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Quantum Mechanical Studies on the BrO + ClO Reaction[†]

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Geometries for possible transition states and energy minima of the potential-energy surface for the reaction between BrO and ClO radicals and for conformers of ClOOBr peroxide have been identified and harmonic frequency calculations have been carried out at the second-order Moller−Plesset perturbation theory level using the 6-311++G(2d) and the 6-311++G(3df) basis sets. The energetics have been studied using the CCSD(T)/6-311++G(3df) methodology at the MP2 calculated geometries. The results assist in the qualitative understanding of the mechanism and the kinetics of the stratospherically important BrO + ClO reaction.

1. Introduction

The gas-phase chemistry of halogen monoxide radicals has long been of atmospheric interest, because of their direct involvement in several catalytic ozone depletion cycles. One of the most important of these processes is the coupling between bromine and chlorine monoxides. This coupling has been shown to play an important role in the development of the "ozone hole" over Antarctica,[1,2] and analogous indications were obtained within the Arctic stratosphere. In addition the BrO + ClO cross reaction was blamed[3] as the primarily responsible pathway for the formation of OClO through the channel

$$\mathrm{ClO + BrO \rightarrow OClO + Br}$$

As a result, the bromine oxide−chlorine oxide disproportionation reaction has given the motive for several experimental kinetic studies[4−11] and for extensive theoretical investigations of the intermediates complexes,[12−14] assumed to be formed during the course of the reaction. Also photoisomerization studies of the chain structure BrOClO and other XOClO (X = Cl and I) species have been performed and have shown direct isomerization to Y-shaped isomers with the X halogen bound to the Cl atom.[15]

The reaction between ClO and BrO radicals is a three- channel process taking place in the following scheme:[11]

$$\mathrm{BrO + ClO \rightarrow ClOO + Br} \quad \Delta H^\circ_{298} = -5.2\ \mathrm{kcal\ mol^{-1}} \qquad \text{(a)}$$

$$\rightarrow \mathrm{OClO + Br} \quad \Delta H^\circ_{298} = -4.7\ \mathrm{kcal\ mol^{-1}} \qquad \text{(b)}$$

$$\rightarrow \mathrm{BrCl + {}^3O_2} \quad \Delta H^\circ_{298} = -50.9\ \mathrm{kcal\ mol^{-1}} \qquad \text{(c)}$$

Similarly to the analogous ClO + ClO reaction, the main channels lead to the formation of chlorine dioxides, i.e., the Br + ClOO or the Br + OClO products, and the third, highly exothermic channel is found to account only for 10% of the overall rate at room temperature. Unlike the ClO + ClO reaction, however, it is a much faster process with a rate coefficient k ranging from 1.08 ± 0.20 to 1.40×10^{-11} cm^3 molecule^{-1} s^{-1} at room temperature.[11] These indications couple with the experimental findings of a significant negative temperature dependence of the overall reaction rate and an increasing importance of the OClO + Br channel as the temperature decreases.[9−11] A plausible explanation assumed the formation of a short-lived intermediate of the type [ClOOBr]* that either leads to channel a or possibly rearranges to a four-centered intermediate and produces the molecular products BrCl and O_2 through the elimination channel c. A short-lived intermediate of the type [BrOClO]* was suggested to be formed, leading to OClO + Br products. Another possibility for symmetric chlorine dioxide formation could be through the intervening formation of the $BrClO_2$ isomer, but no evidence of such a sequence was ever suggested. The hypothesis of the formation of short-lived intermediate complexes was employed to rationalize the negative temperature dependence observed experimentally. On the basis of the absence of any pressure dependence in the experimental rate constant, it was concluded that decomposition of the intermediates toward reactants is substantially favored at lower temperatures over stabilization because of the collision of the reactants.

Various theoretical studies have determined possible energy minima in the ClO + BrO potential-energy profile. Guha and Francisco[13] carried out density-functional calculations of the different isomers of the $BrClO_2$ system using the very large 6-311++G(3df, 3pd) basis set. Gomez and Pacios[14] performed an extensive investigation of the $BrClO_2$ isomers in which they made an interesting comparison of MP2 and CCSD(T) methodologies versus B3LYP calculations for the study of such systems. In all cases, the nonplanar ClOOBr conformer was found to be the most stable geometry followed first by the Y-shaped $ClBrO_2$ and $BrClO_2$ forms and then by the linear geometry type ClOBrO and BrOClO isomeric complexes. These studies, however, have concentrated only on the thermodynamic stability of ClOOBr isomers and discuss nothing about the energy barriers involved in isomerization and dissociation channels.

In view of the assumptions made for the mechanism of ClO and BrO coupling, it would be interesting to investigate possible

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transition states and potential interconversion processes between the various isomeric and conformeric forms of the $BrClO_2$ system. Knowledge of the energy barriers is very important to elucidate what intermediates are predominantly involved or whether they interconvert during the three pathways of the reaction. In this work, we present ab initio quantum mechanical calculations of the structures, vibrational spectra, energies, and energy differences for the transition states of BrO + ClO reaction and the conformeric forms of ClOOBr peroxide. The calculations were performed at the second-order Moller−Plesset perturbation theory level using the 6-311++G(2d) and 6-311++G(3df) basis sets. Also CCSD(T)/6-311++G(3df) single-point calculations at the MP2 calculated geometries were performed to reproduce the proper energy ordering of the various structures determined.

