

## Research Article

# Theoretical Investigation of Halogen-Oxygen Bonding and Its Implications in Halogen Chemistry and Reactivity

Agnie Mylona Kosmas

*Division of Physical Chemistry, Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece*

Received 27 September 2006; Revised 18 January 2007; Accepted 29 March 2007

Recommended by Konstantinos Tsipis

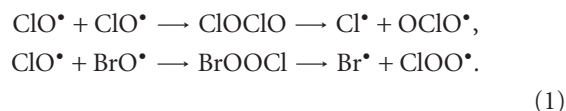
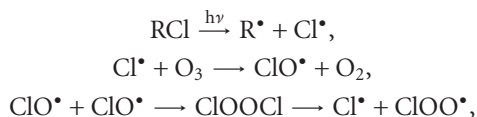
Trends in the properties of normal valent and multivalent halogen-oxygen bonding are examined for the isomers of the halogen polyoxide families of the types (YXO<sub>2</sub>) and (YXO<sub>3</sub>), Y=Cl, Br, I, H, CH<sub>3</sub>, X=Cl, Br, I. A qualitative model is formulated on the relationship between the X-O bond distance variations, the ionic character of the bonding, and the degree of halogen valence. The relative stability and enthalpy of formation of each species are also suggested to correlate with the ionic nature of the X-O bonding and the electrostatic character of the Y, YO fragments. In the model presented, halogen hypervalence is interpreted to be the result of partial p → d promotion of lone-pair valence electrons followed by the formation of two, four, or six additional pd hybrid bonds around the halogen atom.

Copyright © 2007 Agnie Mylona Kosmas. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

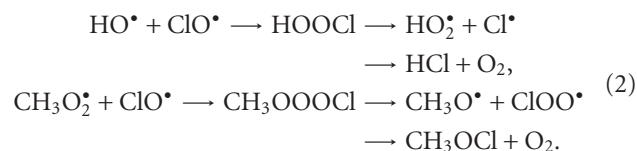
## 1. INTRODUCTION

High-level quantum mechanical electronic structure methodologies have known a spectacular development over the past two decades [1, 2], improving dramatically the accuracy of molecular geometry and energy calculations. For instance, it is currently possible to predict heat of formation values and reaction enthalpies to within 0.5 kcal mol<sup>-1</sup>, depending on the size of the system and the degree to which the molecule is well described by a single reference function. An area that has largely profited from this progress is the class of “highly correlated” molecules, that is, species possessing relatively low lying excited electronic states that affect the description of the ground or reference state through coupling from the correlation operator. A well-known set of highly correlated compounds are those that contain different electronegative elements bonded together as several species of atmospheric significance do, which contain halogen-oxygen bonds.

In stratospheric chemistry, halogen peroxides and their isomers are formed as intermediate complexes in the coupling of halogen monoxides



The halogen atoms thus released reattack new ozone molecules leading to a catalytic ozone depletion cycle. Systematic experimental studies have observed IR absorption spectra for several simple and cross halogen peroxides and polyoxides while some members have been isolated at 220° K which is the temperature prevailing in the stratospheric layer. The halogen monoxide radicals also interact with the hydroxyl HO<sup>•</sup>, methyl CH<sub>3</sub><sup>•</sup>, hydroperoxy HO<sub>2</sub><sup>•</sup>, and methylperoxy CH<sub>3</sub>O<sub>2</sub><sup>•</sup> radicals species abundant in the lower and upper atmosphere and give interesting reactions that participate in tropospheric ozone depletion cycles and in various hydrocarbon oxidation processes in atmospheric and combustion chemistry



Due to their importance [3–9], the study of halogen polyoxides, (YXO<sub>2</sub>) and (YXO<sub>3</sub>), Y = Cl, Br, I, H, CH<sub>3</sub>, X = Cl, Br, I, has known intense theoretical and experimental

investigations and has become one of the major chapters in halogen physical inorganic chemistry [10, 11].

The purpose of the present study is to examine the significant differences in the properties of normal valent and multivalent halogen-oxygen bonding in a series of chlorine, bromine and iodine containing polyoxides. This examination allows us to formulate a qualitative correlation model that links the structural variations and the energy stabilization tendencies among the various members with the degree of halogen valence, the ionicity of X–O bonding, and the electrostatic character of the Y, YO fragments.

## 2. COMPUTATIONAL DETAILS

As noted in the introduction, the quantum mechanical characterization of halogen polyoxides has been a subject of continuous and intense investigations in the recent literature. In the present work, the (YXO<sub>2</sub>) and (YXO<sub>3</sub>) isomers have been systematically optimized, all species at the same level of theory to allow a proper comparison of various molecular properties. More than fifty structures have been investigated in total. The MP2 method in combination with the 6-311G(d,p) basis set [12] has been used for all members of the Cl and Br families. For the treatment of I in the iodine polyoxides, the LANL2DZ basis set [13] has been employed, augmented with additional two-d and one-f polarization functions taken from the Stuttgart-Bonn quantum chemistry package [14]. The computations have been carried out using the Gaussian 98 series of programs [15].

The calculated equilibrium geometries have been found consistent with the literature results wherever available [16–54], that have been obtained by employing either higher ab initio methodologies or density functional theory techniques combined with very large basis sets, depending on the computational resources available. For instance, Guha and Francisco have carried out the investigation of the (YBrO<sub>2</sub>), Y = H, Cl, Br, and (YBrO<sub>3</sub>), Y = H, CH<sub>3</sub>, isomers using the B3LYP functional in combination with the large 6-311++G(3df,3pd) basis set and the QCISD/6-31D(d) methodology [22, 34, 42]. In our laboratory, the members of the (CH<sub>3</sub>XO<sub>2</sub>) series, X = Cl, Br, I, have also been investigated at various levels of theory [40, 44, 48].

Regarding the energy computations, higher than MP2 theory calculations are required to make a reliable study of the energetics of all these systems. Opposite to the equilibrium geometry optimizations, accurate energy and relative stability computations for these adducts have been found to be very demanding and are very frequently quite sensitive to the theoretical method applied with severe discrepancies from one method to another. Such methodologies are beyond the capability of the present investigation, taking into account the large number of systems examined. However, the good agreement of the present optimizations, with various higher level structural calculations reported, allows us to use energy results previously published to analyze the dependence of the thermodynamic stability on the properties of X–O bonding. Thus, we discuss the relative energy and heat of formation tendencies and the correlation with the halogen

TABLE 1: Harmonic vibrational frequencies (cm<sup>-1</sup>) for the isomers of (ClBrO<sub>2</sub>), (ClIO<sub>3</sub>) families.

