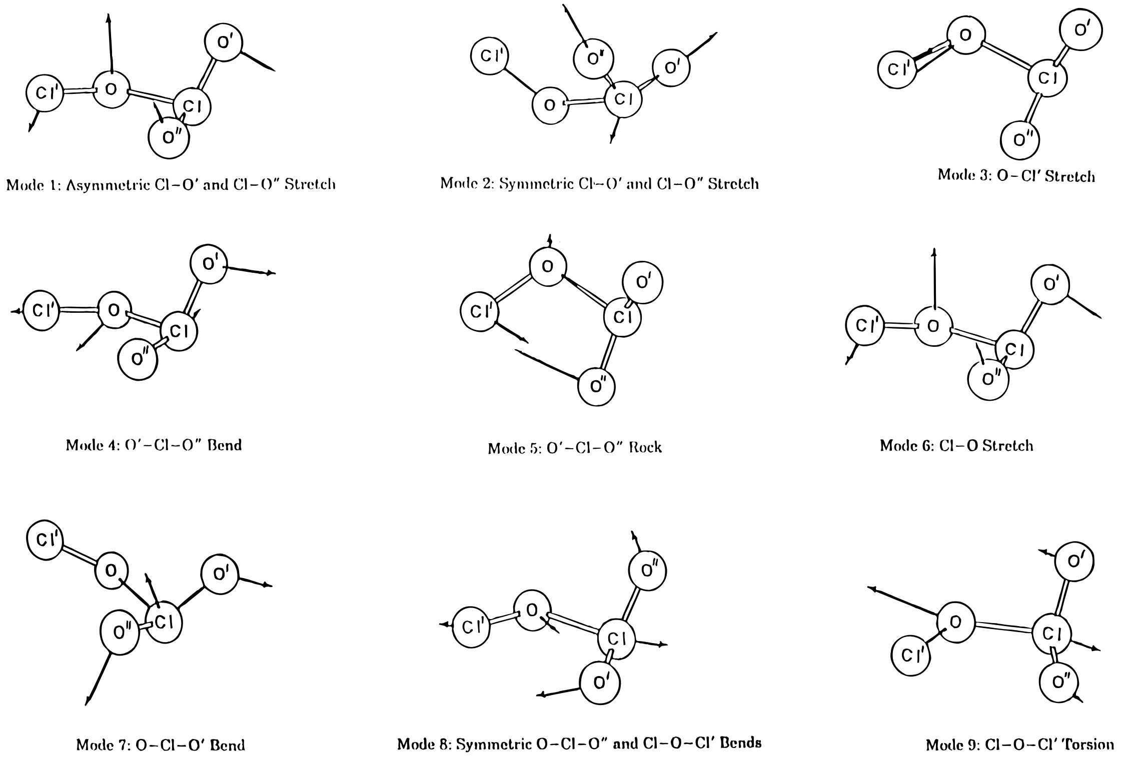


Figure 3. Potential energy surface for internal rotation in ClOCl(O)O.



Mode 1: Asymmetric Cl–O′ and Cl–O″ Stretch

Mode 2: Symmetric Cl–O′ and Cl–O″ Stretch

Mode 3: O–Cl′ Stretch

Mode 4: O′–Cl–O″ Bend

Mode 5: O′–Cl–O″ Rock

Mode 6: Cl–O Stretch

Mode 7: O–Cl–O′ Bend

Mode 8: Symmetric O–Cl–O″ and Cl–O–Cl′ Bends

Mode 9: Cl–O–Cl′ Torsion

Figure 4. Vibrational mode vectors for mode assignments for ClOCl(O)O [A].

Also in Table 4 are vibrational frequencies for $ClClO_3$. The vibration mode vectors for the mode assignments for $ClClO_3$ are shown in Figure 5. The structures of $ClClO_3$ may be derived from the perchlorate ion, ClO_4^-, by substitution of a chlorine for one oxygen. The structure has C_{3v} symmetry and only six distinct fundamental vibrations. There should be three totally symmetric, parallel vibrations of a_1 symmetry and three doubly degenerate fundamentals of e symmetry. These span the representation $3a_1 + 3e$. All the vibrational modes are infrared active. Because there are no experimental reports of the spectral characterization of the $ClClO_3$ isomer, we use two models to aid in assessing whether or not the B3LYP/6-311+G(3df)