2. Computational Methods

The electronic molecular orbital calculations were carried out using the Gaussian 98 series of programs.[16] All equilibrium and transition-state geometries were fully optimized at the MP2 level of theory with all electrons included in the correlation calculations, using the 6-311++G(2d) and 6-311++G(3df) basis sets. It has been observed, however,[17,18] that the correct energetic ordering of XOO and OXO (X = Cl and Br) triatomics cannot be achieved at the MP2 level. The ClOO radical is thermodynamically more stable than OClO, although it readily dissociates into Cl + O_2 products. Yet MP2 methodologies usually produce the wrong energetic ordering and repeatedly place ClOO higher than OClO as it has been again the case with our MP2 calculations.

Two important reasons are the usual sources of problems in the theoretical treatment of halogen oxide species with MP2 methodologies, spin contamination, and higher order correlation effects. Species of high spin multiplicity like the XO_2 doublet radicals are known to suffer from contamination of unwanted spin states in UMP2 procedures that may lead eventually to distortions of the potential-energy surface and the wrong energetic ordering. Schlegel[19] has suggested a method where spin contamination is projected out of the correlated wave function and labeled this PMP2 with single annihilations of the spin contamination because removal of more than the first two components seems impractical for routine use.[20] The doublet species under study exhibit UHF $\langle S^2\rangle$ values in optimized MP2-(full) structures equal to 0.7588 for Br, 0.7697 for ClO, 0.7724 for BrO, 0.7696 for ClOO, and 0.7871 for OClO, which at a first glance indicate no significant spin contamination. Annihilation of the first spin contaminant reduced $\langle S^2\rangle$ to 0.7500 for Br, 0.7503 for ClO, 0.7504 for BrO, 0.7503 for ClOO, and 0.7510 for OClO. To treat the electron correlation we employed the singles and doubles coupled-cluster method including a perturbational correction for associated triple excitations. Thus, single-point CCSD(T)/6-311++G(3df) calculations within the frozen core approximation were carried out at the MP2(full)/6−311++G(3df) determined geometries for all species under consideration, to establish the correct energetic ordering of product channels and intermediate adducts. The results place the ClOO + Br product channel 0.32 kcal mol^{-1} including ZPE corrections below the OClO + Br channel which is consistent with the difference in the experimental exothermicities at 298 K, 0.5 kcal mol^{-1} mentioned by Turnipseed et al.[11] A theoretical energy difference of more than 9 kcal mol^{-1} is reported by other workers,[17,18] whereas the experimental estimate derived from the difference in the two dissociation energies $D_e(OClO \rightarrow Cl + O_2)$ and $D_e(ClOO \rightarrow Cl + O_2)$ places it at 4 ± 2 kcal mol^{-1}.[17] The recent spin-restricted B3LYP/6-311+G(3df, 2p) calculations of Beltran et al.[21] yield 2.45 kcal mol^{-1}.

The harmonic vibrational frequencies were analytically evaluated for all species involved at the MP2(full)/6−311++G(3df) level of theory, but the chlorine dioxide calculations were found in trouble again. The error in the vibrational frequencies from spin contamination will mainly depend on the magnitude of $d\langle S^2\rangle/dq$. Large values of the $\langle S^2\rangle$ geometrical derivative indicate that the potential curve rises too steeply with the q coordinate as more and more high energy states mix into the UMP2 wave function, which in turn leads to higher frequencies.[22] As a result, poor harmonic frequencies compared to those of the experimental data[24−28] are calculated for both ClOO and OClO. For example, the asymmetric bond stretching in ClOO is found to be 1950 cm^{-1} vs 1479 and 1443 cm^{-1} for the experimental values. For OClO, the MP2(full)/6-311++G(3df) harmonic vibrational frequency of the asymmetric bond stretching mode was found to be almost twice the experimental value and consequently totally unacceptable. To achieve a better consistency with the experiment, a restricted-open-shell MP2(full)/6-311++G(3df)[30,31] optimization was performed in the case of OClO. The ROMP2(full)/6-311++G(3df) frequencies were obtained by double numerical differentiation of the energy with a step size equal to 0.05 Å. This calculation produced a more realistic set of harmonic frequencies to use in the ZPE corrections, in which the highest deviation from the experiment is for the asymmetric stretching mode, 1284 cm^{-1} vs 1108 and 1110 cm^{-1} for the experimental values. The CCSD(T) energy results for OClO calculated at the ROMP2/6-311++G(3df) geometries were less than 0.07 kcal mol^{-1} different than the CCSD(T)//UMP2(full)/6-311++G(3df), and so the latter could still be used for the evaluation of the energy difference among the various reaction channels.

