

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/41620221>

# Thermodynamic properties of the $\text{XO}_2$ , $\text{X}_2\text{O}$ , $\text{XYO}$ , $\text{X}_2\text{O}_2$ , and $\text{XYO}_2$ ( $\text{X}, \text{y} = \text{Cl}, \text{Br}, \text{and I}$ ) Isomers

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · FEBRUARY 2010

Impact Factor: 2.69 · DOI: 10.1021/jp911320p · Source: PubMed

CITATIONS

22

READS

34

7 AUTHORS, INCLUDING:



Minh Tho Nguyen

University of Leuven

748 PUBLICATIONS 10,835 CITATIONS

SEE PROFILE



Kirk A Peterson

Washington State University

273 PUBLICATIONS 16,080 CITATIONS

SEE PROFILE



David A Dixon

University of Alabama

766 PUBLICATIONS 22,167 CITATIONS

SEE PROFILE

# Thermodynamic Properties of the $\text{XO}_2$ , $\text{X}_2\text{O}$ , $\text{XYO}$ , $\text{X}_2\text{O}_2$ , and $\text{XYO}_2$ ( $\text{X}, \text{Y} = \text{Cl}, \text{Br}$ , and $\text{I}$ ) Isomers

Daniel J. Grant,<sup>†</sup> Edward B. Garner III,<sup>†</sup> Myrna H. Matus,<sup>†,‡</sup> Minh Tho Nguyen,<sup>†,§</sup> Kirk A. Peterson,<sup>||</sup> Joseph S. Francisco,<sup>⊥</sup> and David A. Dixon<sup>\*,†</sup>

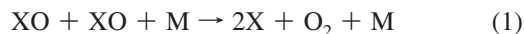
Chemistry Department, The University of Alabama, Shelby Hall, Box 870336, Tuscaloosa, Alabama 35487-0336, Unidad de Servicios de Apoyo en Resolución Analítica, Universidad Veracruzana, A. P. 575, Xalapa, Veracruz, México, Department of Chemistry, Washington State University, Pullman, Washington 99164-4630, Department of Chemistry, H. C. Brown Laboratory, Purdue University, West Lafayette, Indiana 47907-1393, and Department of Chemistry, Katholieke Universiteit Leuven, B-3001 Leuven, Belgium

Received: November 29, 2009; Revised Manuscript Received: February 3, 2010

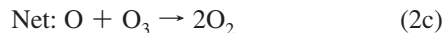
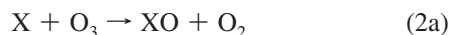
High level ab initio electronic structure calculations at the coupled cluster level with a correction for triples extrapolated to the complete basis set limit have been made for the thermodynamics of the  $\text{BrBrO}_2$ ,  $\text{IIO}_2$ ,  $\text{ClBrO}_2$ ,  $\text{ClIO}_2$ , and  $\text{BrIO}_2$  isomers, as well as various molecules involved in the bond dissociation processes. Of the  $\text{BrBrO}_2$  isomers,  $\text{BrOOBr}$  is predicted to be the most stable by 8.5 and 9.3 kcal/mol compared to  $\text{BrBrO}_2$  and  $\text{BrOBrO}$  at 298 K, respectively. The weakest bond in  $\text{BrOOBr}$  is the  $\text{O}-\text{Br}$  bond with a bond dissociation energy (BDE) of 15.9 kcal/mol, and in  $\text{BrBrO}_2$ , it is the  $\text{Br}-\text{Br}$  bond of 19.1 kcal/mol. The smallest BDE in  $\text{BrOBrO}$  is for the central  $\text{O}-\text{Br}$  bond with a BDE of 12.6 kcal/mol. Of the  $\text{IIO}_2$  isomers,  $\text{IIO}_2$  is predicted to be the most stable by 3.3, 9.4, and 28.9 kcal/mol compared to  $\text{IOIO}$ ,  $\text{IOOI}$ , and  $\text{OIIO}$  at 298 K, respectively. The weakest bond in  $\text{IIO}_2$  is the  $\text{I}-\text{I}$  bond with a BDE of 22.2 kcal/mol. The smallest BDEs in  $\text{IOIO}$  and  $\text{IOOI}$  are the terminal  $\text{O}-\text{I}$  bonds with values of 19.0 and 5.2 kcal/mol, respectively.

## Introduction

There is substantial interest in the role of halogen oxides in the stratosphere, especially for ozone depletion.<sup>1–3</sup> One of the key reactions involving halogen oxides that lead to the catalytic destruction of stratospheric ozone is the self-reaction of halogen oxides (reaction 1)



The halogen atom ( $\text{X}$ ) resulting from this reaction can participate in known catalytic reactions to destroy ozone via reaction sequence (2)



This above catalytic cycle, originally proposed by Rowland and Molina,<sup>1</sup> is used to describe ozone destruction by both chlorine and bromine in the stratosphere. In regions where oxygen atom abundances are low, but halogen oxide concentrations are high, a halogen oxide dimer or “ $\text{XO}$  dimer” mechanism for the destruction of ozone plays an important role in catalytically

destroying ozone via reaction sequence 3, which yields the net reaction (2c).



There are several major assumptions with the above chemistry. One assumption is that when two  $\text{XO}$  radicals combine in a three-body collision, a  $\text{XOOX}$  dimer is formed. The second assumption is that the resulting  $\text{XOO}$  radical that is formed from the photodissociation of the  $\text{XOOX}$  dimer is only marginally stable to render its facile decomposition into  $\text{X}$  atoms and  $\text{O}_2$ .

In addition to the well-known role of the chlorine oxides in the atmospheric process of ozone depletion, the analogous bromine oxides also play an important role. Bromine’s potential for ozone depletion is  $\sim 40$  times larger as compared to that of chlorine.<sup>4–7</sup> An estimated 40% of the ozone depletion in the Antarctic and Arctic stratosphere may be due to bromine oxides.<sup>8,9</sup> In addition, iodine oxides could play a role in ozone depletion if the iodo compounds reach the stratosphere. In order to better understand the chemistry of these halogen oxides, there have been a number of experimental studies of the atmospheric chemistry of bromine and its oxides, especially for its impact on ozone reduction.<sup>10–23</sup> There is also considerable interest in the role of iodine chemistry in the troposphere due to formation of its compounds in the marine boundary layer (MBL), and its potential for the destruction of  $\text{O}_3$  by cycles involving  $\text{IO}$ ,  $\text{HOI}$ ,

\* To whom correspondence should be addressed, dadixon@bama.ua.edu.

<sup>†</sup> University of Alabama.

<sup>‡</sup> Universidad Veracruzana.