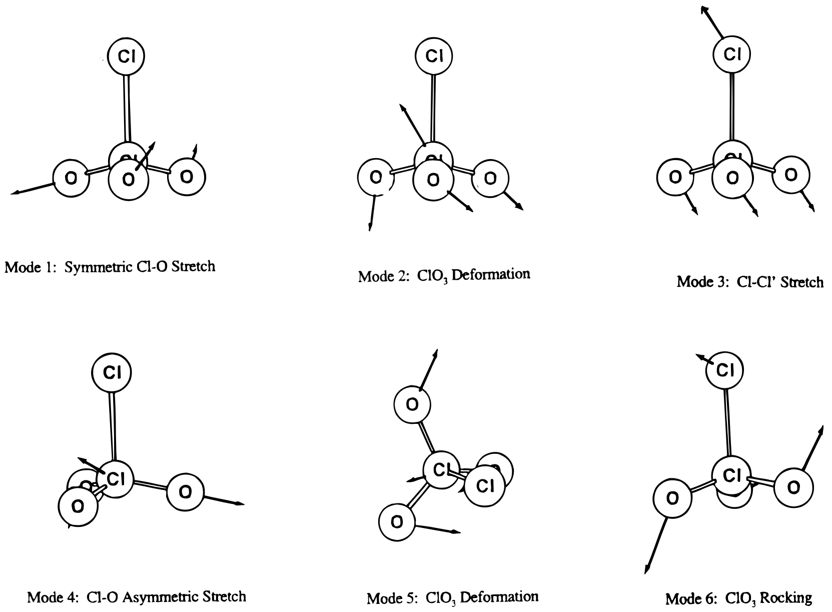


Figure 5. Vibrational mode vectors for mode assignments for $ClClO_3$.

TABLE 4: Vibrational Frequencies and Intensities for Cl_2O_3 Isomers

			vibrational frequencies (cm^{-1})						experimental			intensity B3LYP/6-311+G(3df)	
			6-31G(d)				6-311+G(3df)						
species	mode no.	mode description	HF	MP2	BLYP	B3LYP	BLYP	B3LYP	Cheng & Lee	Zabel	Burkholder	absolute	relative
ClOCl(O)O [A]	1	ClO′ asym. stretch	1315	1281	1032	1161	1093	1233	1226.1	1224	1225	179	1.0
	2	ClO′ sym. stretch	1137	1083	886	1002	934	1062	1058.4	1057	1057	129	0.7
	3	Cl′O stretch	889	789	721	755	736	765	730.9	740	740	14	0.1
	4	O′ClO bend	742	474	435	502	471	539	565.4	560	560	15	0.1
	5	O′ClO″ rock	593	371	356	405	377	433				10	0.1
	6	ClO stretch	474	271	310	362	324	366				28	0.2
	7	OClO′ bend	382	208	184	232	201	255				3	0
	8	OClO″ bend	224	162	138	172	143	183				1	0
	9	ClOCl′ torsion	93	115	88	62	80	54				2	0
ClOCl(O)O [B]	1	ClO′ asym. stretch	1315	1281	1035	1161	1105	1233				179	1.0
	2	ClO′ sym. stretch	1138	1081	890	1002	945	1062				129	0.7
	3	Cl′O stretch	889	792	723	756	732	764				14	0.1
	4	O′ClO bend	742	472	437	502	472	539				15	0.1
	5	O′ClO″ rock	593	369	357	405	379	433				10	0.1
	6	ClO stretch	474	270	312	362	327	368				28	0.2
	7	OClO′ bend	381	209	180	231	201	255				3	0
	8	OClO″ bend	224	160	142	172	152	186				1	0
	9	ClOCl′ torsion	92	111	83	63	79	53				2	0
ClOOOCl	1	OO asym. stretch	1086	820	1281	876	1297	867				3	0.1
	2	OO sym. stretch	1085	724	757	739	792	738				21	1.0
	3	OOO bend	849	688	555	661	547	668				1	0
	4	ClO asym. stretch	831	576	473	557	470	563				5	0.2
	5	OOO out-of-plane wag	665	554	410	513	370	508				8	0.4
	6	ClO sym. stretch	557	476	290	427	269	441				14	0.7
	7	ClOO sym. bend	307	255	198	249	195	255				0_2	0
	8	ClOO asym. bend	158	154	133	156	129	158				0_5	0
	9	ClOO torsion	73	67	79	68	81	68				0_2	0
$ClClO_3$	1 (a_1)	ClO stretch	1076	1091	857	950	929	1027				101	0.5
	2 (a_1)	ClO_3 deformation	707	587	513	570	567	621				187	1.0
	3 (a_1)	ClCl stretching	411	281	243	298	290	340				16	0.1
	4 (e)	ClO stretch	1320	1336	1069	1177	1153	1261				185	1.0
	5 (e)	ClO_3 deformation	585	508	439	485	493	539				141	0.1
	6 (e)	ClO_3 rock	333	269	225	228	258	289				0_1	0