We used C_1 point group symmetry for each species as the initial geometry of the optimization procedure, and we fully optimized all of the redundant internal coordinates. The resulting point group symmetries and ground states are $C_{\infty v}$ for ClO, BrO, and BrCl; C_{2v} for OClO; C_s for $BrClO_2$, ClOO, *cis*- and *trans*-BrOOCl conformers, and TS(a); and finally C_1 for the nonplanar BrOOCl, BrOClO, TS(b), and Ts(c) structures.

3. Energy Minima and Transition States

Results of equilibrium geometries and harmonic frequency calculations for isomeric forms of the BrOOCl system that are possibly involved in the course of ClO + BrO reaction, i.e., skewed BrOOCl peroxide, BrOClO linear chain, and Y-shaped $BrClO_2$, are shown in Table 1 where they are compared with the corresponding results of Guha and Francisco[13] and Gomez and Pacios.[14] The agreement is very satisfactory, especially with the MP2/AREP-TZ(2df) results of Gomez and Pacios[14] with bond length differences less than 0.02 and with one only exception, that of OCl bond distance in BrOClO, where the difference between the two values is somewhat larger. Also differences in bond angles are smaller than 2.0°. The agreement between harmonic frequency results is equally satisfactory.

The ClO_2 geometrical and harmonic frequency results for both the symmetric and asymmetric forms along with the results for all reactants and products are included in Table 2. It is readily seen that our MP2 and ROMP2/6-311++G(3df) calculations are in fair consistency with the reported theoretical and experimental values.

Investigation of possible transition states in the lowest singlet potential-energy surface under study have led to three configurations fully characterized by vibrational frequency analysis-

TABLE 1: Optimized Geometries (Å and Degrees) and Harmonic Frequencies (cm^{-1}) for ClOOBr Isomers

species	coordinate	MP2/ 6-311++G(3df)[a]	B3LYP/ 6-311++G(3df, 3pd)[b]	MP2/ AREP-TZ(2df)[c]
ClOOBr	OO	1.400	1.347	1.412
	ClO	1.703	1.757	1.710
	BrO	1.855	1.914	1.859
	ClOO	109.3	111.8	109.0
	OOBr	109.6	112.8	109.4
	ClOOBr	83.3	86.0	82.4
	frequencies[d]	776, 676, 595	864, 602, 533	761, 671, 595
		431, 296, 103	412, 280, 110	427, 295, 101
$BrClO_2$	BrCl	2.423	2.416	2.440
	ClO	1.430	1.445	1.441
	BrClO	104.1	114.7	104.5
	OClO	114.1	104.7	115.0
	frequencies[d]	1187, 528, 407	1043, 512, 407	1186, 521, 398
		189, 1337, 214	201, 1213, 213	201, 1330, 188
BrOClO	BrO	1.846	1.895	1.843
	OCl	1.735	1.679	1.792
	ClO′	1.479	1.498	1.489
	BrOCl	111.9	116.2	109.9
	OClO′	114.0	113.6	114.2
	BrOClO′	74.9	79.2	67.9
	frequencies[d]	1192, 591, 460	1013, 546, 428	1206, 602, 412
		340, 222, 92	348, 235, 104	326, 197, 66

[a] Results of present work. [b] Results of ref 13. [c] Results of ref 14. [d] A description of normal modes for each harmonic frequency for BrOOCl isomers has been conducted elsewhere.[13,14]

TABLE 2: Optimized Geometries (Å and Degrees), Harmonic Frequencies (cm^{-1}), Electronic Energies, and ZPE Corrections for Reactants and Products

species	coordinate	MP2/6-311++G(3df)[a]	CMRCI[b]	ROB3LYP	exp
ClOO′	ClO	2.142	2.139	1.929[k]	1.83[d]
	OO′	1.154	1.201	1.215	1.23[d]
	ClOO	118.3	115.7	115.7	110[d]
	E_{el}[c] (ZPE)	−609.788 61 (3.78)			
	frequencies	223, 473	181, 391	308, 549	215, 432
		1950	1506	1397	1479[e]
					192, 408
					1443[f]
OClO	OCl	1.476	1.480	1.479[k]	1.470[g]
	OClO	118.4	117.8	117.3	117.4[e]
	E_{el}[c] (ZPE)	−609.787 84 (3.69)			
	frequencies	975, 324	945, 452	451, 968	945, 448
		1284	1095	1120	1110[h]
					945, 449
					1108[f]

	r_e	ν	E_{el}[c]	ZPE[c]
ClO	1.546	858	−534.728 21	1.23[a]
	1.576	861[k]		
BrO	1.701	732	−2647.573 18	1.05[a]
	1.725	728	−2647.707 25[l]	
Br			−2572.516 24[a]	
BrCl	2.125	470	−3032.259 24	0.67[a]
$(^3\Sigma_g^-)O_2$	1.215	1501	−150.128 21	2.15[a]

[a] Results of present work. [b] Results of ref 17. [c] Electronic energy in hartrees at the CCSD(T)//MP2/6-311++G(3df) level of theory and ZPE correction in kcal mol^{-1}. [d] Results of ref 23. [e] Results of ref 24. [f] Results of ref 25. [g] Results of ref 26. [h] Results of refs 27 and 28. [k] Results of ref 21. [l] Results of ref 28 at the CCSD(T)/ANO4 level of theory.

