

Research Article

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

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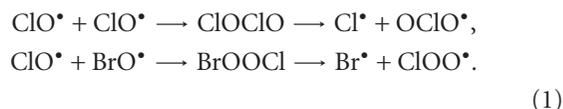
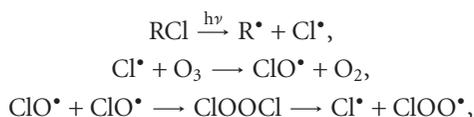
Trends in the properties of normal valent and multivalent halogen-oxygen bonding are examined for the isomers of the halogen polyoxide families of the types (YXO₂) and (YXO₃), Y=Cl, Br, I, H, CH₃, X=Cl, Br, I. A qualitative model is formulated on the relationship between the X-O bond distance variations, 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.

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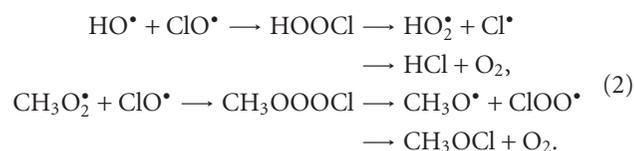
1. INTRODUCTION

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⁻¹, 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[•], methyl CH₃[•], hydroperoxy HO₂[•], and methylperoxy CH₃O₂[•] 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, (YXO₂) and (YXO₃), Y = Cl, Br, I, H, CH₃, 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 (YXO₂) and (YXO₃) 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 (YBrO₂), Y = H, Cl, Br, and (YBrO₃), Y = H, CH₃, 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 (CH₃XO₂) 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⁻¹) for the isomers of (ClBrO₂), (ClIO₃) families.

| | |
|--------------------|--|
| ClOOBr | 776, 676, 595, 431, 296, 103 |
| ClBrO ₂ | 832, 331, 297, 211, 876, 168 |
| BrClO ₂ | 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 ₂ | 965, 952, 774, 465, 332, 290, 238, 136, 45 |
| IOClO ₂ | 1231, 995, 675, 494, 443, 359, 221, 175, 101 |
| ClIO ₃ | 920, 392, 295, 981, 308, 195 |
| IClO ₃ | 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 (ClBrO₂) and (IClO₃) families.

3. RESULTS AND DISCUSSION

Selected structural results for the (YClOn), (YBrOn), and (YIO_n), Y = Cl, Br, I, H, CH₃, *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 (YClO₂), (YBrO₂), and (YIO₂) families, Y=Cl, Br, I, H, CH₃

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 (YClO₂) and (YClO₃) isomeric structures.

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

YXO₂. 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 ClClO₂, a striking shrinkage of ~ 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 (YBrO₂) family, for instance, the Br–O equilibrium length varies from 1.905 Å to 1.597 Å, again a range of the order of ~ 0.3 Å.

3.2. Trends in the structural parameters of (YXO₃) species

For Y = halogen atom, three types of isomers are obtained, the peroxide form, YOOOX, the fully hypervalent, YXO₃, and the mixed one, YOXO₂. As an example, Figure 1 displays the optimized structures of (IClO₃) family. When Y = H, CH₃, a fourth isomeric structure has been determined, that is, the HOOXO, CH₃OOXO geometries. In all (YXO₃), 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 YXO₃. The Cl–O bond distance in ClClO₃, 1.418 Å, is the shortest ever calculated for a Cl–O bond while the bridged O-bridged Cl in ClOClO₂, 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 (YBrO₂) and (YBrO₃) isomeric structures.

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

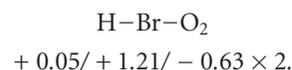
observed in (YXO₂) are observed in the (YXO₃). However, the deviations between largest and shortest bond lengths are even more emphasized in the (YXO₃) than in the (YXO₂) series.