<sup>§</sup> Katholieke Universiteit Leuven.

<sup>||</sup> Washington State University.

<sup>⊥</sup> Purdue University.

OIO, and  $\text{INO}_3$ .<sup>24–32</sup> It is known that iodine at the MBL can lead to the activation of chlorine and bromine from sea-salt aerosol<sup>33</sup> due to the presence of iodocarbons in the open ocean.<sup>34</sup>

There have been several experimental investigations into the thermodynamic properties, specifically the heats of formation, of the halogen oxides.<sup>35–37</sup> The experimental heats of formation of the diatomics  $\text{ClO}$ ,<sup>38</sup>  $\text{BrO}$ ,<sup>39,40</sup>  $\text{IO}$ ,<sup>41–44</sup>  $\text{Cl}_2$ ,  $\text{Br}_2$ ,<sup>37</sup>  $\text{I}_2$ ,<sup>37</sup>  $\text{BrCl}$ ,<sup>37</sup>  $\text{ICl}$ ,<sup>37</sup> and  $\text{IBr}$ <sup>37</sup> have been reported. The experimental heats of formation of the triatomic chlorine oxide molecules and  $\text{ClOOC}$  are available.<sup>37,45–47</sup> The heats of formation of  $\text{Br}_2\text{O}$  and  $\text{OBrO}$  have been reported from photoionization studies.<sup>36,48,49</sup> In addition, the  $\text{Br}-\text{OO}$  bond dissociation energy (BDE) has been estimated to be 1 kcal/mol from a study of the recombination rate constants of the  $\text{Br}$  with  $\text{O}_2$  reaction.<sup>50</sup> Additional experiments provide data relevant to the chemistry of these oxides.  $\text{OBrO}$  has been identified in the gas phase reactions<sup>51</sup> of  $\text{Br}_2 + \text{O}$ , as well as being spectroscopically identified in the gas phase as an intermediate of the  $\text{BrO} + \text{O}_3$  reaction.<sup>52</sup> The visible spectrum of gaseous  $\text{OBrO}$  has been reported.<sup>53</sup> Crossed molecular beam reactive scattering of ground-state oxygen atoms with  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  show that complexes can be formed and that the lifetime of the complex is related to the initial translational energy distribution.<sup>54–57</sup>

High-level electronic structure methods (coupled cluster<sup>58</sup> or multireference configuration interaction (MRCI)<sup>59</sup>) combined with the correlation-consistent basis sets, which extrapolate to the complete basis set (CBS) limit,<sup>60</sup> implemented on high-performance computers allow us to predict the structures and energies of medium size molecules to chemical accuracy.<sup>61</sup> Such approaches have already been used for the diatomic halogen oxides  $\text{XO}$ .<sup>62</sup> The heat of formation of  $\text{FOO}$  has been reported at a CCSD(T)/CBS level plus additional higher order corrections.<sup>63</sup> The  $\text{Cl}_2\text{O}_2$ ,  $\text{Cl}_2\text{O}$ , and  $\text{ClO}_2$  isomers have been previously studied at a comparably high level.<sup>64</sup> Heats of formation of the fluorine and chlorine oxides have been reported at the W4 level.<sup>65</sup> The molecular structures, thermochemistry, and electron affinities have been reported for the  $\text{Cl}_2\text{O}_n/\text{Cl}_2\text{O}_n^-$  ( $n = 1-4$ ) systems from density functional theory (DFT) calculations with a DZP++ basis set and four exchange-correlation functionals.<sup>66</sup> In addition, lower level calculations are also available in the literature.<sup>67</sup> Enthalpies of formation of  $\text{OXO}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ) have been calculated at the B3LYP, MP2, and CCSD(T) levels<sup>68</sup> and those for  $\text{OCIO}$  and  $\text{OBrO}$  at the MRCI level.<sup>69</sup> A series of triatomic bromine molecules,  $\text{Br}_2\text{O}$ ,  $\text{BrBrO}$ ,  $\text{ClOBr}$ ,  $\text{ClBrO}$ , and  $\text{BrClO}$ , have been studied at the CCSD(T)/TZ2P level.<sup>70</sup> Enthalpies of formation of the bromine oxides have been estimated via isodesmic reactions at the CCSD(T)/AREP/TZ(2df)//UMP2/AREP/TZ(2df) level.<sup>71</sup> The electron affinities of  $\text{Br}_2\text{O}_n$  ( $n = 0-4$ )<sup>72</sup> and  $\text{BrO}_n$  ( $n = 1-4$ )<sup>73</sup> have been reported from DFT calculations with a DZP++ basis set and a number of exchange-correlation functionals. The reactions of  $\text{BrO}$  with  $\text{BrO}$ ,  $\text{OBrO}$ , and  $\text{Br}_2\text{O}_2$  have been studied at the (QCISD)(T)/6-311++G(2df)//QCISD/6-311G\* level.<sup>74</sup> The structure, vibrational spectra, and energetics of  $\text{OBrO}$  have been reported at the MP2, MP4, and CCSD(T) levels of theory.<sup>75</sup> Heats of formation of the iodine oxides were calculated at a modified G2 level.<sup>76</sup> The electronic and geometric structures of several iodine-containing species have been predicted using ab initio molecular orbital and density functional approaches.<sup>77</sup> Peterson has reported very high level calculations similar to the approach given below using MRCI as well as CCSD(T) and the use of the electron affinities to predict the properties of the low-lying states of  $\text{OIO}$ , the ground state of  $\text{IOO}$ , and improved values for  $\text{IO}$ .<sup>78</sup>

We have used high-level molecular orbital theory following the methods we developed for accurate thermochemical predictions<sup>61</sup> to predict the structures, vibrational frequencies, heats of formation, and BDEs of the  $\text{XO}_2$ ,  $\text{X}_2\text{O}$ ,  $\text{XYO}$ ,  $\text{X}_2\text{O}_2$ , and  $\text{XYO}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ) isomers. We note that there are three relevant isomers with the formula  $\text{X}_2\text{O}_2$ :  $\text{XOOX}$ ,  $\text{XXO}_2$ , and  $\text{XOXO}$ , and five isomers for  $\text{XYO}_2$ ,  $\text{XOOY}$ ,  $\text{XYO}_2$ ,  $\text{YXO}_2$ :  $\text{XOYO}$ , and  $\text{YOXO}$  for ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ).