ClOOBr	776, 676, 595, 431, 296, 103
ClBrO <sub>2</sub>	832, 331, 297, 211, 876, 168
BrClO <sub>2</sub>	1182, 528, 407, 192, 1335, 212
ClOBrO	795, 575, 348, 224, 174, 90
BrOCIO	1162, 574, 445, 338, 215, 91
ClOOOI	853, 746, 651, 580, 553, 435, 212, 144, 52
ClOIO <sub>2</sub>	965, 952, 774, 465, 332, 290, 238, 136, 45
IOClO <sub>2</sub>	1231, 995, 675, 494, 443, 359, 221, 175, 101
ClIO <sub>3</sub>	920, 392, 295, 981, 308, 195
IClO <sub>3</sub>	1075, 624, 218, 1290, 527, 232

valence and the Y, YO electronegativities, on the basis of collected literature results that have been obtained with the use of three different high level methodologies, namely, G2MP2, CCSD(T), and QCISD(T).

Harmonic vibrational frequencies have also been calculated along with the structural optimizations. They verify that all isomeric structures investigated represent energy minima on the corresponding potential energy surfaces. As an example, Table 1 summarizes the calculated harmonic vibrational frequencies for the isomers of the (ClBrO<sub>2</sub>) and (IClO<sub>3</sub>) families.

## 3. RESULTS AND DISCUSSION

Selected structural results for the (YClOn), (YBrOn), and (YIO<sub>n</sub>), Y = Cl, Br, I, H, CH<sub>3</sub>, *n* = 2, 3 isomers, calculated as described above, are collected in Tables 2–4. Depending on the position of the oxygen atom within the molecule, two kinds of X–O bonds (X = halogen atom) are distinguished, that is, with the O atom either located at a terminal position or within the molecule bound to another atom (bridged oxygen). When the X–O bond involves a terminal oxygen atom, it presents multiple bond properties and the corresponding halogen atom is characterized as hypervalent displaying more than 8 electrons in the valence shell. The interesting feature of the bonds between multivalent halogen atoms and terminal oxygen atoms is the severe tightening of the bond distance that does not correlate with the bond strength. Multiple X–O bonds exhibit a strikingly smaller equilibrium distance compared to the normal valent X–O length, a difference much more pronounced in the halogen case than, for instance, the difference in bond length between single and multiple carbon bonds.

### 3.1. Trends in the structural parameters of (YClO<sub>2</sub>), (YBrO<sub>2</sub>), and (YIO<sub>2</sub>) families, Y=Cl, Br, I, H, CH<sub>3</sub>

Three types of isomeric structures have been determined in this series, the peroxide normal valent YOOX form, the YOXO structure which contains both bridged and terminal oxygen-halogen bonds, and the fully hypervalent structure

TABLE 2: Bridged and terminal Cl–O bond distances (Å) in (YClO<sub>2</sub>) and (YClO<sub>3</sub>) isomeric structures.

Species	ClOOCl	ClOClO	ClClO <sub>2</sub>	
Cl–O bridged	1.756	1.909		
Cl–O terminal		1.512	1.469	
Terminal Cl–O		1.713		
Species	BrOOCl	BrOClO	BrClO <sub>2</sub>	
Cl–O bridged	1.703	1.735		
Cl–O terminal		1.489	1.430	
Species	IOOCl	IOClO	IClO <sub>2</sub>	
Cl–O bridged	1.716	1.749		
Cl–O terminal		1.492	1.450	
Species	HOOCl	HOCLO	HClO <sub>2</sub>	
Cl–O bridged	1.739	1.754		
Cl–O terminal		1.513	1.488	
Species	CH <sub>3</sub> OOCl	CH <sub>3</sub> OClO	CH <sub>3</sub> ClO <sub>2</sub>	
Cl–O bridged	1.761	1.763		
Cl–O terminal		1.520	1.489	
Species	ClOOOCl	ClOClO <sub>2</sub>	ClClO <sub>3</sub>	
Cl–O bridged	1.704	2.032		
Cl–O terminal		1.464	1.418	
Terminal Cl–O		1.632		
Species	BrOOOCl	BrOClO <sub>2</sub>	BrClO <sub>3</sub>	
Cl–O bridged	1.725	2.045		
Cl–O terminal		1.440	1.424	
Species	IOOCl	IOClO <sub>2</sub>	IClO <sub>3</sub>	
Cl–O bridged	1.707	2.097		
Cl–O terminal		1.460	1.426	
Species	HOOOCl	HOOCLO	HOCLO <sub>2</sub>	HClO <sub>3</sub>
Cl–O bridged	1.750	1.874	1.754	
Cl–O terminal		1.511	1.452	1.427
Species	CH <sub>3</sub> OOOCl	CH <sub>3</sub> OOCLO	CH <sub>3</sub> OClO <sub>2</sub>	CH <sub>3</sub> ClO <sub>3</sub>
Cl–O bridged	1.742	1.864	1.786	
Cl–O terminal		1.510	1.473	1.461

YXO<sub>2</sub>. The equilibrium X–O distances calculated present a wide range of values from the normal valent peroxide to the other isomers. For example, the Cl–O distance decreases from 1.756 Å in ClOOCl to 1.469 Å in ClClO<sub>2</sub>, a striking shrinkage of  $\sim 0.3$  Å. The ClOClO isomer presents three different types of Cl–O bonding. The bond that involves bridged Cl and O atoms is the longest, 1.909 Å, becoming 1.716 Å for the terminal Cl-bridged O bond and 1.512 Å between bridged Cl and terminal O, a net decrease of 0.4 Å. For comparison reasons, we may note that the Cl–O distance in free ClO radical has been calculated to be 1.576 Å at the same theory level. Similar large changes take place in all other halogen families with fully hypervalent halogen-terminal oxygen bond distance considerably tighter than the normal valent bonding. In the (YBrO<sub>2</sub>) family, for instance, the Br–O equilibrium length varies from 1.905 Å to 1.597 Å, again a range of the order of  $\sim 0.3$  Å.