vibrational frequencies are reasonable. The two chemical models are ClO_4^- and $FClO_3$. For ClO_4^- the molecule is of T_d symmetry. Its IR vibrations[17] are 932 cm^{-1} (a_1), 460 cm^{-1} (e), 1110 cm^{-1} (f_2), and 626 cm^{-1} (f_2). The correlation (see Table 5) with C_{3v} requires that the f_2 symmetry species split into one a_1 and one e symmetry representations. The f_2 bending of ClO_4^- will split into a pair of a_1 and e vibrations separated by not more than about 100 cm^{-1} from the parent 626 cm^{-1}, while the f_2 symmetry species for the stretching mode will split into a pair of symmetric (a_1) and degenerate (e) stretching vibrations separated by ca. 200 cm^{-1}. Using this as a model, we would predict that 1110 cm^{-1} (f_2) splits into two components of 1210 cm^{-1} and 1010 cm^{-1}. Our B3LY/6-311+G(3df) calculations predict ν_1 of a_1 symmetry representing a ClO stretching mode to be at 1027 cm^{-1} and ν_4 of e symmetry to be at 1261 cm^{-1}. The ClO_4^- model suggests that the 626 cm^{-1} (f_2) bending modes would split into two components of 675 cm^{-1} and 575 cm^{-1}. These are consistent with the B3LYP/6-311+G(3df) predictions of ν_2 (a_1) of 621 cm^{-1} and ν_5 (e) of 539 cm^{-1}. The e rocking mode of ClO_4^- would be expected to shift toward lower

TABLE 5: Correlation Table for Splitting of Vibrational Modes of ClO_4^- [a]

symmetry	ν_1	ν_2	ν_3	ν_4
T_d	a_1	e	f_2	f_2
	R	R	i.r., R	i.r., R
C_{3v}	a_1	e	a_1 + e	a_2 + e
	i.r., R	R	a11 i.r., R	a11 i.r., R
C_{2v}	a_1	$a_1 + a_2$	a_1 + b, + b_2	a_1 + b
	i.r., R	i.r., R; R	a11 i.r., R	a11 i.r., R
C_s	a′	a′ + a″	2a′ + a″	2a′ + a″
	i.r., R	a11 i.r., R	a11 i.r., R	a11 i.r., R

[a] i.r. refers to infrared; R to Raman.

frequency from the pure 460 cm^{-1} mode in unperturbed ClO_4^-. Its symmetry character would be preserved. The ν_6 (e) ClO_3 rocking mode for $ClClO_3$ is predicted to 289 cm^{-1}, consistent with this model prediction.

Another model to compare with $ClClO_3$ is $FClO_3$. In this molecule, ν_1 (a) for the ClO stretch has been determined to be 1063 cm^{-1} and the ν_4 (e) for the ClO stretch is 1317 cm^{-1}. The ν_2 (a_1) and ν_5 (e) ClO_3 deformation modes for $FClO_3$, which are 550 and 590 cm^{-1}, are consistent with those predicted for $ClClO_3$. Both the ClO_4^- and $FClO_3$ chemical models suggest that the B3LYP/6-311+G(3df) vibrational frequencies may be reasonably well predicted for $ClClO_3$.

The vibrational frequencies and intensities for the ClOOOCl isomer calculated at the B3LYP/6-311+G(3df) level of theory are given in Table 4, and its mode vectors for the mode assignments are shown in Figure 6.

Our predictions of the vibrational spectra and the assignments of the vibrational modes for Cl_2O_3 isomers using B3LYP/6-311+G(3df) wave functions appear reasonable. As shown in Table 4 our calculations predict a mean deviation between the B3LYP and the few experimental observed frequencies for ClOCl(O)O of 11.3 cm^{-1}, which is well within the mean absolute deviation (13.3 cm^{-1}) between B3LYP and observed frequencies of many small gas phase molecules.