## Computational Approach

All thermochemical calculations were done with the R/UCCS-D(T) method<sup>79</sup> with the augmented correlation consistent basis sets,<sup>60</sup> aug-cc-pVnZ ( $n = \text{D}, \text{T}, \text{Q}, 5$ ) for H, O, F, Cl, and Br. Only the spherical component subset (e.g., five-term  $d$  functions, seven-term  $f$  functions, etc.) of the Cartesian polarization functions were used. The iodine basis set is discussed below. Tight  $d$  functions are necessary for calculating accurate atomization energies for second-row elements,<sup>80</sup> so we included additional tight  $d$  functions in our calculations giving the aug-cc-pV( $n+d$ )Z basis set on the second-row atom Cl. We use aVnZ to represent the combination of aug-cc-pVnZ on H, O, F, and Br and aug-cc-pV( $n+d$ )Z on Cl. Core–valence (CV) calculations were carried out with the weighted core–valence basis set cc-pwCVTZ.<sup>81,82</sup> The core–valence correction is then taken as the difference in energy between the valence electron correlation calculation and that with the nearest core electrons included using basis sets with additional functions the cc-pwCVTZ basis set in both cases.

For Br, we performed additional calculations using a relativistic effective core potential (RECP) and the associated correlation consistent basis sets for an RECP.<sup>85</sup> For Br, the RECP subsumes the ( $1s^2, 2s^2, 2p^6$ ) orbital space into the 10-electron core set, leaving the ( $3s^2, 3p^6, 4s^2, 3d^{10}, \text{and } 4p^5$ ) space with 25 electrons to be handled explicitly, and only the ( $4s^2, 4p^5$ ) electrons are active in our valence correlation treatment. We use aVnZ-PP to represent the combination of aVnZ basis set on the other atoms and the aug-cc-pVnZ-PP basis set on Br. CV calculations (25 electrons outside the RECP core) were carried out with the weighted core–valence basis set wCVTZ for O and Cl<sup>81</sup> and wCVTZ-PP for Br.<sup>83</sup>

For molecules containing I as a substituent, we used a different approach due to issues described elsewhere.<sup>84</sup> We used the new effective core potential/correlation consistent basis sets developed by Peterson and co-workers.<sup>62,85</sup> The RECP for I subsumes the ( $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$ ) orbital space into the 28-electron core set, leaving the ( $4s^2, 4p^6, 5s^2, 4d^{10}, \text{and } 5p^5$ ) space with 25 electrons to be handled explicitly. We have previously shown that inclusion of the nearest core electrons in the valence electron correlation energy calculations for the iodine fluoride compounds was critical for the prediction of reliable energetics.<sup>84</sup> We included all 25 electrons outside the RECP core in our iodine calculations with the aug-cc-pwCVnZ-PP basis sets for D, T, and Q for I and aug-cc-pwCVnZ on O, Cl, and Br. We abbreviate the combination of aug-cc-pwCVnZ on O, Cl, and Br and aug-cc-pwCVnZ-PP on I basis sets as awCVnZ.

Geometries were optimized at the CCSD(T) level with the aVDZ and aVTZ basis sets, at the valence-only level with the aVnZ-PP basis set and RECP on I and the aVnZ basis set on O, Cl, and Br. For the awCVnZ calculations, the geometries obtained with the aVDZ basis set were used in single point awCVDZ calculations and that with the aVTZ basis set used in the single point awCVTZ and awCVQZ calculations. The harmonic frequencies were calculated at the CCSD(T)/aVTZ

level and used to calculate the zero point energy ( $\Delta E_{\text{ZPE}}$ ) without scaling. Bond distances, harmonic frequencies, and anharmonic constants for the diatomics were obtained from a fifth order fit<sup>86</sup> of the potential energy surface at the CCSD(T)/aVQZ level.

The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form

$$E(n) = E_{\text{CBS}} + A \exp[-(n - 1)] + B \exp[-(n - 1)^2] \quad (4)$$

with  $n = 2$  (aVDZ), 3 (aVTZ), and 4 (aVQZ), as first proposed by Peterson et al.<sup>87</sup>

The scalar relativistic corrections ( $\Delta E_{\text{SR}}$ ) were carried out at the CCSD(T)/Douglas–Kroll–Hess level<sup>88</sup> with the VTZ-DK basis sets for compounds with O, Cl, and Br. For the compounds containing I, the RECP already accounts for the scalar relativistic correction on I. For these compounds,  $\Delta E_{\text{SR}}$  (which accounts for scalar relativistic effects primarily for atoms other than I) was evaluated from the expectation values for the two dominant terms in the Breit–Pauli Hamiltonian (the mass-velocity and one-electron Darwin (MVD) corrections)<sup>89</sup> from configuration interaction singles and doubles (CISD) calculations with a VTZ basis set at the CCSD(T)/aVTZ geometry. We have shown that any “double counting” of the relativistic effect on I when applying a MVD correction to an energy, which already includes most of the relativistic effects via the RECP, is small.<sup>90,91</sup>

We have previously shown that one can use isodesmic reactions to calculate the heats of formation of compounds like HOOX<sup>92</sup> (an XO type compound with  $X = \text{OH}$ ) as the use of total atomization energies (TAE) leads to considerable disagreement between the experimental and theoretical values due to the neglect of higher order correlation effects. For example, for FOO, the higher order correlation correction has been estimated to be  $2.40 \pm 0.5$  kcal/mol.<sup>93</sup> For the XOOX compounds which also contain an O–O bond, the higher order correlation corrections are expected to be much smaller on the basis of our previous calculations<sup>64</sup> on ClOOCl, and we have used our normal TAE approach to predicting their heats of formation. In order to better predict the heats of formation of the molecules, we used the following isodesmic reaction 5 to account for the higher order correlation effects



where  $X = \text{Cl, Br, and I}$ . The results from the isodesmic reactions are presented in Table 2. For  $\Delta H_f^{\circ}(\text{FOO})$ , we used the calculated value of Feller et al.<sup>63,93</sup> of  $6.4 \pm 0.7$ , which is in good agreement with the experimental values of  $6.1 \pm 0.5$ ,<sup>37</sup>  $5.49 \pm 0.40$ ,<sup>94</sup> and  $6.24 \pm 0.50$  kcal/mol.<sup>95</sup> For HOOF, we used our previously calculated value,<sup>92</sup> and for the remaining HOOX molecules ( $X = \text{Cl, Br, and I}$ ), we calculated the values and these are reported. The heats of formation of ClOO and BrOO (Table 3) are derived from isodesmic reaction energies calculated at the CBS (Q5) level (see Table 1, footnote *j*),<sup>63,64</sup> while that of IOO was based on energy at the CBS (DTQ) level.