### 3.2. Trends in the structural parameters of (YXO<sub>3</sub>) species

For Y = halogen atom, three types of isomers are obtained, the peroxide form, YOOOX, the fully hypervalent, YXO<sub>3</sub>, and the mixed one, YOXO<sub>2</sub>. As an example, Figure 1 displays the optimized structures of (IClO<sub>3</sub>) family. When Y = H, CH<sub>3</sub>, a fourth isomeric structure has been determined, that is, the HOOXO, CH<sub>3</sub>OOXO geometries. In all (YXO<sub>3</sub>), the largest X–O distances are found for the bonds in which both halogen and oxygen atoms are bridged while the shortest X–O bond lengths have been calculated for the fully hypervalent structures YXO<sub>3</sub>. The Cl–O bond distance in ClClO<sub>3</sub>, 1.418 Å, is the shortest ever calculated for a Cl–O bond while the bridged O-bridged Cl in ClOClO<sub>2</sub>, 2.032 Å, is the largest calculated for bound species. Similar large changes take place in the other halogen families and the same trends

TABLE 3: Bridged and terminal Br–O bond distances (Å) in (YBrO<sub>2</sub>) and (YBrO<sub>3</sub>) isomeric structures.

Species	BrOOBr	BrOBrO	BrBrO <sub>2</sub>	
Br–O bridged	1.878	1.897		
Br–O terminal		1.648	1.618	
Terminal Br–O		1.815		
Species	ClOOBr	ClOBrO	ClBrO <sub>2</sub>	
Br–O bridged	1.884	1.892		
Br–O terminal		1.659	1.613	
Species	IOOBr	IOBrO	IBrO <sub>2</sub>	
Br–O bridged	1.870	1.872		
Br–O terminal		1.634	1.597	
Species	HOObBr	HOBrO	HBrO <sub>2</sub>	
Br–O bridged	1.883	1.868		
Br–O terminal		1.676	1.645	
Species	CH <sub>3</sub> OOBr	CH <sub>3</sub> OBrO	CH <sub>3</sub> BrO <sub>2</sub>	
Br–O bridged	1.899	1.905		
Br–O terminal		1.666	1.647	
Species	ClOOOBr	ClOBrO <sub>2</sub>	ClBrO <sub>3</sub>	
Br–O bridged	1.887	2.084		
Br–O terminal		1.613	1.601	
Species	IOOOBr	IOBrO <sub>2</sub>	IBrO <sub>3</sub>	
Br–O bridged	1.859	2.167		
Br–O terminal		1.610	1.582	
Species	HOOOBr	HOObBrO	HOBrO <sub>2</sub>	HBrO <sub>3</sub>
Br–O bridged	1.867	1.919	1.844	
Br–O terminal		1.635	1.598	1.586
Species	CH <sub>3</sub> OOOBr	CH <sub>3</sub> OOBrO	CH <sub>3</sub> OBrO <sub>2</sub>	CH <sub>3</sub> BrO <sub>3</sub>
Br–O bridged	1.898	1.977	1.882	
Br–O terminal		1.653	1.620	1.615

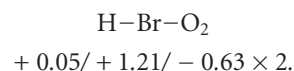
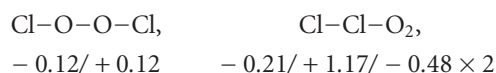
observed in (YXO<sub>2</sub>) are observed in the (YXO<sub>3</sub>). However, the deviations between largest and shortest bond lengths are even more emphasized in the (YXO<sub>3</sub>) than in the (YXO<sub>2</sub>) series.

### 3.3. Trends in relative energetics and thermodynamic stability

Relative energy values, displayed with respect to the electronic energies of the normal valent peroxide compounds, are summarized in Tables 5-6. They are mainly based on literature results calculated with the G2MP2 method but CCSD(T) and QCISD(T) reported values are also discussed when discrepancies with the G2MP2 values are encountered.

The general feature emerging from the inspection of the relative energy results is the absence of evidence for any correlation between the magnitude of the X–O bond length and the stabilization of the corresponding isomer. In fact, the fully hypervalent structures of the type YXO<sub>3</sub> that contain the shortest X–O distances and the highest degree of halogen multivalence are the most unstable. On the other hand, the stabilization tendencies show an interesting dependence on the electronegativity of the Y, YO partners, a factor that must be examined in combination with the halogen partial

atomic charge distributions. For example, the following Mulliken atomic charge distributions have been determined:



These examples readily demonstrate that multivalent halogens exhibit considerable positive partial charge distributions increasing from hypervalent Cl to hypervalent I and indicating that the corresponding X–O bonds are highly ionic. A direct consequence is the increase in stabilization achieved when the strongly electropositively charged hypervalent halogen combines with an electronegative Y, YO partner. Several examples may be considered that demonstrate this correlation. For instance, the ClBrO<sub>2</sub> structure is more stable than BrClO<sub>2</sub> since the more electropositively charged hypervalent Br is connected to the more electronegative normal valent Cl. Another example is the YOClO<sub>2</sub>, YOBrO<sub>2</sub>, Y = H, CH<sub>3</sub> compounds where the hypervalent, positively charged Cl, Br atoms connect to the

TABLE 4: Bridged and terminal I–O bond distances (Å) in (YIO2) and (YIO3) isomeric structures.

Species	IOOI	IOIO	IIO <sub>2</sub>	
I–O bridged	2.065	2.066		
I–O terminal		1.820	1.790	
Terminal I–O		2.046		
Species	CIOOI	CIOIO	ClIO <sub>2</sub>	
I–O bridged	2.060	2.064		
I–O terminal		1.818	1.783	
Species	BrOOI	BrOIO	BrIO <sub>2</sub>	
I–O bridged	2.064	2.065		
I–O terminal		1.819	1.786	
Species	HOOI	HOIO	HIO <sub>2</sub>	
I–O bridged	2.058	1.992		
I–O terminal		1.815	1.784	
Species	CH <sub>3</sub> OOI	CH <sub>3</sub> OIO	CH <sub>3</sub> IO <sub>2</sub>	
I–O bridged	2.005	1.948		
I–O terminal		1.777	1.749	
Species	CIOOOI	CIOIO <sub>2</sub>	ClIO <sub>3</sub>	
I–O bridged	2.018	2.001		
I–O terminal		1.744	1.733	
Species	BrOOOI	BrOIO <sub>2</sub>	BrIO <sub>3</sub>	
I–O bridged	2.019	1.980		
I–O terminal		1.744	1.735	
Species	HOOOI	HOOIO	HOIO <sub>2</sub>	HIO <sub>3</sub>
I–O bridged	2.012	1.982	1.919	
I–O terminal		1.835	1.795	1.794
Species	CH <sub>3</sub> OOOI	CH <sub>3</sub> OOIO	CH <sub>3</sub> OIO <sub>2</sub>	CH <sub>3</sub> IO <sub>3</sub>
I–O bridged	2.003	1.992	1.994	
I–O terminal		1.786	1.762	1.738

TABLE 5: Relative stabilities of (YXO2) isomers (kcal mol<sup>-1</sup>) compared to the normal valent peroxide species YOOX in each family<sup>(a)</sup>.