.They are summarized in Table 3, and their schematic representation is given in Figure 1. A first transition state is located at a large O−O distance formed during the approach of the two radicals. This configuration denoted hereafter as TS(a) represents a low energy barrier at the entrance valley of the reaction, placed only 0.14 kcal mol^{-1} above reactants at the CCSD(T)//MP2/6-311++G(3df) level and representing a bimolecular pathway leading directly to products ClOO + Br. In this sense, it resembles direct pathways that have been obtained in OH + ClO and OH + BrO systems[32,33] and which are usually of minor importance because the reactions between two radical centers prefer the barrierless association channels.

Two transition states, denoted TS(b) and TS(c), have been determined in the investigation of two interesting isomeric interconversion pathways, i.e., the [BrOOCl→ $BrClO_2$] and [$BrClO_2$→ BrOClO] processes, in order of decreasing stability of the resulting isomer. The two structures exhibit some similarities with the isomerization transition states determined by Guha and Francisco in the study of $HBrO_2$ system,[34,35] but important deviations are present as well, considering the different masses involved and the different isomerization pathways examined. TS(b) represents the energy barrier for the interconversion of BrOOCl to $BrClO_2$, which may take place from an elongation of BrO bond in BrOOCl toward the Cl edge

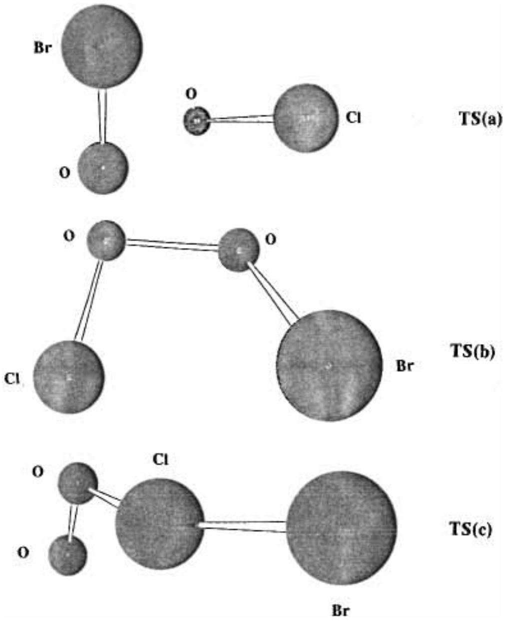

Figure 1. Transition-state structures TS(a), TS(b), and TS(c).

TABLE 3: MP2 Optimized Geometries (Å and Degrees) and Harmonic Frequencies (cm^{-1}) for Transition States in the ClO + BrO Reaction

species	coordinate	MP2/ 6-311++G(2d)	MP2/ 6-311++G(3df)		
				normal mode	ν
TS(a)	ClO	1. 506	1.576	ClO str A′	830
	BrO′	1.721	1.731	BrO str A′	687
	OO′	2.273	2.114	OO str A′	326
	ClOO′	120.2	122.4	OOBr bd A′	85
	BrOO′	92.4	91.6	OOCl bd A″	62
				reac coor A′	172i
TS(b)	ClO	1.806	1.668	OO str A	1717
	BrCl	3.021	2.442	ClOO bend	615
	OO′	1.373	1.290	ClOO wag	358
	BrClO	160.2	151.2	OCl str	247
	ClOO′	116.9	117.3	ClBr str	148
	ClBrO′	18.6	19.1	reac coor	238i
	BrClOO′	94.0	92.8		
TS(c)	ClO	1.518	1.494	ClO str A	1250
	ClO′	1.469	1.449	ClOO bnd	686
	BrO	2.355	2.265	ClOO wag	472
	O’ClO	118.5	117.6	OClO bnd	282
	ClOBr	115.7	115.8	BrClO bnd	118
	BrOClO′	83.1	82.6	reac coor	357i

TABLE 4: Total Electronic and Zero-Point Energies for Various Species Involved in the ClO + BrO Reaction

species	E_{elec} (hartree)[a]		ZPE (kcal mol^{-1})	ΔE (kcal mol^{-1})[b]
TS(a)	−3182. 821 62	−3182. 300 71	2.84	0.14
TS(b)	−3182.806 91	−3182. 285 36	4.41	12.21
TS(c)	−3182.825 95	−3182.307 94	4.01	−2.35
ClOOBr	−3182.849 37	−3182.335 78 −3182.335 20[c]	4.11	−19.76
$BrClO_2$	−3182.860 07	−3182.325 63 3182.326 08[c]	5.52	−11.95
BrOClO	−3182. 842 23	−3182.317 57 −3182.317 79[c]	4.14	−8.28
cis-ClOOBr	−3182.834 57	−3182.319 23	3.47	−9.99
trans-ClOOBr	−3182.842 78	−3182.327 79	3.86	−14.97
BrO + ClO	−3182.787 85	−3182.301 39	2.27	0.0
Br + ClOO	−3182.802 37	−3182.304 85	3.78	−0.66 (−1.68)[d]
Br + OClO	−3182.826 63	−3182.304 19	3.69	−0.34 (−1.36)[d]
BrCl + O_2	−3182.901 46	−3182.387 45	2.82	−53.45