Atomic spin orbit corrections ( $\Delta E_{\text{SO}}$ ) were taken from the tables of Moore.<sup>96</sup> Spin–orbit corrections for the dissociation energies of the diatomics were taken from the literature.<sup>97–99,97–99</sup> The spin–orbit corrections to the heats of formation of ClOO, BrOO, and IOO were calculated for the isodesmic reaction (5) at the DFT level with the B3LYP exchange–correlation functional.<sup>100</sup> Spin–orbit corrections were obtained at the DFT

B3LYP level for the TAE of all iodine compounds. For the spin–orbit calculations, the ECPs developed by Ermler and co-workers including spin–orbit operators<sup>101</sup> for the F, Cl, Br, and I atoms were used. The basis sets associated with these ECPs were augmented with the addition of the most diffuse *s* and two most diffuse *d* functions from the aVDZ (F, Cl, Br) and aVDZ-PP (I) basis sets. For O, the aVDZ basis set was used as the test calculations on O<sub>2</sub> gave erroneous dissociation energies if the ECP was utilized.

The total atomization energy ( $\text{TAE} = \sum D_0$ ) is calculated from eq 6.

$$\sum D_0 = \Delta E_{\text{elec}}(\text{CBS}) - \Delta E_{\text{ZPE}} + \Delta E_{\text{CV}} + \Delta E_{\text{SR}} + \Delta E_{\text{SO}} \quad (6)$$

Heats of formation were calculated by combining our computed  $\sum D_0$  values with the known enthalpies of formation at 0 K for the elements ( $\Delta H_f^{\circ}(\text{O}) = 58.98 \pm 0.02$  kcal/mol,  $\Delta H_f^{\circ}(\text{Cl}) = 28.59 \pm 0.001$  kcal/mol,  $\Delta H_f^{\circ}(\text{Br}) = 28.18 \pm 0.001$  kcal/mol, and  $\Delta H_f^{\circ}(\text{I}) = 25.61$  kcal/mol). We obtain enthalpies of formation at 298 K by following the procedures outlined by Curtiss et al.<sup>102</sup> We estimate that the error bars for the calculated heats of formation of the XO are  $\pm 1.5$  kcal/mol considering errors in the energy extrapolation, frequencies, and other electronic energy components as well as the use of the isodesmic reaction approach.

All CCSD(T) calculations were performed with either the MOLPRO-2006<sup>103</sup> program system on a single processor of an SGI Origin computer, the DMC at the Alabama Supercomputer Center, or a Dell Cluster at the University of Alabama, or with NWChem<sup>104</sup> and MOLPRO on the massively parallel HP Linux cluster in the Molecular Science Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory. The initial DFT calculations were done with the Gaussian program system<sup>105</sup> and the spin–orbit calculations with NWChem.

## Results and Discussion

**Geometries and Vibrational Frequencies.** The molecular geometries are given in the Supporting Information (Tables SI-1–Table SI-6). For the diatomics, the agreement of the predicted structures calculated at the CCSD(T)/CBS level with the experimental geometries<sup>110</sup> is in general excellent, within a few thousandths of an angstrom, with the largest difference being the  $r(\text{IO})$  distance that is predicted to be too long by 0.02 Å. The experimental geometries of OBrO<sup>106,107</sup> and BrOBr<sup>107,108</sup> have been reported, and our CCSD(T)/aVTZ values are in excellent agreement, with the largest difference predicted for the  $\angle \text{BrOBr}$  that was calculated to be 0.8° larger than that obtained by experiment. The experimental geometries for the remaining polyatomics are not available, but our work on the Cl<sub>2</sub>O<sub>2</sub> isomers<sup>64</sup> showed reasonable agreement with experiment<sup>109</sup> to within 0.02 Å, and we expect this quality for these molecules.

There are been a number experimental studies measuring the vibrational frequencies of the compounds of interest.<sup>110–126</sup> The calculated harmonic vibrational frequencies are given in the Supporting Information (Table SI-7) and serve as an additional test of the accuracy of the present results. We use the values calculated at the CCSD(T)/aVTZ level unless specified otherwise. For the diatomic molecules, the harmonic frequencies calculated at the CCSD(T)/aVQZ level are within 15 cm<sup>−1</sup> of the experimental values.<sup>110,111</sup> For BrOO, the calculated harmonic frequencies are in excellent agreement,