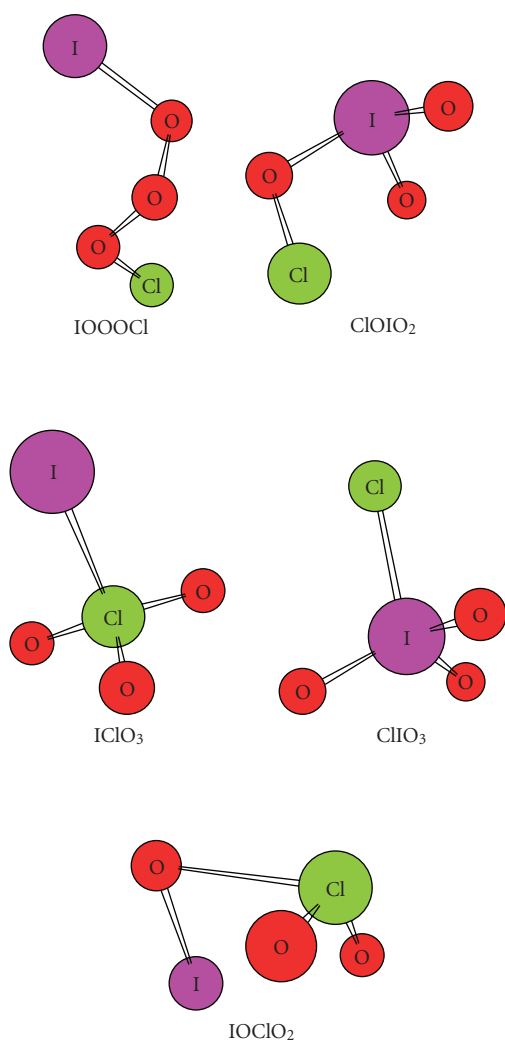
Species	CIOClO	BrOCIO	IOClO	HOCIO	CH <sub>3</sub> OClO
ΔE	14.5 <sup>(a)</sup> 13.3 <sup>(b)</sup>	10.5 <sup>(c)</sup> 5.2 <sup>(d)</sup>	12.4 <sup>(e)</sup>	8.3 <sup>(f)</sup>	8.4 <sup>(g)</sup>
Species	BrOBrO	ClOBrO	IOBrO	HOBrO	CH <sub>3</sub> OBrO
ΔE	11.0 <sup>(h)</sup> 8.7 <sup>(d)</sup>	13.1 <sup>(c)</sup> 8.6 <sup>(d)</sup>	3.8 <sup>(e)</sup>	2.9 <sup>(d)</sup>	6.3 <sup>(i)</sup>
Species	ClOIO	BrOIO	IOIO	HOIO	CH <sub>3</sub> OIO
ΔE	-5.0 <sup>(e)</sup>	-6.4 <sup>(e)</sup>	-8.2 <sup>(e)</sup> -7.9 <sup>(j)</sup>	-13.2 <sup>(k)</sup>	-0.2 <sup>(l)</sup>
Species	ClClO <sub>2</sub>	BrClO <sub>2</sub>	IClO <sub>2</sub>	HClO <sub>2</sub>	CH <sub>3</sub> ClO <sub>2</sub>
ΔE	5.1 <sup>(a)</sup> 3.4 <sup>(b)</sup>	6.8 <sup>(c)</sup> 7.8 <sup>(d)</sup>	22.6 <sup>(e)</sup>	49.7 <sup>(f)</sup>	30.8 <sup>(g)</sup>
Species	BrBrO <sub>2</sub>	ClBrO <sub>2</sub>	IBrO <sub>2</sub>	HBrO <sub>2</sub>	CH <sub>3</sub> BrO <sub>2</sub>
ΔE	8.2 <sup>(h)</sup> 6.8 <sup>(d)</sup>	3.4 <sup>(c)</sup> 2.4 <sup>(d)</sup>	9.3 <sup>(e)</sup>	52.6 <sup>(d)</sup>	33.4 <sup>(i)</sup>
Species	IIO <sub>2</sub>	ClIO <sub>2</sub>	BrIO <sub>2</sub>	HIO <sub>2</sub>	CH <sub>3</sub> IO <sub>2</sub>
ΔE	-14.6 <sup>(e)</sup> -12.9 <sup>(j)</sup>	-32.3 <sup>(e)</sup>	-23.6 <sup>(e)</sup>	59.5 <sup>(k)</sup>	18.5 <sup>(l)</sup>

<sup>(a)</sup> Reference [37], <sup>(b)</sup> reference [16], <sup>(c)</sup> reference [36], <sup>(d)</sup> reference [22], <sup>(e)</sup> reference [39], <sup>(f)</sup> reference [17], <sup>(g)</sup> reference [44], <sup>(h)</sup> reference [29], <sup>(i)</sup> reference [40], <sup>(j)</sup> reference [25], <sup>(k)</sup> reference [45], <sup>(l)</sup> reference [48].

TABLE 6: Relative stabilities of (YXO<sub>3</sub>) isomers in kcal mol<sup>-1</sup> compared to the normal valent peroxide species YOOOX in each family.