[a] Results of present work. The first column corresponds to MP2/6-311++G(3df) results and the second to the CCSD(T)/6-311++G(3df) level of theory using the MP2/6-311++G(3df) geometries. [b] Energy differences with respect to reactants (based on the present CCSD-(T) results and including ZPE values). [c] The CCSD(T)//B3LYP/6-311++G(3df,3dp) results of ref 13. [d] ΔE values in parentheses include SOC corrections: for atomic Br, $^1/_3$ of the fine structure splitting given in Moore's compilations[47] yields a correction of 3.51 kcal mol^{-1}, $^1/_2$ of the BrO experimental splitting[48] of 968 cm^{-1} yields a correction of 1.38 kcal mol^{-1} for BrO, and $^1/_2$ of 318 cm^{-1} amounts to 0.45 kcal mol^{-1} for ClO.[49]

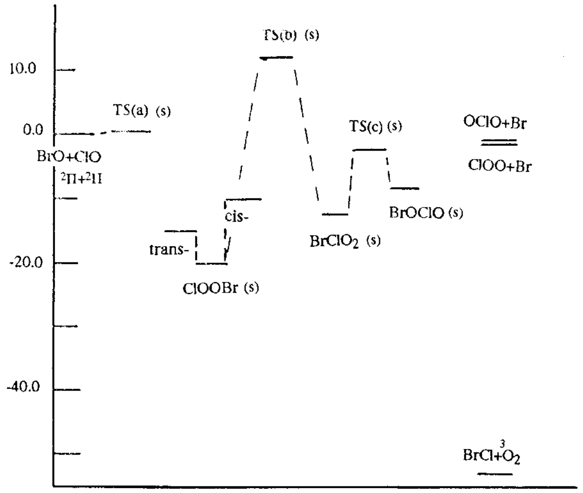

Figure 2. Relative energetics of dissociation and isomerization pathways for ClO + BrO reaction, (s) represents singlet states of these adducts.

of the molecule, eventually leading to isomerization into $BrClO_2$. The geometrical changes accompanying such an inerconversion may be easily visualized, for example, the shrinkage of the ClO bond (1.703 → 1.668 Å) and of O−O bond (1.400 → 1.290 Å) compared to BrOOCl minimum and the approach of Br and Cl atoms at 2.442 Å to reach eventually the 2.423 Å bond distance in $BrClO_2$ minimum. Similarly, TS(c) which represents an interconversion path of $BrClO_2$ to BrOClO shows the extension of ClO bond in $BrClO_2$ (1.430 → 1.494 Å) and the approach of Br and O atoms. All transition-state structures display imaginary frequencies, suggesting that these conformations are first-order saddle points.

The total electronic energies and relative energetics with regard to reactants at the CCSD(T)/MP2/6-311++G(3df) level including ZPEs for all minima and transition states are summarized in Table 4. A relative stability diagram with respect to reactants is also depicted in Figure 2. The relative stabilities of the three isomers are 7.8 kcal mol^{-1} for $BrClO_2$ and 11.5 kcal mol^{-1} for BrOClO, higher than BrOOCl. These values are in good agreement with the corresponding CCSD(T)//B3LYP/6-311++G(3df, 3dp) results, 6.8 and 10.5 kcal mol^{-1} of Guha and Francisco.[13] No attempt to calculate spin−orbit or relativistic effects has been carried out in the present work, but such corrections are expected to further improve the energetics of the reaction by affecting both reactants and products. For example, when spin−orbit corrections reported for BrO, Br, and ClO are included in Table 4, the energy differences between reactants and products becomes 1.68 and 1.36 kcal mol^{-1} for channels a and b, respectively.

To summarize the role of the calculated saddle point configurations, it is easily observed that TS(a) represents a low transition-state configuration that the reactants assume leading directly into products. TS(b) and TS(c) represent the two barriers for interconversion of the most stable form BrOOCl to the next one $BrClO_2$ and of this to the least stable form BrOClO, respectively. TS(b) exhibits a considerable energy barrier of 32.0

TABLE 5: MP2 Optimized Geometries (Å and Degrees) and Harmonic Frequencies (cm^{-1}) for the ClOOBr and BrOOBr Conformeric Forms at the MP2/6-311++G(3df) Level of Theory

	cis-ClOOBr	*trans*-ClOOBr		*cis*-ClOOBr	*trans*-ClOOBr
Coordinate			Normal Mode		
OO	1.560	1.495	ClO stretch A′	795	790
ClO	1.642	1.668	OO stretch A′	396	740
BrO	1.793	1.817	ClOO bend A′	644	679
ClOO	114.8	103.1	BrOO bend A′	175	281
OOBr	115.6	102.9	BrO stretch A′	420	211
			reaction coor A″	182i	23i

	cis-BrOOBr	*trans*-BrOOBr		*cis*-BrOOBr	*trans*-BrOOBr
Coordinate			Normal Mode		
OO	1.526	1.491	OO stretch A1	505	A 762
BrO	1.803	1.819	BrO stretch B2	736	A 711
BrOO	1116.9	102.9	BrO stretch A1	590	B 638
			BrOO bnd B2	372	A 215
			BrOO bnd A1	139	B 193
			reaction coor A1	205i	A 21i