TABLE 1: Components for CCSD(T) Atomization Energies (kcal/mol)<sup>a</sup>

molecule	CBS <sup>b</sup>	$\Delta E_{\text{ZPE}}^c$	$\Delta E_{\text{SR}}^d$	$\Delta E_{\text{CV}}^e$	$\Delta E_{\text{SO}}^f$	$\Sigma D_0$ (0 K) <sup>g</sup>	molecule	CBS <sup>b</sup>	$\Delta E_{\text{ZPE}}^c$	$\Delta E_{\text{SR}}^d$	$\Delta E_{\text{CV}}^e$	$\Delta E_{\text{SO}}^f$	$\Sigma D_0$ (0 K) <sup>g</sup>
ClO ( $C_{\infty v}^{-2}\Pi$ ) <sup>h</sup>	64.75	1.24	-0.32	0.22	-0.61	62.80	BrIO ( $C_s^{-1}A'$ )	91.52	1.64	-0.26		-8.85	80.77
BrO ( $C_{\infty v}^{-2}\Pi$ )	58.34	1.03	-0.72	0.10	-2.05	54.54	BrIO ( $C_s^{-3}A''$ )	75.16	1.34	-0.11		-9.08	64.62
IO ( $C_{\infty v}^{-2}\Pi$ )	57.89	0.95	-0.10		-3.35	53.49	IBrO ( $C_s^{-1}A'$ )	75.92	1.65	-1.64		-8.62	64.02
Cl <sub>2</sub> ( $D_{\infty h}^{-1}\Sigma_g^+$ ) <sup>h</sup>	60.00	0.79	-0.37	0.22	-1.68	57.39	ClOOCl ( $C_2^{-1}A'$ ) <sup>h</sup>	148.94	4.19	-0.56	0.24	-2.12	142.30
Br <sub>2</sub> ( $D_{\infty h}^{-1}\Sigma_g^+$ )	51.56	0.46	0.02	0.47	-6.60	44.98	ClOClO ( $C_1^{-1}A'$ ) <sup>h</sup>	140.55	4.06	-0.68	0.43	-2.12	134.12
I <sub>2</sub> ( $D_{\infty h}^{-1}\Sigma_g^+$ )	47.97	0.31	0.00		-12.01	35.65	ClClO <sub>2</sub> ( $C_s^{-1}A'$ ) <sup>h</sup>	154.04	5.38	-1.39	0.57	-2.12	145.71
BrCl ( $C_{\infty v}^{-1}\Sigma^+$ )	56.00	0.63	-0.35	0.29	-4.14	51.17	BrOOBr ( $C_2^{-1}A'$ )	141.42	3.73	-0.43	0.47	-7.44	130.28
ICl ( $C_{\infty v}^{-1}\Sigma^+$ )	56.45	0.56	-0.15		-6.46	49.28	BrOBrO ( $C_1^{-1}A'$ )	134.27	3.45	-1.90	-0.26	-7.44	121.22
IBr ( $C_{\infty v}^{-1}\Sigma^+$ )	51.39	0.39	-0.28		-8.93	41.79	BrBrO <sub>2</sub> ( $C_s^{-1}A'$ )	137.79	4.07	-3.33	-1.12	-7.44	121.83
OCIO ( $C_{2v}^{-2}B_1$ ) <sup>h</sup>	127.51	3.61	-0.98	0.47	-1.28	122.10	IOOI ( $C_2^{-1}A'$ )	140.25	3.45	-0.34		-11.71	124.75
ClOCl ( $C_{2v}^{-1}A_1$ ) <sup>h</sup>	101.30	2.35	-0.45	0.24	-1.90	96.84	IOIO ( $C_1^{-1}A'$ )	146.00	3.20	-0.34		-11.89	130.58
ClClO ( $C_s^{-1}A'$ ) <sup>h</sup>	88.37	2.27	-0.53	0.27	-1.90	83.94	IIIO ( $C_s^{-1}A'$ )	150.44	3.51	-0.28		-12.76	133.89
ClClO ( $C_s^{-3}A''$ ) <sup>h</sup>	67.31	1.37	-0.31	0.22	-1.90	63.95	OIOI ( $C_2^{-1}A'$ )	120.25	2.72	-0.26		-10.96	106.31
OBrO ( $C_{2v}^{-2}B_1$ )	113.75	2.90	-2.73	-0.93	-3.94	103.24	ClOOBr ( $C_1^{-1}A'$ )	144.73	3.96	-0.34	0.33	-4.78	135.98
BrOBr ( $C_{2v}^{-1}A_1$ )	95.04	1.96	-0.70	0.39	-7.22	85.54	ClOBrO ( $C_1^{-1}A'$ )	136.73	3.65	-1.59	-0.32	-4.78	126.39
BrBrO ( $C_s^{-1}A'$ )	81.36	1.76	-1.07	0.04	-7.22	71.36	BrOCIO ( $C_1^{-1}A'$ )	136.69	3.88	-0.61	0.47	-4.78	127.88
BrBrO ( $C_s^{-3}A''$ )	63.99	1.28	-0.27	0.13	-7.22	55.35	ClBrO <sub>2</sub> ( $C_s^{-1}A'$ )	145.60	4.32	-3.65	-1.59	-4.78	131.26
BrBrO ( $C_s^{-3}A'$ )	59.70	1.31	-0.65	0.27	-7.22	50.79	BrClO <sub>2</sub> ( $C_s^{-1}A'$ )	143.82	5.09	-0.52	0.80	-4.78	134.23
OIO ( $C_{2v}^{-2}B_1$ )	121.76	2.65	-0.25		-4.81	114.05	ClOOI ( $C_1^{-1}A'$ )	144.32	3.81	-0.45		-6.41	133.64
IOI ( $C_{2v}^{-1}A_1$ )	96.29	1.73	-0.18		-11.47	82.90	ClOIO ( $C_1^{-1}A'$ )	147.23	3.48	-0.47		-6.69	136.60
IIO ( $C_s^{-1}A'$ )	84.89	1.53	-0.12		-12.21	71.03	IOClO ( $C_1^{-1}A'$ )	137.97	3.78	-0.78		-6.35	127.06
IIO ( $C_{\infty v}^{-3}\Sigma^-$ )	60.60	1.05	-0.11		-7.29	52.16	ClIO <sub>2</sub> ( $C_s^{-1}A'$ )	169.15	3.91	-0.38		-7.33	157.52
ClOBr ( $C_s^{-1}A'$ )	97.84	2.13	-0.42	0.30	-4.56	91.03	IClO <sub>2</sub> ( $C_s^{-1}A'$ )	137.35	4.81	-1.27		-6.13	125.14
ClBrO ( $C_s^{-1}A'$ )	87.04	1.94	-1.26	-0.32	-4.56	78.95	BrOOI ( $C_1^{-1}A'$ )	140.58	3.58	-0.70		-8.54	127.77
ClBrO ( $C_s^{-3}A''$ )	69.64	1.73	-0.07	-0.05	-4.56	63.22	BrOIO ( $C_1^{-1}A'$ )	144.71	3.28	-0.82		-8.77	131.84
ClBrO ( $C_s^{-3}A'$ )	59.71	1.16	-0.65	0.12	-4.56	53.45	IOBrO ( $C_1^{-1}A'$ )	134.41	3.36	-2.39		-8.54	120.12
BrClO ( $C_s^{-1}A'$ )	81.77	2.08	-0.09	0.48	-4.56	75.52	BrIO <sub>2</sub> ( $C_s^{-1}A'$ )	159.98	3.68	-0.30		-9.48	146.52
BrClO ( $C_s^{-3}A''$ )	60.47	1.49	-0.09	0.35	-4.56	54.68	IBrO <sub>2</sub> ( $C_s^{-1}A'$ )	128.25	3.87	-4.40		-8.69	111.28
BrClO ( $C_s^{-3}A'$ )	65.33	1.30	-0.19	0.24	-4.56	59.52	OIOBr ( $C_1^{-1}A'$ )	114.78	2.77	-1.67		-8.43	101.91
ClOI ( $C_s^{-1}A'$ )	98.52	2.03	-0.33		-6.30	89.86	HOOF ( $C_1^{-1}A'$ ) <sup>i,j</sup>	209.07	11.23	-0.27		-0.83	196.83
ClIO ( $C_s^{-1}A'$ )	98.53	1.83	-0.25		-6.61	89.84	HOOCI ( $C_1^{-1}A'$ ) <sup>j</sup>	208.65	10.54	-0.31	0.26	-1.28	196.39
ClIO ( $C_s^{-3}A''$ )	81.73	1.50	-0.25		-6.94	73.04	HOObBr ( $C_1^{-1}A'$ ) <sup>j</sup>	204.43	10.33	-0.46	0.37	-3.94	190.08
IClO ( $C_s^{-1}A'$ )	77.91	1.93	-0.48		-6.14	69.37	HOOI ( $C_1^{-1}A'$ )	203.23	10.12	-0.39		-7.68	185.04
BrOI ( $C_s^{-1}A'$ )	95.52	1.82	-0.69		-8.41	84.60							