Species	ClOClO <sub>2</sub>	BrOClO <sub>2</sub>	IOClO <sub>2</sub>	HOOCIO	HOClO <sub>2</sub>	CH <sub>3</sub> OOCIO	CH <sub>3</sub> OClO <sub>2</sub>
ΔE	-2.2 <sup>(a)</sup> -2.1 <sup>(b)</sup>	-3.0 <sup>(c)</sup>	-5.7 <sup>(a)</sup>	21.1 <sup>(d)</sup>	-2.8 <sup>(d)</sup>	12.4 <sup>(e)</sup>	-7.9, 4.2 <sup>(f)</sup>
Species	ClOBrO <sub>2</sub>	IOBrO <sub>2</sub>	HOObro	HOBrO <sub>2</sub>	CH <sub>3</sub> OObro	CH <sub>3</sub> OBrO <sub>2</sub>	
ΔE	-0.5 <sup>(c)</sup>	-14.1 <sup>(a)</sup>	14.5 <sup>(g)</sup>	-5.7 <sup>(g)</sup>	12.3 <sup>(h)</sup>	-5.6 <sup>(h)</sup> , 1.4 <sup>(i)</sup>	
Species	ClOIO <sub>2</sub>	BrOIO <sub>2</sub>	HOIO	HOIO <sub>2</sub>	CH <sub>3</sub> OIO	CH <sub>3</sub> OIO <sub>2</sub>	
ΔE	-37.4 <sup>(a)</sup>	-39.7 <sup>(a)</sup>	-0.1 <sup>(j)</sup>	-39.9 <sup>(j)</sup>	-1.3 <sup>(k)</sup>	-31.2 <sup>(k)</sup>	
Species	ClClO <sub>3</sub>	BrClO <sub>3</sub>	IClO <sub>3</sub>	HClO <sub>3</sub>	CH <sub>3</sub> ClO <sub>3</sub>		
ΔE	10.6 <sup>(a)</sup> 4.6 <sup>(b)</sup>	8.1 <sup>(c)</sup>	23.4 <sup>(a)</sup>	42.7 <sup>(d)</sup>	47.2 <sup>(f)</sup>		
Species	ClBrO <sub>3</sub>	IBrO <sub>3</sub>	HBrO <sub>3</sub>	CH <sub>3</sub> BrO <sub>3</sub>			
ΔE	16.2 <sup>(c)</sup>	10.5 <sup>(a)</sup>	59.8 <sup>(g)</sup>	37.2 <sup>(h)</sup>			
Species	ClIO <sub>3</sub>	BrIO <sub>3</sub>	HIO <sub>3</sub>	CH <sub>3</sub> IO <sub>3</sub>			
ΔE	-35.5 <sup>(a)</sup>	-27.3 <sup>(a)</sup>	29.9 <sup>(j)</sup>	13.3 <sup>(k)</sup>			

<sup>(a)</sup>Reference [46], <sup>(b)</sup>reference [23], <sup>(c)</sup>reference [24], <sup>(d)</sup>reference [19], <sup>(e)</sup>reference [43], <sup>(f)</sup>reference [43] at the G2MP2 and the CCSD(T), QCISD(T) levels, respectively, <sup>(g)</sup>reference [27], <sup>(h)</sup>reference [34], <sup>(i)</sup>reference [42], <sup>(j)</sup>reference [49], <sup>(k)</sup>reference [53]

FIGURE 1: The optimized structures of (IClO<sub>3</sub>) isomers.

highly electronegative YO fragments. These complexes compete in stability with the peroxide normal valent forms YOOOCl, YOOOBr, and their classification is very sensitive to the method applied. At the CCSD(T)/6-311G(d,p), QCISD(T)/6-311G(d,p) levels of theory [42, 43], they are placed only ~1-2 kcal/mol above the normal valent peroxide structures, while at the G2MP2 level they are found to be even more stable by ~2-3 kcal/mol [19, 34, 43]. The corresponding I containing isomer, the iodic acid HOIO<sub>2</sub>, presents particular stability and it is far more stable than the normal valent peroxide isomer HOOOI, as we will see in the next paragraph. On the other hand, the high instability of the fully hypervalent configurations HClO<sub>2</sub>, HBrO<sub>2</sub>, CH<sub>3</sub>ClO<sub>2</sub>, CH<sub>3</sub>BrO<sub>2</sub>, HClO<sub>3</sub>, HBrO<sub>3</sub>, CH<sub>3</sub>ClO<sub>3</sub>, CH<sub>3</sub>BrO<sub>3</sub> may be readily explained when it is realized that the electropositively charged hypervalent halogen is necessarily connected to the electropositive H, CH<sub>3</sub> partners. We suggest that the correlation of the ionic character of X-O bonding and the electrostatic character of the Y, YO fragments is a major factor affecting the stabilization of the corresponding polyoxide, that has not been given so far the appropriate attention required.

A related parameter that also influences the relative stability order appears to be the degree of valence on the halogen. The isomers ClOClO, BrOBrO are less stable than ClClO<sub>2</sub>, BrBrO<sub>2</sub> despite having the hypervalent halogen also connected to an electronegative fragment such as ClO and BrO. The difference must most probably rely on the lower degree of halogen valence in the former compounds, which evidently plays also an important role in the stabilization process and becomes another significant factor affecting the stability of the compound. It has been suggested [11] that the multivalent configuration on the halogen is achieved when one, two, or three lone-pair valence electrons acquire a considerable amount of d character and form two, four, or six additional pd hybrid halogen bonds. The “energetic cost”



of the first partial p→d promotion in the YOxO species is obviously only partly recovered by the X–O double bond. Once however, some pd hybridization has taken place, the energy level decreases and the mixing of the second lone-pair electrons is suggested [11] to occur much easier. This analysis [11] indicates that hypervalent halogen species with more than five bonds, such as the YXO<sub>3</sub> species which contain seven bonds on the valence shell, will require the participation of the third halogen valence lone-pair electrons, that is, the s valence electrons [11] having already acquired some p character. Such a hybridization is obviously very costly and the YXO<sub>3</sub> species are quite unstable thermodynamically as shown from the calculated results. We may conclude by saying that there appears to be an optimum degree of valence for stabilization which is five bonds around the halogen atom.

### 3.4. Particular features of the iodine oxides

The tendencies described above are most convincingly demonstrated in the hypervalent I series. The lower electronegativity of I compared to Cl, Br allows hypervalent iodine to carry a much larger positive charge distribution and enhances remarkably the ionic nature of I–O bonding. We have for example the following partial charge distributions:

$$\begin{aligned} & \text{H-O-O-I} \\ & + 0.44/ - 0.38/ - 0.39/ + 0.33 \\ & \text{H-O-I-O} \\ & + 0.47/ - 0.91/ + 1.37/ - 0.93 \\ & \text{H-I-O}_2 \\ & + 0.12/ + 2.11/ - 0.99 \times 2. \end{aligned}$$

As a result, the oxides containing hypervalent iodine are usually more stable than the normal valent isomers. Thus, in contrast to the YOClO, YOBrO species discussed above, YOIO isomers are more stable than the normal valent peroxide compounds YOOI, despite the lower degree of valence involved. In fact, the hypervalent I compounds are usually very stable thermodynamically and one of them, iodic acid HOIO<sub>2</sub>, a white powdered solid, is even stable at room temperature. Also methyl iodate CH<sub>3</sub>OIO<sub>2</sub>, because of its thermodynamic stability, is found to operate as a reservoir species for iodine in the marine boundary layer [52]. The only exceptions are the fully hypervalent HIO<sub>2</sub>, HIO<sub>3</sub>, CH<sub>3</sub>IO<sub>2</sub>, CH<sub>3</sub>IO<sub>3</sub> isomers where the hypervalent I may only form a weak bond with the electropositive H, CH<sub>3</sub> fragments producing also unstable adducts like the Cl, Br analogues.