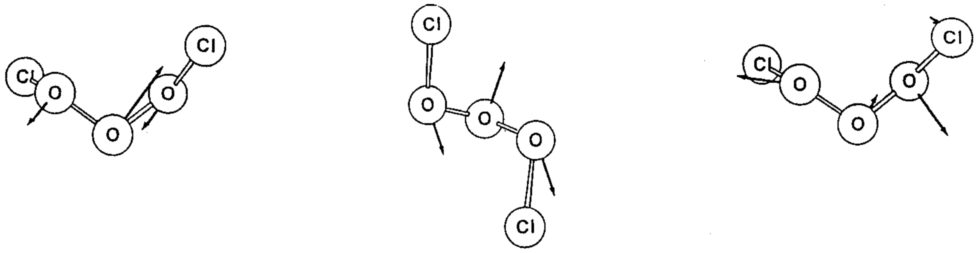
D. Thermochemical Properties of Cl_2O_3 and Its Isomers. The thermochemical properties of Cl_2O_3 have been a point of some debate in the literature. The experimental work of Hayman and Cox[3] deduced an enthalpy of formation of Cl_2O_3 of 33.9 ± 2.9 kcal mol^{-1} and a standard entropy of 79.6 ± 11.9 cal mol^{-1} K^{-1}. The enthalpy of formation obtained by Hayman and Cox corresponds to a reaction enthalpy of −14.8 ± 2.9 kcal mol^{-1} for the formation of Cl_2O_3 via

$$ClO + OClO + M \rightarrow Cl_2O_3 + M$$

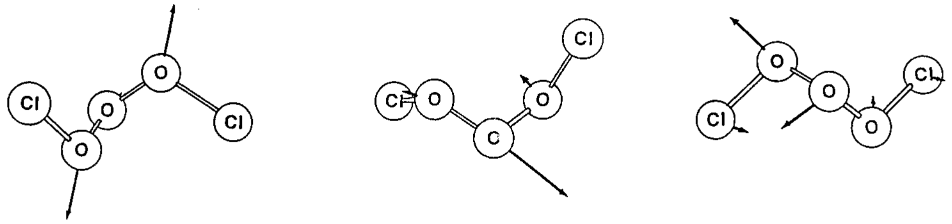
Work by Burkholder et al.,[4] however, suggested a much larger entropy, 95 ± 19 cal mol^{-1} K^{-1}, and a larger enthalpy of formation of 36.5 kcal mol^{-1}, calculated from a smaller reaction enthalpy of −11.1 kcal mol^{-1}. While the two experimental results are in a broad range, they are consistent with one another, but the two results have different implications for the atmospheric lifetime for Cl_2O_3.

In order to shed some light on these experimental results, we have used two ab initio schemes to estimate the heat of formation for ClOCl(O)O. The first approach determines the heat of formation using G2 theory.[18,19] In the second approach we estimate the heat of reaction for ClO + OClO → ClOCl(O)O, and using the experimental heats of formation[20,21] for ClO of 24.2 ± 0.5 kcal mol^{-1} and OClO of 24.9 ± 1.5 kcal mol^{-1}, we can determine the heat of formation for ClOCl(O)O. Our estimate for the heat of formation for ClOCl(O)O at the G2 level is 44.5 kcal mol^{-1}. These results are summarized in Table 6. At the CCSD(T)/6-311+G(3df)// B3LYP/6-311+G(3df) level of theory, using reaction 1, we estimate the heat of formation for ClOCl(O)O to be 38.2 ± 2 kcal mol^{-1}. If we use the heat of formation for OClO of 23.2 kcal mol^{-1} from Nickolaisen et al.,[22] the heat of formation for $ClOClO_2$ is estimated to be 36.5 kcal mol^{-1}. This is in excellent agreement with the Burkholder et al.[4] result. The G2 estimated heat of formation value may have a large uncertainty associated with it because in the G2 formalism, both scaled Hartree−Fock frequencies and the MP2 geometries are used in the energy estimation. As one can see from Table 1, the MP2 geometry for ClOCl(O)O may be inadequate for determining the G2 energy. The more reliable estimate comes from the CCSD(T)/6-311+G(3df)//B3LYP/6-311+G(3df) level of theory, where the B3LYP/6-311+G(3df) geometry is used. Our heat of formation for ClOCl(O)O obtained at this level of theory compares well with the experimental estimate of Burkholder et al.[4] To estimate the heats of formation for the other isomers, we add their energy separation values from Table 2 to the heat of formation determination value at the CCSD(T)/6-311+G(3df)//B3LYP/6-311+G(3df) level of theory. The G2 estimates for isomers ClOOOCl and $ClClO_3$ are in reasonable agreement with the CCSD(T) results. (These methods have been tested on a series of molecules having well-established geometries and experimental values for their dissociation energies. The mean deviation between experimental and G2 values is ±1.5 kcal mol^{-1}.[18,19])