kcal mol^{-1} that makes very unlikely the possibility of interconversion of BrOOCl to BrClO$_2$. Thus, the pathway through the BrOOCl intermediate complex formation leads directly into products that must be channel a, ClOO + Br. TS(c), however, presents a much lower energy barrier of only 9.6 kcal mol^{-1}, and it is located 2.35 kcal mol^{-1} below that of the reactants, which makes feasible an interconversion process between these two isomers. Consequently the second pathway leading to OClO + Br may be anticipated as following either the direct intermediate formation of BrOClO or possibly the intermediate interconversion of BrClO$_2$ to BrOClO and then to products.

4. BrOOCl Conformeric Forms

The third channel leading to molecular products BrCl + ($^3\Sigma_g^-$)O$_2$ must involve a kind of a cyclic intermediate complex formation. Such a geometry might be suggested to be the cis conformation of the peroxide isomer. It would be interesting in this sense to characterize the conformeric forms of BrOOCl to investigate possible participation of such geometries in the mechanism of the reaction. Of course, there is a problem here with such an assumption, as in all related XO + YO systems, concerning the different multiplicities associated with the intermediate states of such a mechanism and the molecular products XY + ^{3}O$_2$. The halogen monoxide radicals being ground-state doublets correlate with both the singlet and triplet states,[36,37] but the intermediate adducts in the lowest singlet states assumingly formed do not. Thus, the singlet *cis*-BrOOCl configuration correlates with ^{1}XY + ^{1}O$_2$ but not with ^{1}XY + ^{3}O$_2$. A spin−orbit induced quenching to ground-state triplet O$_2$ may be suggested to occur somewhere in the exit channel, or alternatively, a removal of spin conservation restriction between singlet and triplet states by a heavy atom such as Br may be also proposed.[38]

Structural parameters for the *cis*- and *trans*-BrOOCl are summarized in Table 5, and electronic energies and relative stabilities are included in Table 4. The various features that have been revealed in the study of rotational barriers of similar systems are obtained here too. We can see the elongation of the O−O bond from the minimum through the trans to the cis configuration, 1.400 → 1.495 → 1.560 Å, and the corresponding shrinkage of the ClO and BrO bonds, 1.703 → 1.668 → 1.642 Å and 1.855 → 1.817 → 1.793 Å, respectively, consistent with what has been observed in the study of the torsional barriers of ClOOCl[39,40] and BrOOBr[41] peroxides. Similar changes are followed for the bond angles. The XOO angles present a maximum in the cis geometry as a result of the high repulsion of the two halogen atoms found on the plane at the closest distance and through the minimum conformation reach their minimum values at the trans geometry where the two halogen atoms assume their largest distance. Optimization of the torsional angle, however, has been very hard to obtain in particular for the trans conformer because the structure appears to display a plateau of energy extending about 10° around the 180° value. Both cis and trans geometries display imaginary frequencies that characterize these forms as saddle points for rotation around the O−O bond, but accurate frequencies were also extremely difficult to obtain. The torsional fundamental for the trans conformer exhibits a very low value at the MP2/6-311++G-(3df) level, 24i, for which it is difficult to evaluate the uncertainty associated with it and which points out to a very loose saddle point configuration compared to the cis geometry. The difficulties associated with the optimization of the torsional angle and the accurate determination of the relevant imaginary frequency made it desirable to have a comparison with an analogous system. For this reason, the conformeric forms of BrOOBr peroxide were also investigated at the same level of theory, MP2/6-311++G(3df), and the results are also included in Table 5. A structural study of the rotational barrier of BrOOBr peroxide has been carried out by Pacios and Gomez,[41] but no frequency characterization of the conformeric forms of any of the XOOY (X and Y = halogen atoms) peroxides has been ever attempted to the best of our knowledge. The BrOOBr study produced similar results, and a weak torsional frequency, 21i, for the trans configuration was calculated in agreement with the BrOOCl case, which thus indicates a loose structure of the trans conformers of XOOY (X and Y = halogen) complexes in general.

TABLE 6: cis and trans Energy Barriers in kcal mol^{-1} for Homo- and Cross-Halogen Peroxides[a]

species	cis	trans	Δ*E*	species	cis	trans	Δ*E*
HOOH	7.3^{a}	1.1^{a}	6.2	BrOOBr	10.3^{h}	5.5^{h}	4.8
	7.4^{b}	1.1^{b}	6.3		9.2^{e}	4.4^{e}	4.8
ClOOCl	9.1^{c}	5.1^{c}	4.0		10.0^{g}	5.6^{g}	4.4
	10.1^{d}	4.4^{d}	5.7	HOOCl[i]	6.0	4.0	2.0
	8.7^{e}	4.4^{e}	4.3	HOOBr[j]	6.9	4.6	2.3
ClOOBr	8.7^{e}	4.3^{e}	4.4				
	10.4^{f}	5.0^{f}	5.4				
	9.3^{g}	4.1^{g}	5.2				

[a] Best estimate of ref 44. [b] The CASPT2 results of ref 45. [c] The QCISD(T)/6-31+G(2df)+ΔZPE results of ref 39. [d] The CCSD(T)/ECP-TZDP(f) of ref 40. [e] The MP2/AREP/TZ(2df) results of ref 41. [f] The CCCSD(T)//MP2/6-311++G(3df) results of the present work. [g] The MP2/6-311++G(3df) results of the present work. [h] The CCSD(T) results of ref 14. [i] Density-functional calculations of ref 32. [j] Density-functional calculations of ref 33.