### 3.5. Heat of formation values

The most appropriate measure of the actual thermodynamic stability of chemical species is the heat of formation values, ΔH<sub>f</sub>, which allow a direct comparison among various compounds. Several computed values in the present laboratory as well as various literature results are summarized in Table 7. For comparison the maternal compound, HOOH, is also included. The table shows that low heat of formation

TABLE 7: Collected heat of formation ΔH<sub>f</sub><sup>o</sup> (kcal mol<sup>-1</sup>) reported values for several halogen polyoxides<sup>(a)</sup>.

(YXO <sub>2</sub> )	ΔH <sub>f</sub> <sup>o</sup>	(YXO <sub>3</sub> )	ΔH <sub>f</sub> <sup>o</sup>
HOOH	-31.0	BrOOCl	49.8
ClClO <sub>2</sub>	33.8	BrOClO <sub>2</sub>	46.8
ClOClO	40.0	ClOBrO <sub>2</sub>	49.3
ClOOCl	32.6	HOOCl	9.1
HOCIO	11.9	HOOCIO	25.3
HClO <sub>2</sub>	56.1	HOCIO <sub>2</sub>	4.2
HOCl	1.6	HClO <sub>3</sub>	46.1
HOBr	8.6	BrClO <sub>3</sub>	57.9
HOBrO	13.2	ClBrO <sub>3</sub>	66.0
HBrO <sub>2</sub>	63.7	ClOOCl	40.3
ClOOBr	38.9	ClOClO <sub>2</sub>	38.2
ClOBrO	48.3	ClClO <sub>3</sub>	44.9
BrOClO	49.4	HOObBr	13.6
ClBrO <sub>2</sub>	41.9	HOBrO <sub>2</sub>	5.7
BrClO <sub>2</sub>	45.7	HOObBrO	26.2
BrOOBr	46.1	HBrO <sub>3</sub>	71.6
BrBrO <sub>2</sub>	52.9	BrOBrO <sub>2</sub>	56.4
BrOBrO	54.8	CH <sub>3</sub> OOObBr	16.2
HOOI	7.6	CH <sub>3</sub> OOBrO	28.5
HOIO	-5.3	CH <sub>3</sub> OBrO <sub>2</sub>	10.6
HIO <sub>2</sub>	26.5	CH <sub>3</sub> BrO <sub>3</sub>	53.4
IOOI	38.7	HOIOI	21.9
IOIO	30.8	HOIOO	21.6
IIO <sub>2</sub>	25.8	HOIO <sub>2</sub>	-17.8
		HIO <sub>3</sub>	51.0

<sup>(a)</sup>Reference [16–53]

values are calculated for the normal-valent cross hydrogen-halogen peroxides of the type HOOX. Among the multivalent species low heat of formation values are computed for the acidic derivatives HOXO, HOXO<sub>2</sub>, and the methyl analogs CH<sub>3</sub>OXO<sub>2</sub>, X = Cl, Br, I, which may be considered relatively stable at room temperature. The polyoxides that involve two halogen atoms are usually unstable and present very short lifetimes, having been detected only spectroscopically as bound short-lived intermediates in the kinetic investigation of various atmospheric processes or in matrix isolation studies. As a rule the iodine containing species are the most stable halogen polyoxides.

## 4. SUMMARY

The halogen-oxygen bonding properties in the (YXO<sub>2</sub>) and (YXO<sub>3</sub>) polyoxides, Y = Cl, Br, I, H, CH<sub>3</sub> and X = Cl, Br, I, have been examined. The analysis shows that multivalent bonding presents a strong ionic nature and affects the structural characteristics and the thermodynamic stabilization trends. The X–O bond distance decreases considerably in the fully hypervalent compounds but its variations do not correlate with energy stability order. From the analysis presented, the thermodynamic stability and the relative stability

order of the various isomers are suggested to result from the combination of three factors: (a) the electrostatic nature of the Y, YO fragments, (b) the electronegativity of the halogen, and (c) the degree of halogen valence in the formation of the hypervalent bonds.