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 YXO₃ 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 ClBrO₂ structure is more stable than BrClO₂ since the more electropositively charged hypervalent Br is connected to the more electronegative normal valent Cl. Another example is the YOClO₂, YOBrO₂, Y = H, CH₃ 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 ₂ | |
| I–O bridged | 2.065 | 2.066 | | |
| I–O terminal | | 1.820 | 1.790 | |
| Terminal I–O | | 2.046 | | |
| Species | CIOOI | CIOIO | ClIO ₂ | |
| I–O bridged | 2.060 | 2.064 | | |
| I–O terminal | | 1.818 | 1.783 | |
| Species | BrOOI | BrOIO | BrIO ₂ | |
| I–O bridged | 2.064 | 2.065 | | |
| I–O terminal | | 1.819 | 1.786 | |
| Species | HOOI | HOIO | HIO ₂ | |
| I–O bridged | 2.058 | 1.992 | | |
| I–O terminal | | 1.815 | 1.784 | |
| Species | CH ₃ OOI | CH ₃ OIO | CH ₃ IO ₂ | |
| I–O bridged | 2.005 | 1.948 | | |
| I–O terminal | | 1.777 | 1.749 | |
| Species | CIOOOI | CIOIO ₂ | ClIO ₃ | |
| I–O bridged | 2.018 | 2.001 | | |
| I–O terminal | | 1.744 | 1.733 | |
| Species | BrOOOI | BrOIO ₂ | BrIO ₃ | |
| I–O bridged | 2.019 | 1.980 | | |
| I–O terminal | | 1.744 | 1.735 | |
| Species | HOOOI | HOOIO | HOIO ₂ | HIO ₃ |
| I–O bridged | 2.012 | 1.982 | 1.919 | |
| I–O terminal | | 1.835 | 1.795 | 1.794 |
| Species | CH ₃ OOOI | CH ₃ OOIO | CH ₃ OIO ₂ | CH ₃ IO ₃ |
| 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⁻¹) compared to the normal valent peroxide species YOOX in each family^(a).

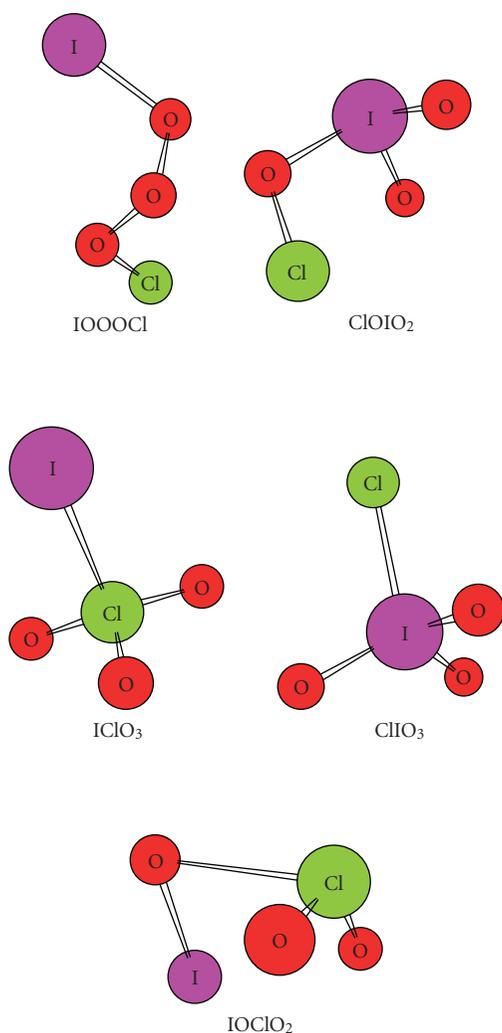
| | | | | | |
|---------|--|---|--|----------------------|----------------------------------|
| Species | CIOClO | BrOClO | IOClO | HOClO | CH ₃ OClO |
| ΔE | 14.5 ^(a) 13.3 ^(b) | 10.5 ^(c) 5.2 ^(d) | 12.4 ^(e) | 8.3 ^(f) | 8.4 ^(g) |
| Species | BrOBrO | ClOBrO | IOBrO | HOBrO | CH ₃ OBrO |
| ΔE |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

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

TABLE 6: Relative stabilities of (YXO₃) isomers in kcal mol⁻¹ compared to the normal valent peroxide species YOOOX in each family.

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

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

FIGURE 1: The optimized structures of (IClO₃) 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 HOIO₂, 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 HClO₂, HBrO₂, CH₃ClO₂, CH₃BrO₂, HClO₃, HBrO₃, CH₃ClO₃, CH₃BrO₃ may be readily explained when it is realized that the electropositively charged hypervalent halogen is necessarily connected to the electropositive H, CH₃ 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 ClClO₂, BrBrO₂ 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 YXO₃ 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 YXO₃ 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 HOIO₂, a white powdered solid, is even stable at room temperature. Also methyl iodate CH₃OIO₂, 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 HIO₂, HIO₃, CH₃IO₂, CH₃IO₃ isomers where the hypervalent I may only form a weak bond with the electropositive H, CH₃ 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_f, 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_f^o (kcal mol⁻¹) reported values for several halogen polyoxides^(a).

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

^(a)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, HOXO₂, and the methyl analogs CH₃OXO₂, 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 (YXO₂) and (YXO₃) polyoxides, Y = Cl, Br, I, H, CH₃ 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.

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