<sup>a</sup> The atomic asymptotes were calculated with the R/UCCSD(T) method. <sup>b</sup> Extrapolated by using eq 1 with the awCVDZ, awCVTZ, and awCVQZ basis sets. <sup>c</sup> The zero point energies were taken as 0.5 the sum of the frequencies from CCSD(T) levels. <sup>d</sup> The scalar relativistic correction is based on a CCSD(T)-DK/VTZ-DK calculation and is expressed relative to the CCSD(T) result without the DK correction. <sup>e</sup> Core-valence corrections were obtained with the cc-pwCVTZ basis sets at the optimized CCSD(T)/aVTZ geometries. <sup>f</sup> Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's tables, ref 96. <sup>g</sup> The theoretical value of  $\Sigma D_0$  (0 K) was computed with the CBS (awCVnZ) estimates. <sup>h</sup> Reference 64. <sup>i</sup> Reference 92. <sup>j</sup> The total atomization energies were obtained by extrapolating the aVQZ and aV5Z values using the formula  $E(I_{\text{max}}) = E_{\text{CBS}} + B/I_{\text{max}}^3$ . Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. J. Chem. Phys., 1997, 106, 9639.

within a few  $\text{cm}^{-1}$ , of the experimental anharmonic values, measured in neon<sup>111</sup> and argon<sup>115</sup> matrices. The calculated harmonic gas-phase frequencies for OBrO and BrOBr are in excellent agreement with the reported anharmonic gas-phase values,<sup>117,119</sup> within  $35 \text{ cm}^{-1}$ . For BrBrO, there is excellent agreement between our calculated values and the argon matrix values.<sup>115,116</sup> The frequencies for OIO are in excellent agreement within  $20 \text{ cm}^{-1}$  with the available experimental values.<sup>122,123,127</sup> The harmonic frequencies for ClIO<sub>2</sub> are in excellent agreement with the available anharmonic experimental values from a matrix isolation study,<sup>125</sup> within  $9 \text{ cm}^{-1}$  for most bands. The only significant difference is for the third  $a'$  frequency mode (IO<sub>2</sub> scissors), which differs from the experimental value by  $135 \text{ cm}^{-1}$ . On the basis of the good agreement for the other bands, it is likely that the experimental value should be reassigned. The calculated harmonic frequencies for ClOBr,<sup>124</sup> ClBrO,<sup>124</sup> BrClO,<sup>124</sup> ClIO,<sup>125</sup> ClOBrO,<sup>126</sup> BrOCIO,<sup>126</sup> BrClO<sub>2</sub>,<sup>126</sup> IOClO,<sup>126</sup> and ICIO<sub>2</sub><sup>126</sup> show a similar excellent agreement with the experimental anharmonic values, within  $21 \text{ cm}^{-1}$  for a maximum discrepancy.

**Heats of Formation.** The energetic components for predicting  $\Sigma D_0$  are given in Table 1. The absolute values for the  $\Delta E_{\text{CV}}$  corrections are all less than 1 kcal/mol, except for BrBrO<sub>2</sub> and

ClBrO<sub>2</sub>, which are  $-1.12$  and  $-1.59 \text{ kcal/mol}$ , respectively. The  $\Delta E_{\text{SR}}$  corrections are in general larger than the  $\Delta E_{\text{CV}}$  corrections. When there is a substantial change in the oxidation state of the central atom in the molecule to the zero oxidation state of the atom,  $\Delta E_{\text{SR}}$  can be significant. The largest corrections are found when Br is the central atom in a high oxidation state. For example,  $\Delta E_{\text{SR}} = -2.73 \text{ kcal/mol}$  for OBrO with Br in the +4 oxidation state, and  $\Delta E_{\text{SR}} = -4.40$ ,  $-3.33$ , and  $-3.65 \text{ kcal/mol}$  for IBrO<sub>2</sub>, BrBrO<sub>2</sub>, and ClBrO<sub>2</sub>, respectively, with the central Br atom in the +5 oxidation state.

The results from the isodesmic reactions are presented in Table 2. The calculated heats of formation at 0 and 298 K are given in Table 3, and we use the values calculated at 298 K in our discussion below. Our calculated values for the diatomics are in good agreement with the experimental values,<sup>37-43</sup> considering the higher order corrections are 0.74, 0.99, and 1.36 kcal/mol for ClO, BrO, and IO, respectively.<sup>62</sup> Use of the higher order corrections with our calculated results would give almost identical results to those obtained previously.

For the triatomics, the calculated heats of formation of OCIO,<sup>38,46</sup> ClOCl,<sup>38</sup> OBrO,<sup>36,49</sup> BrOBr,<sup>36,48</sup> and OIO are within 1 kcal/mol of experiment,<sup>38</sup> if the most recent values of  $23.53 \pm 0.24$ ,<sup>46</sup>  $39.2 \pm 1.1$ ,<sup>49</sup> and  $28.1 \pm 0.5 \text{ kcal/mol}$ <sup>128</sup> are used for

**TABLE 2: Isodesmic Reactions for Calculating Heats of Formation of ClOO, BrOO, and IOO in kcal/mol**

isodesmic reactions	$\Delta E_{\text{CBS}}$		$\Delta E_{\text{ZPE}}$	$\Delta E_{\text{CV}}$	$\Delta E_{\text{SR}}$	$\Delta E_{\text{SO}}$	$\Delta E_{\text{Total}}$	
	(DTQ)	(Q5) <sup>a</sup>					(DTQ)	(Q5) <sup>a</sup>
HOOCI + FOO → HOOF + ClOO	9.40	8.21	0.10	0.20	−0.08	−0.02	9.59	8.40
HOObR + FOO → HOOF + BrOO	8.26	8.27	0.13	−0.06	−0.44	−0.42	7.46	4.47
HOOI + FOO → HOOF + IOO	−0.46		−0.20		−0.05	−3.78	−4.39	