## REFERENCES

- [1] D. R. Yarkony, Ed., *Modern Electronic Structure Theory—Parts I & II*, World Scientific, Singapore, 1995.
- [2] T. J. Lee and G. E. Scuseria, "Achieving chemical accuracy with coupled-cluster theory," in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, S. R. Langhoff, Ed., p. 47, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1995.
- [3] B. J. Finlayson-Pitts and J. N. Pitts, *Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Diego, Calif, USA, 2000.
- [4] M. J. Molina and F. S. Rowland, "Stratospheric sink for chlorofluoromethanes: chlorine atom catalysed destruction of ozone," *Nature*, vol. 249, no. 5460, pp. 810–812, 1974.
- [5] R. S. Stolarski and R. J. Cicerone, "Stratospheric chlorine: a possible sink for ozone," *Canadian Journal of Chemistry*, vol. 52, no. 8, pp. 1610–1615, 1974.
- [6] S. C. Wofsy, M. B. McElroy, and Y. L. Yung, "The chemistry of atmospheric bromine," *Geophysical Research Letters*, vol. 2, no. 6, pp. 215–218, 1975.
- [7] O. Zafririou, "Photochemistry of halogens in the marine atmosphere," *Journal of Geophysical Research*, vol. 79, no. 18, pp. 2730–2732, 1974.
- [8] S. Solomon, R. R. Garcia, and A. R. Ravishankara, "On the role of iodine in ozone depletion," *Journal of Geophysical Research*, vol. 99, no. D10, pp. 20491–20499, 1994.
- [9] M. Xieqi, B. Cicek, and S. M. Senkan, "Chemical structures of fuel-rich and fuel-lean flames of  $\text{CCl}_4/\text{CH}_4$  mixtures," *Combustion and Flame*, vol. 94, no. 1–2, pp. 131–145, 1993.
- [10] S. P. Sander, R. R. Friedl, and J. S. Francisco, "Experimental and theoretical studies of atmospheric inorganic chlorine chemistry," in *Current Problems and Progress in Atmospheric Chemistry*, D. R. Barker, Ed., chapter 19, World Scientific, Singapore, 1998.
- [11] T. J. Lee, C. E. Dateo, and J. E. Rice, "An analysis of chlorine and bromine oxygen bonding and its implications for stratospheric chemistry," *Molecular Physics*, vol. 96, no. 4, pp. 633–643, 1999.
- [12] J. B. Foresman and Æ. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian, Pittsburgh, Pa, USA, 1996.
- [13] W. R. Wadt and P. J. Hay, "Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi," *The Journal of Chemical Physics*, vol. 82, no. 1, pp. 284–298, 1985.
- [14] A. Bergner, M. Dolg, W. Küchle, H. Stoll, and H. Preuß, "Ab initio energy-adjusted pseudopotentials for elements of groups 13–17," *Molecular Physics*, vol. 80, no. 6, pp. 1431–1441, 1993.
- [15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., *Gaussian 98 (Revision A.7)*, Gaussian, Pittsburgh, Pa, USA, 1998.
- [16] M. P. McGrath, K. C. Clemitshaw, F. S. Rowland, and W. J. Hehre, "Structures, relative stabilities, and vibrational spectra of isomers of  $\text{Cl}_2\text{O}_2$ : the role of the chlorine oxide dimer in antarctic ozone depleting mechanisms," *The Journal of Physical Chemistry*, vol. 94, no. 15, pp. 6126–6132, 1990.
- [17] T. J. Lee, C. M. Rohlfing, and J. E. Rice, "An extensive ab initio study of the structures, vibrational spectra, quadratic force fields, and relative energetics of three isomers of  $\text{Cl}_2\text{O}_2$ ," *The Journal of Chemical Physics*, vol. 97, no. 9, pp. 6593–6605, 1992.
- [18] J. S. Francisco, S. P. Sander, T. J. Lee, and A. P. Rendell, "Structures, relative stabilities, and spectra of isomers of  $\text{HClO}_2$ ," *The Journal of Physical Chemistry*, vol. 98, no. 22, pp. 5644–5649, 1994.
- [19] D. H. Phillips and G. E. Quelch, "Normal-valent  $\text{ClO}_n\text{X}$  compounds for  $n = 2, 3$  and  $\text{X} = \text{Cl, H}$ : an MCSCF investigation," *The Journal of Physical Chemistry*, vol. 100, no. 27, pp. 11270–11275, 1996.
- [20] J. S. Francisco and S. P. Sander, "Structures, relative stabilities, and vibrational spectra of isomers of  $\text{HClO}_3$ ," *The Journal of Physical Chemistry*, vol. 100, no. 2, pp. 573–579, 1996.
- [21] J. T. Gleghorn, "A G1 study of the isomers of  $\text{ClOOBr}$  and related systems," *Chemical Physics Letters*, vol. 271, no. 4–6, pp. 296–301, 1997.
- [22] W.-K. Li and C.-Y. Ng, "Gaussian-2 ab initio study of isomeric  $\text{Cl}_2\text{O}_2$  and  $\text{Cl}_2\text{O}_2^+$  and their dissociation reactions," *The Journal of Physical Chemistry A*, vol. 101, no. 2, pp. 113–115, 1997.
- [23] S. Guha and J. S. Francisco, "A density functional study of the structure, vibrational spectra, and relative energetics of  $\text{XBrO}_2$  isomers (where  $\text{X} = \text{H, Cl, and Br}$ )," *The Journal of Physical Chemistry A*, vol. 101, no. 29, pp. 5347–5359, 1997.
- [24] J. Clark and J. S. Francisco, "Study of the stability of  $\text{Cl}_2\text{O}_3$  using ab initio methods," *The Journal of Physical Chemistry A*, vol. 101, no. 38, pp. 7145–7153, 1997.
- [25] J. S. Francisco and J. Clark, "Study of the stability of  $\text{BrClO}_3$  isomers," *The Journal of Physical Chemistry A*, vol. 102, no. 12, pp. 2209–2214, 1998.
- [26] A. Misra and P. Marshall, "Computational investigations of iodine oxides," *The Journal of Physical Chemistry A*, vol. 102, no. 45, pp. 9056–9060, 1998.
- [27] S. Guha and J. S. Francisco, "A density functional study of the equilibrium structure, vibrational spectrum, and heat of formation of  $\text{Br}_2\text{O}_3$ ," *The Journal of Physical Chemistry A*, vol. 102, no. 33, pp. 6702–6705, 1998.
- [28] S. Guha and J. S. Francisco, "Structures, vibrational spectra, and relative energetics of  $\text{HBrO}_3$  isomers," *The Journal of Physical Chemistry A*, vol. 102, no. 11, pp. 2072–2079, 1998.
- [29] L. F. Pacios and P. C. Gómez, "Bonding in bromine oxides: isomers of  $\text{BrO}_2$ ,  $\text{Br}_2\text{O}_2$  and  $\text{BrO}_3$ ," *Journal of Molecular Structure: THEOCHEM*, vol. 467, no. 3, pp. 223–231, 1999.
- [30] D. Papayannis, A. M. Kosmas, and V. S. Melissas, "Ab initio calculations for  $(\text{BrO})_2$  system and quasiclassical dynamics study of  $\text{BrO}$  self-reaction," *Chemical Physics*, vol. 243, no. 3, pp. 249–262, 1999.
- [31] R. Sumathi and S. D. Peyerimhoff, "Density functional characterization of  $[\text{HClO}_2]$  potential energy surface," *The Journal of Physical Chemistry A*, vol. 103, no. 37, pp. 7515–7521, 1999.
- [32] K. H. Kim, Y.-K. Han, and Y. S. Lee, "Basis set effects on the stability of the  $\text{Cl}_2\text{O}_3$  isomers using B3P86 and B3LYP methods of density functional theory," *Journal of Molecular Structure: THEOCHEM*, vol. 460, no. 1–3, pp. 19–25, 1999.
- [33] A. Beltrán, J. Andrés, S. Noury, and B. Silvi, "Structure and bonding of chlorine oxides and peroxides:  $\text{ClO}_x$ ,  $\text{ClO}_x^-$  ( $x = 1–4$ ), and  $\text{Cl}_2\text{O}_x$  ( $x = 1–8$ )," *The Journal of Physical Chemistry A*, vol. 103, no. 16, pp. 3078–3088, 1999.
- [34] P. C. Gómez and L. F. Pacios, "Bromine and mixed bromine chlorine oxides: wave function (CCSD(T) and MP2) versus density functional theory (B3LYP) calculations," *The Journal of Physical Chemistry A*, vol. 103, no. 6, pp. 739–743, 1999.