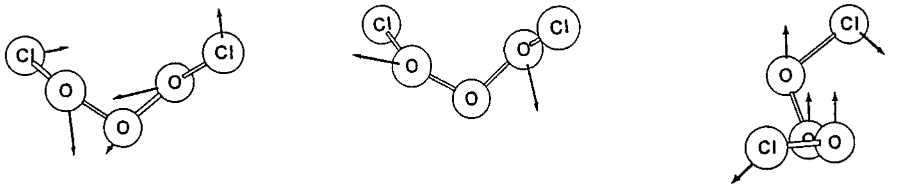
Burkholder et al.[4] derived the entropy two different ways: by a van t'Hoff analysis (second law) and from a direct calculation using spectroscopic data. However, they found discrepancies in their analyses of kinetic and thermochemical data which they suggested was an indication that the entropy of Cl_2O_3 is not calculated correctly from the experimental rotational constants of Friedl et al.[6] and the ab initio vibrational frequencies provided to them by Hehre.[8] They suggested that the calculated entropy is very sensitive to low-frequency vibrational modes, which was not well-known. In order to shed some light on this, from the calculated B3LYP/6-311+G(3df) geometry optimizations and vibrational frequency calculations we are able to calculate entropies of formation for the Cl_2O_3 isomers. We have also calculated entropies for ClO and OClO to estimate some degree of uncertainty in these values. Probable uncertainties from ClO and OClO are within ±1.2 cal mol^{-1} K^{-1} for our estimate of the entropy of formation for Cl_2O_3 isomers. Calculated entropy of formation for ClOCl(O)O is 78.5 cal mol^{-1} K^{-1}. We find that our entropy of formation value is in good agreement with the estimate of Hayman and Cox[3] of 79.6 ± 11.9 cal mol^{-1} K^{-1} and Abramowitz and Chase[20] of 77.8 cal mol^{-1} K^{-1}. The entropy value that Burkholder et al.[4] calculated from using spectroscopic data was found to be in good agreement with our calculated value and the result of Hayman and Cox.[3] However, the entropy value derived from the van t'Hoff (second law) analysis by Burkholder et al.[4] is highly discrepant with our theoretical estimate, those of Hayman and Cox,[3] and those of Abramowitz and Chase.[20] Burkholder et al.[4] preferred the value from the second-law analysis because it is based on their equilibrium constant measurements. Interesting, the equilibrium constant data from Hayman and Cox[3] and Burkholder et al.[4] are in good agreement except at the lowest temperature (233 K). This point is quite far off Hayman and Cox's van't Hoff line based on their data from 243−273 K. However, Burkholder et al.[4] neglect this point in the fit, which leads to an entropy that is significantly different. Neglecting the 233 K point leads to the discrepancy between the two methods. It is also interesting to note that the entropy value determined by Burkholder et al.[4] from the second



Mode 1: O-O Asymmetric Stretch Mode 2: O-O Symmetric Stretch Mode 3: O-O'-O" Bend



Mode 4: Cl-O Asymmetric Stretches Mode 5: O-O-O Out of Plane Wag Mode 6: Cl-O Symmetric Stretches



Mode 7: Cl-O-O Symmetric Bend Mode 8: Cl-O-O Asymmetric Bend Mode 9: Cl-O-O-O Tortion

Figure 6. Vibrational mode vectors for mode assignments for ClOOOCl.