<sup>a</sup> Table 1, footnote j.**TABLE 3: Calculated Heats of Formation (kcal/mol) at 0 and 298 K**

molecule	calcd (0 K)	calcd (298 K)	expt/calcd (298 K)	molecule	calcd (0 K)	calcd (298 K)	expt/calcd (298 K)
ClO ( $C_{\infty v}^{-2}\Pi$ )	24.8 <sup>a</sup>	24.8 <sup>a</sup>	24.29 ± 0.03 <sup>b</sup>	ClBrO ( $C_s^{-3}A''$ )	52.5	50.6	
			24.2 ± 0.3 <sup>c</sup>	ClBrO ( $C_s^{-3}A'$ )	62.3	60.4	
BrO ( $C_{\infty v}^{-2}\Pi$ )	32.6	30.8	29.5 ± 0.1 <sup>d</sup>	BrClO ( $C_s^{-1}A'$ )	40.2	38.1	42.8 calcd <sup>g</sup>
			30.2 ± 0.4 <sup>e</sup>	BrClO ( $C_s^{-3}A''$ )	61.1	59.0	
			29.9 ± 0.6 <sup>c</sup>	BrClO ( $C_s^{-3}A'$ )	56.2	54.1	
IO ( $C_{\infty v}^{-2}\Pi$ )	31.1	30.6	31 ± 3 <sup>f</sup>	ClOI ( $C_s^{-1}A'$ )	23.3	22.5	18.2 ± 2.4 calcd <sup>b,r</sup>
			29 ± 2 <sup>g</sup>	ClIO ( $C_s^{-1}A'$ )	23.3	22.7	
			28.8 ± 0.5 <sup>h</sup>	ClIO ( $C_s^{-3}A''$ )	40.2	39.2	
			29.9 ± 0.6 <sup>c</sup>	IClO ( $C_s^{-1}A'$ )	43.8	43.2	39.7 ± 2.4 calcd <sup>b,r</sup>
			28.9 calc. <sup>i</sup>	BrOI ( $C_s^{-1}A'$ )	28.2	25.6	
			29.2 <sup>+0.4</sup> −0.2 <sup>j</sup>	BrIO ( $C_s^{-1}A'$ )	32.0	29.2	
Cl <sub>2</sub> ( $D_{\infty h}^{-1}\Sigma_g^+$ )	−0.2 <sup>a</sup>	−0.2 <sup>a</sup>	0.0 <sup>k</sup>	BrIO ( $C_s^{-3}A''$ )	48.2	45.4	
Br <sub>2</sub> ( $D_{\infty h}^{-1}\Sigma_g^+$ )	11.4	7.9	7.39 ± 0.03 <sup>k</sup>	IBrO ( $C_s^{-1}A'$ )	48.8	46.0	
I <sub>2</sub> ( $D_{\infty h}^{-1}\Sigma_g^+$ )	15.6	14.8	14.92 ± 0.02 <sup>k</sup>	ClOOCl ( $C_2^{-1}A$ )	32.9 <sup>a</sup>	31.6 <sup>a</sup>	30.5 ± 0.7 <sup>b</sup>
BrCl ( $C_{\infty v}^{-1}\Sigma^+$ )	5.6	3.8	3.5 ± 0.3 <sup>k</sup>				31.3 ± 0.7 <sup>u</sup>
ICl ( $C_{\infty v}^{-1}\Sigma^+$ )	4.9	4.5	4.18 ± 0.03 <sup>k</sup>	ClOClO ( $C_1^{-1}A$ )	41.0 <sup>a</sup>	39.9 <sup>a</sup>	41.9 calcd <sup>b,v</sup>
IBr ( $C_{\infty v}^{-1}\Sigma^+$ )	12.0	9.9	9.77 ± 0.02 <sup>k</sup>	ClClO <sub>2</sub> ( $C_s^{-1}A'$ )	29.4 <sup>a</sup>	28.5 <sup>a</sup>	36.9 calcd <sup>b,v</sup>
OCIO ( $C_{2v}^{-2}B_1$ )	24.5 <sup>a</sup>	23.9 <sup>a</sup>	22.6 ± 0.3 <sup>b</sup>	BrOOBr ( $C_2^{-1}A$ )	44.1	39.7	41 ± 1 calcd <sup>p</sup>
			23.53 ± 0.24 <sup>l</sup>	BrOBrO ( $C_1^{-1}A$ )	53.1	49.0	51 ± 4 calcd <sup>p</sup>
ClOO ( $C_s^{-2}A''$ )	25.3	25.1	23.4 ± 1.0 <sup>m</sup>	BrBrO <sub>2</sub> ( $C_s^{-1}A'$ )	52.5	48.2	51 ± 6 calcd <sup>p</sup>
			24.30 ± 0.32 calcd <sup>n</sup>	IOOI ( $C_2^{-1}A$ )	4.5	42.5	37.5 ± 4 calcd <sup>b,r</sup>
ClOCl ( $C_{2v}^{-1}A_1$ )	19.3 <sup>a</sup>	18.9 <sup>a</sup>	19.4 ± 0.4 <sup>b</sup>				43.0 ± 2.2 calc <sup>s</sup>
ClClO ( $C_s^{-1}A'$ )	32.2 <sup>a</sup>	31.9 <sup>a</sup>	22 ± 7 <sup>b</sup>	IOIO ( $C_1^{-1}A$ )	38.6	36.4	29.7 ± 4 calcd <sup>b,r</sup>
ClClO ( $C_s^{-3}A''$ )	52.2 <sup>a</sup>	52.4 <sup>a</sup>					33.8 ± 2.2 <sup>s</sup>
OBRO ( $C_{2v}^{-2}B_1$ )	42.9	40.6	39.2 ± 1.1 <sup>o</sup>	IIO <sub>2</sub> ( $C_s^{-1}A'$ )	35.3	33.1	24.6 ± 4 calcd <sup>b,r</sup>
			36 ± 6 est <sup>k</sup>				37.7 ± 2.2 <sup>s</sup>
			30 ± 3 calcd <sup>p</sup>	OIO ( $C_2^{-1}A$ )	62.9	62.0	53.5 ± 4 calcd <sup>b,r</sup>
BrOO ( $C_s^{-2}A''$ )	30.9	28.9	26 ± 10 <sup>o</sup>	ClOOBr ( $C_1^{-1}A$ )	38.8	36.2	
			26 ± 1 calcd <sup>p</sup>	ClOBrO ( $C_1^{-1}A$ )	48.4	46.0	
BrOBr ( $C_{2v}^{-1}A_1$ )	29.8	25.9	25.7 ± 0.8 <sup>o</sup>	BrOCIO ( $C_1^{-1}A$ )	46.9	44.5	
			29.1 calcd <sup>q</sup>	ClBrO <sub>2</sub> ( $C_s^{-1}A'$ )	43.5	40.9	
BrBrO ( $C_s^{-1}A'$ )	44.0	40.2	43.7 calcd <sup>q</sup>	BrClO <sub>2</sub> ( $C_s^{-1}A'$ )	40.5	37.8	
BrBrO ( $C_s^{-3}A''$ )	60.0	56.4	40 ± 5 est <sup>o</sup>	ClOOI ( $C_1^{-1}A$ )	38.5	36.9	30.0 ± 2.4 calcd <sup>b,r</sup>
BrBrO ( $C_s^{-3}A'$ )	64.6	60.1		ClOIO ( $C_1^{-1}A$ )	35.6	34.2	25.6 ± 2.4 calcd <sup>b,r</sup>
OIO ( $C_{2v}^{-2}B_1$ )	29.5	28.6	18 ± 4 calcd <sup>b,r</sup>	IOClO ( $C_1^{-1}A$ )	45.1	43.6	36.7 ± 2.4 calcd <sup>b,r</sup>
			38 ± 6 est <sup>k</sup>	ClIO <sub>2</sub> ( $C_s^{-1}A'$ )	14.7	13.6	2.6 ± 2.4 calcd <sup>b,r</sup>
			26.3 ± 2.2 <sup>s</sup>	IClO <sub>2</sub> ( $C_s^{-1}A'$ )	47.0	45.8	44.9 ± 2.4 calcd <sup>b,r</sup>
			28.5 calcd <sup>i</sup>	BrOOI ( $C_1^{-1}A$ )	44.0	40.6	
			28.1 ± 0.5 <sup>f</sup>	BrOIO ( $C_1^{-1}A$ )	39.9	36.4	
IOO ( $C_s^{-2}A''$ )	21.2	20.9	23 ± 4 calcd <sup>b,r</sup>	IOBrO ( $C_1^{-1}A$ )	51.7	48.4	
			28 ± 10 est <sup>k</sup>	BrIO <sub>2</sub> ( $C_s^{-1}A'$ )	25.3	22.1	
			23.6 calcd <sup>i</sup>	IBrO <sub>2</sub> ( $C_s^{-1}A'$ )	60.5	57.3	
IOI ( $C_{2v}^{-1}A_1$ )	27.3	25.7	22 ± 4 calcd <sup>b,r</sup>	OIBrO ( $C_1^{-1}A$ )	69.9	65.4	
			29 ± 6 est <sup>k</sup>	HOOF ( $C_1^{-1}A$ )	−8.8 <sup>w</sup>	−10.2 <sup>w</sup>	
IIO ( $C_s^{-1}A'$ )	39.2	37.8	32 ± 4 calcd <sup>b,r</sup>	HOOCI ( $C_1^{-1}A$ )	1.4	0.1	
IIO ( $C_{\infty v}^{-3}\Sigma^-$ )	58.1	56.0	26 ± 10 est <sup>b,r</sup>	HOObR ( $C_1^{-1}A$ )	7.7	4.7	
ClOBr ( $C_s^{-1}A'$ )	24.7	22.5	24.6 calcd <sup>q</sup>	HOOI ( $C_1^{-1}A$ )	10.2	8.6	
ClBrO ( $C_s^{-1}A'$ )	36.8	34.7	36.1 calcd <sup>q</sup>				