The *cis*-BrOOCl conformation is found to be a well characterized tight saddle-point geometry, with the two halogen atoms being at their closest distance from all geometries. It may be assumed then to represent a transition state through which the intermediate formed BrOOCl minimum leads to the molecular products BrCl + ^{3}O$_2$ through some sort of spin−orbit induced quenching, as mentioned above, and it has been suggested in the corresponding BrO + BrO reaction.[42] The significant energy barrier associated with it explains the very low branching ratio to channel c.

Finally, in Table 6, we summarize the relative heights of cis and trans torsional barriers for rotation of the XO group around the O−O bond for all of the known cases of XOOY peroxides, X and Y = H, Cl, and Br, with the exception of the highly correlated fluorine case that has been found very large.[43] This motion is quite analogous to the rotational motion of hydrogen peroxide, HOOH, one of the simplest molecular rotors for which the torsional potential has been recently well established[44,45] at a very high level of theory and experimentally as well, yielding a trans barrier lower than a cis one. We can see the general tendency for decreasing energy differences between the cis and trans barriers of the conformeric forms among the various species starting from HOOH as the hydrogen atoms are replaced by halogens.

Because of the importance of these species extensive theoretical studies have been reported by various workers. The first studies of chlorine peroxide rotational potential include a preliminary investigation of the cis- and trans-planar forms of ClOOCl by McGrath et al.,[50] who characterized these geometries as first-order saddle points corresponding to the two transition states for rotation around the O−O bond. Birk et al.[51] made an experimental determination of the internal rotational potential for ClOOCl and found the trans barrier to be between 1.7 and 2.1 times larger as than the cis barrier. This observation, quite contradictive to what was admitted for the HOOH case, gave the opportunity for detailed quantum calculations on the internal rotational barrier of ClOOCl[39,40] that definitely established the cis conformer as being higher than the trans one. Pacios and Gomez made an MP2/6−311(2d) structural study[41] of the torsional potential of BrOOBr, and they have also determined the E_{cis} and E_{trans} barrier heights of ClOOBr.[14] Sumathi and Peyerimhoff determined the $\mathrm{E}_{\mathrm{cis}}$ and $\mathrm{E}_{\mathrm{trans}}$ barrier heights of HOOBr[32] and the harmonic frequencies associated and also the corresponding barrier heights of HOOCl.[33] Finally, empirical relationships have been developed by Grela and Colussi[46] for the contribution of the peroxide bond to the heat of formation of XOOY that involved interesting correlations with the halogen electronegativity.

5. Summary

The present studies established transition-state configurations in the lowest singlet potential-energy surface of BrO + ClO reaction. A very low transition state was determined at the entrance valley which yields a direct pathway to ClOO + Br products. Two other important transition-state geometries were also determined which consist of two possible interconversion processes among the BrOOCl isomers in order of decreasing stability, i.e., [BrOOCl→ $\mathrm{BrClO_2}$] and [$\mathrm{BrClO_2}$→ BrOClO]. Of the latter, the first one being adequately high makes prohibitive the interconversion between BrOOCl and $\mathrm{BrClO_2}$ at thermal temperatures, whereas the low barrier associated with the second isomerization process and located below the reactants energy level makes feasible an interconversion between $\mathrm{BrClO_2}$ and BrOClO. Thus, channel b seems to be favored by the formation of both the BrOClO and $\mathrm{BrClO_2}$ intermediate complexes. The calculations also demonstrated that the general features of torsional barriers in halogen peroxides seem to a great extent independent of the particular halogen involved with regard to the structural distortion accompanying the internal rotation. The energy differences between the trans and cis configurations show a decreasing tendency along with the heavier halogens.

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References and Notes

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

(2) Solomon, S. *Nature* **1990**, *347*, 347.

(3) Tung, K. K.; Ko, M. K. W.; Rodriguez, J. M.; Sze, N. D. *Nature* **1986**, *322*, 811.

(4) Basco, N.; Dogra, S. K. *Proc. R. Soc. London Ser. A* **1971**, *323*, 417.

(5) Clyne, M. A. A.; Watson, R. T. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1169.

(6) Hills, A. J.; Cicerone, R. J.; Calvert, J. G.; Birks, J. W. *J. Phys. Chem.* **1988**, *92*, 1853.

(7) Toohey, D. W.; Anderson, J. G. *J. Phys. Chem.* **1988**, *92*, 1705.

(8) Poulet, G.; Lancar, I. T.; Laverdet, G.; Le Bras, G. *J. Phys. Chem.* **1990**, *94*, 278.