- [35] S. Guha and J. S. Francisco, "Structures, vibrational spectra, and relative energetics of  $\text{CH}_3\text{BrO}_3$  isomers," *The Journal of Physical Chemistry A*, vol. 104, no. 14, pp. 3239–3245, 2000.
- [36] W.-K. Li, K.-C. Lau, C. Y. Ng, H. Baumgärtel, and K.-M. Weitzel, "Gaussian-2 and Gaussian-3 study of the energetics and structures of  $\text{Cl}_2\text{O}_n$  and  $\text{Cl}_2\text{O}_n^+$ ,  $n = 1 - 7$ ," *The Journal of Physical Chemistry A*, vol. 104, no. 14, pp. 3197–3203, 2000.
- [37] D. K. Papayannis, A. M. Kosmas, and V. S. Melissas, "Quantum mechanical studies on the  $\text{BrO} + \text{ClO}$  reaction," *The Journal of Physical Chemistry A*, vol. 105, no. 11, pp. 2209–2215, 2001.
- [38] D. K. Papayannis, V. S. Melissas, and A. M. Kosmas, "A quantum mechanical study of the structure, vibrational spectra and relative energetics of  $\text{XOOI}$ ,  $\text{XIO}_2$  and  $\text{XOIO}$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) isomers," *Chemical Physics Letters*, vol. 349, no. 3-4, pp. 299–306, 2001.
- [39] R. S. Zhu and M. C. Lin, "Ab initio studies of  $\text{ClO}_x$  reactions. IV. Kinetics and mechanism for the self-reaction of  $\text{ClO}$  radicals," *The Journal of Chemical Physics*, vol. 118, no. 9, pp. 4094–4106, 2003.
- [40] V. S. Melissas, D. K. Papayannis, and A. M. Kosmas, "Structural and relative stability studies of  $\text{IOOX}$  peroxides ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and their isomers," *Journal of Molecular Structure: THEOCHEM*, vol. 626, no. 1–3, pp. 263–269, 2003.
- [41] D. K. Papayannis, V. S. Melissas, and A. M. Kosmas, "Quantum mechanical studies of methyl bromoperoxide isomers and the  $\text{CH}_3\text{O} + \text{BrO}$  reaction," *Physical Chemistry Chemical Physics*, vol. 5, no. 14, pp. 2976–2980, 2003.
- [42] Z.-F. Xu, R. Zhu, and M. C. Lin, "Ab initio studies of  $\text{ClO}_x$  reactions. 3. Kinetics and mechanism for the  $\text{OH} + \text{OClO}$  reaction," *The Journal of Physical Chemistry A*, vol. 107, no. 7, pp. 1040–1049, 2003.
- [43] S. Guha and J. S. Francisco, "An ab initio study of the pathways for the reaction between  $\text{CH}_3\text{O}_2$  and  $\text{BrO}$  radicals," *The Journal of Chemical Physics*, vol. 118, no. 4, pp. 1779–1793, 2003.
- [44] E. Drougas, A. F. Jalbout, and A. M. Kosmas, "Quantum mechanical studies of  $\text{CH}_3\text{ClO}_3$  isomers and the  $\text{CH}_3\text{O}_2 + \text{ClO}$  reaction pathways," *The Journal of Physical Chemistry A*, vol. 107, no. 51, pp. 11386–11390, 2003.
- [45] E. Drougas and A. M. Kosmas, "Quantum mechanical studies of isomeric and conformeric structures of methylchloro-peroxide," *International Journal of Quantum Chemistry*, vol. 98, no. 3, pp. 335–341, 2004.
- [46] N. Begović, Z. Marković, S. Anić, and L. Kolar-Anić, "Computational investigation of  $\text{HIO}$  and  $\text{HIO}_2$  isomers," *The Journal of Physical Chemistry A*, vol. 108, no. 4, pp. 651–657, 2004.
- [47] D. K. Papayannis and A. M. Kosmas, "Structural and relative stability studies of  $(\text{IClO}_3)$  and  $(\text{IBrO}_3)$  polyoxides," *Molecular Physics*, vol. 102, no. 8, pp. 789–795, 2004.
- [48] A. M. Kosmas, E. Drougas, and D. K. Papayannis, "Theoretical structural and stability studies of  $\text{XClO}_2$  and  $\text{XBrO}_2$  molecules ( $\text{X}=\text{H}, \text{HO}, \text{CH}_3, \text{CH}_3\text{O}, \text{Cl}, \text{Br}, \text{I}$ )," *MATCH: Communications in Mathematical and in Computer Chemistry*, vol. 53, no. 2, pp. 261–268, 2005.
- [49] E. Drougas and A. M. Kosmas, "Computational investigation of isomeric and conformeric structures of methyl iodoperoxide," *Canadian Journal of Chemistry*, vol. 83, no. 1, pp. 9–15, 2005.
- [50] E. Drougas and A. M. Kosmas, "Computational studies of  $(\text{HIO}_3)$  isomers and the  $\text{HO}_2 + \text{IO}$  reaction pathways," *The Journal of Physical Chemistry A*, vol. 109, no. 17, pp. 3887–3892, 2005.
- [51] J. M. C. Plane, D. M. Joseph, B. J. Allan, S. H. Ashworth, and J. S. Francisco, "An experimental and theoretical study of the reactions  $\text{OIO} + \text{NO}$  and  $\text{OIO} + \text{OH}$ ," *The Journal of Physical Chemistry A*, vol. 110, no. 1, pp. 93–100, 2006.
- [52] J. S. Francisco and J. N. Crowley, "Theoretical investigation of product channels in the  $\text{CH}_3\text{O}_2 + \text{Br}$  reaction," *The Journal of Physical Chemistry A*, vol. 110, no. 10, pp. 3778–3784, 2006.
- [53] A. M. Kosmas and E. Drougas, "The quantum mechanical description of normal valent and multivalent iodine in the polyoxides of the type  $\text{IO}_n\text{X}$ ,  $\text{X}=\text{H}, \text{CH}_3$ ,  $n = 1, 2, 3$ ," *Computational Materials Science*, vol. 38, no. 3, pp. 502–505, 2007.
- [54] E. Drougas and A. M. Kosmas, "Ab initio characterization of  $\text{CH}_3\text{IO}_2$  isomers and the  $\text{CH}_3\text{O}_2 + \text{IO}$  reaction pathways," *The Journal of Physical Chemistry A*, vol. 111, no. 17, pp. 3402–3408, 2007.