TABLE 6: Heat of Formation for Cl_2O_3 Isomers

	$\Delta H^\circ_{f,0}$		
species	G2	CCSD(T)/6-311+G(3df)/-/B3LYP/6-311+G(3df)	expt
ClOCl(O)O	44.5	38.2[d] 36.5[e]	36.5[a] 33.9 ± 2.9[b] 33.6[c]
ClOOOCl	41.9	40.3 38.6[e]	
$ClClO_3$	46.2	44.9 43.2[e]	

[a] Reference 4. [b] Reference 3. [c] Reference 20. [d] Based on OClO heat of formation value of 24.9 ± 1.5 kcal mol^{-1} from ref 21. [e] Based on OClO heat of formation value of 23.2 ± 1 kcal mol^{-1} (0 K) and 22.6 ± 1 kcal mol^{-1} at 298 K from ref 22.

TABLE 7: Entropy of Formation for Cl_2O_3 Isomers

	S (cal mol^{-1} K^{-1})	
species	B3LYP/6-311+G(3df)	expt
ClO	52.8	53.8[a]
OClO	62.7	61.5[a]
ClOCl(O)O	78.5	79.6 ± 11.9[b] 77.8[a] 95 ± 19[c]
ClOOOCl	78.7	
$ClClO_3$	72.5	

[a] References 20 and 21. [b] Reference 3. [c] Reference 4.

law analysis does not fit any of the other Cl_2O_3 isomers determined by these calculations.

Using the results from Tables 6 and 7, we calculate for reaction 1 that the heat of reaction is −10.9 kcal mol^{-1} using CCSD(T)/6-311+G(3df)//B3LYP/6-311+G(3df) results, and the ΔS is −37 cal mol^{-1} K^{-1}. These results suggest that the heat of reaction energetics is in good agreement with the experimental results of Burkholder et al.,[4] while our entropy change for the reaction is in better agreement with the experimental results of Hayman and Cox.[3]

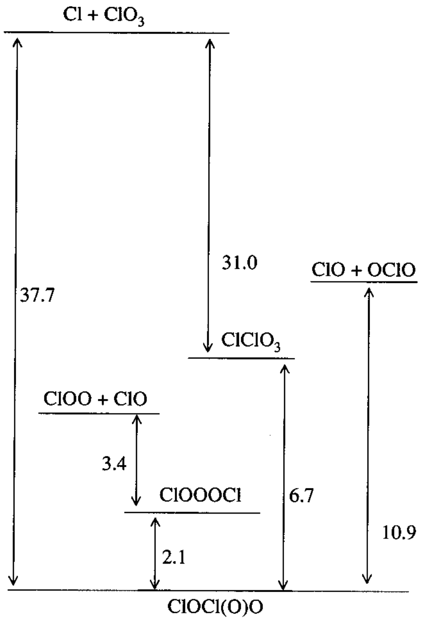


Figure 7. Relative energy diagram for dissociation pathways for Cl_2O_3 isomers. Numbers are in units of kcal mol^{-1}.

From experimental heats of formation,[20−24] for Cl, ClO, ClOO, OClO, and ClO_3 of 28.6 ± 0.0, 24.2 ± 0.5, 24.1 ± 0.4, 24.9 ± 1.5, and 47.3 ± 2 kcal mol^{-1}, respectively, we have calculated relative energy values for dissociation pathways for Cl_2O_3 isomers considered in this study. The relative energy diagram is shown in Figure 7. The common experimental approach to forming ClOCl(O)O in the laboratory has been by the reaction of ClO radicals and OClO. However, we see from Figure 7 that another probable pathway could result in the formation of ClOCl(O)O by the reaction of Cl atoms with ClO_3. This pathway is thermodynamically favorable. We also see that this reaction may also be a route to the formation of the $ClClO_3$ isomer. To form the chained ClOOOCl isomer requires that ClO radicals react with short-lived ClOO radicals. The likelihood of forming ClOOOCl in the atmosphere will have low probability. If ClO_3 radicals are produced in the atmosphere in sufficient abundances and the NO_x abundances are also low, the probability of forming $ClClO_3$ as a temporary or long-term chlorine reservoir from the Cl_2O_3 family cannot be ruled out.

IV. Summary

Four minimum energy structural conformers of Cl_2O_3 have been identified using various ab initio methods. The geometry vibrational frequencies, rotational constants, and thermodynamic properties have been determined for each of these structures. The results from these calculations support observations that the Cl_2O_3 observed in the various experiments are due to the ClOCl(O)O structure.

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