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

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

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

(12) Gleghorn, J. T. *Chem. Phys. Lett.* **1997**, *271*, 296.

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

(14) Gomez, P. C.; Pacios, L. F. *J. Phys. Chem. A* **1999**, *103*, 739.

(15) Johnsson, K.; Engdahl, A.; Kolm, J.; Nieminen, J.; Nelander, B. *J. Phys. Chem.* **1995**, *99*, 3902.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewsky, V. G.; Montgomery, J. A.; Stratman, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Gammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Peterson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Gioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.

(17) Peterson, K. A.; Werner, H. J. *J. Chem. Phys.* **1992**, *96*, 8948.

(18) Pacios, L. F.; Gomez, P. C. *J. Phys. Chem. A* **1997**, *101*, 1767.

(19) Schlegel, H. B. *J. Phys. Chem.* **1986**, *84*, 4530.

(20) Knowles, P. J.; Handy, N. C. *J. Phys. Chem.* **1988**, *88*, 6991; **1988**, *92*, 3097.

(21) Beltran, A.; Andres, J.; Noury, S.; Silvi, B. *J. Phys. Chem. A*, **1999**, *103*, 3078.

(22) Jensen, K. *Chem. Phys. Lett.* **1990**, *169*, 519.

(23) Arkell, A.; Schwager, I. *J. Am. Chem. Soc.* **1967**, *89*, 5999.

(24) Muller, H. S. P.; Willner, H. *J. Phys. Chem.* **1993**, *97*, 10589.

(25) Johnsson, K.; Engdahl, A.; Nelander, B. *J. Phys. Chem*. **1993**, *97*, 9603.

(26) Miyazaki, K.; Tanoura, M.; Tanaka, K.; Tanaka, T. *J. Mol. Spectrosc.* **1986**, *116*, 435.

(27) Ortigoso, J.; Escribano, R.; Burkholder, J. B.; Howard, C. J.; Lafferty, W. J. *J. Mol. Spectrosc.* **1991**, *148*, 346.

(28) Ortigoso, J.; Escribano, R.; Burkholder, J. B.; Lafferty, W. J. *J. Mol. Spectrosc.* **1992**, *155*, 25.

(29) Francisco, J. S.; Pathiban, S.; Lee, T. J. *J. Chem. Phys. A* **1998**, *109*, 10818.

(30) Lauderdal, W. J.; Stanton, J. F.; Gauss, J.; Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 6606.

(31) Knowles, P. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *186*, 130.

(32) Sumathi, R.; Peyerimhoff, S. D. *J. Phys. Chem. A* **1999**, *103*, 7515.

(33) Sumathi, R.; Peyerimhoff, S. D. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3973.

(34) Guha, S; Francisco, J. S. *Chem. Phys.* **1999**, *247*, 387.

(35) Guha, S; Francisco, J. S. *Chem. Phys. Lett.* **2000**, *319*, 650.

(36) Bogan, D. J.; Thorn, R. P.; Nesbitt, F. L.; Stief, L. J. *J. Phys. Chem.* **1996**, *100*, 14383.

(37) Phillips, L. F. *J. Phys. Chem*. **1990**, *94*, 7482.

(38) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(39) Fransisco, J. S. *J. Chem. Phys.* **1995**, *103*, 8921.

(40) Gomez, P. C.; Pacios, L. F. *J. Phys. Chem*. **1996**, *100*, 8731.

(41) Pacios, L. F.; Gomez, P. C. *J. Mol. Struct.* **1999**, *467*, 223.

(42) Papayannis, D.; Kosmas, A. M.; Melissas, V. S. *Chem. Phys.* **1999**, *243*, 249.

(43) Dixon, D. A.; Angzelm, J.; Fitzerald, G.; Wimmer, E. *J. Phys. Chem.* **1991**, *95*, 9197.

(44) Koput, J.; Carter, S.; Handy, N. C. *J. Phys. Chem. A* **1998**, *102*, 6325 and references therein.

(45) Kuhn, B.; Rizzo, T. R.; Luckhaus, D.; Quack, M.; Suhm, M. A. *J. Chem. Phys. A* **1999**, *111*, 2565.

(46) Grela, M. A.; Colussi, A. J. *J. Phys. Chem.* **1996**, *100*, 10150.

(47) Moore, C. E. *Natl. Stand. Ref. Data Ser. (US, Natl. Bur. Stand.)* **1971**, Vols. I, II, and III, 35.

(48) McKellar, A. R.; *J. Mol. Spec.* **1981**, *86*, 43.

(49) Huber, K. P.; Herzberg, G. *Molecular spectra and molecular structure, constants of diatomic molecules*; van Nostrand Reinhold: New York, 1979.

(50) McGrath, M. P.; Clemitshaw, K. C.; Rowland, F. S.; Hehre, W. J. *J. Phys. Chem.* **1990**, *94*, 6126.

(51) Birk, M.; Fiedl, R. R.; Cohen, E. A.; Pickett, H. M.; Sander, S. P. *J. Chem. Phys.* **1989**, *91*, 6588.