<sup>a</sup> Reference 64. <sup>b</sup> Reference 35. <sup>c</sup> Reference 62. <sup>d</sup> Reference 39. <sup>e</sup> Reference 40. <sup>f</sup> Reference 41. <sup>g</sup> Reference 42. <sup>h</sup> Reference 43. <sup>i</sup> Reference 78.  $\Delta H_f^{298}(\text{OIO})$  and  $\Delta H_f^{298}(\text{IOO})$  were obtained from the 0 K values in the reference plus our 0 to 298 K calculated temperature correction. <sup>j</sup> Reference 44. <sup>k</sup> Reference 37. <sup>l</sup> Reference 46. <sup>m</sup> Reference 45. <sup>n</sup> Reference 65. <sup>o</sup> Reference 36. <sup>p</sup> Reference 71. <sup>q</sup> Reference 70. <sup>r</sup> Reference 76. <sup>s</sup> Reference 77. <sup>t</sup> Reference 128. Calculated from the 0 K value of 29.18 ± 0.48 kcal/mol plus our 0 to 298 K calculated temperature correction. <sup>u</sup> Reference 47. <sup>v</sup> Reference 67. Estimated from calculated values and  $\Delta H_f$  (ClOOCl). <sup>w</sup> Reference 92.

OCIO, OBrO, and OIO, respectively. The calculated heat of formation of ClOO is in excellent agreement with the experimental value,<sup>45</sup> differing by 1.7 kcal/mol, just outside the ±1.5 kcal/mol error bar expected for XOO, and is in very good agreement with Martin and co-workers' value<sup>65</sup> of 24.30 ± 0.32

kcal/mol from W4 calculations. Our calculated value for ClClO differs from the experimental value,<sup>38</sup> outside the ±7 kcal/mol error bar. The calculated heat of formation of BrOO is 2.9 kcal/mol higher than the estimated experimental value,<sup>36,71</sup> within the ±7 kcal/mol error bar, and we expect our value for BrOO

to be good to  $\pm 1.5$  kcal/mol. Our calculated value for  $\Delta H_f^{298K}(\text{BrOO})$  is also in good agreement with a lower level theoretical value from CCSD(T)/AREP/TZ(2df) calculations.<sup>71</sup> Our calculated values for BrBrO, IOO, and the I<sub>2</sub>O isomers show larger differences compared to the estimated experimental and previous calculated (modified G2) values.<sup>36,70,76,77</sup> Our calculated value for  $\Delta H_f^{298K}(\text{IOO})$  differs from that of Peterson<sup>78</sup> by 2.7 kcal/mol. This difference is most likely due to the fact that the multireference character in IOO is substantially larger than that in the other XO compounds so that this additional contribution could be missed by our isodesmic approach. There may also be some error in the spin-orbit correction.

Looking further into other thermodynamic properties of the triatomics, the singlet-triplet (S-T) splitting of BrBrO is 16.2 kcal/mol compared to that of 20.5 kcal/mol for ClClO. The S-T splitting of IIO increases slightly by 2 kcal/mol to a value of 18.2 kcal/mol compared to that of BrBrO. The S-T splitting of ClBrO is 15.9 kcal/mol, essentially the same as that of BrBrO, indicating a minimal effect of Cl on the S-T splitting. Similarly, the S-T splitting of BrClO is 20.9 kcal/mol, essentially the same as that of ClClO. The S-T splittings of ClIO and BrIO are 16.5 and 16.2 kcal/mol, respectively, slightly lower than that of IIO and more like that in ClBrO.

We have previously shown that the calculated value<sup>64</sup> for ClOOCl is in excellent agreement within 0.3 kcal/mol of the experimental value of  $31.3 \pm 0.7$  kcal/mol from Cox and Hayman and the recent photoionization study<sup>129,130</sup> and is 1.1 kcal/mol higher than the previous value of  $30.5 \pm 0.7$  kcal/mol.<sup>131</sup> We predict that ClClO<sub>2</sub> is 3.1 kcal/mol more stable than ClOOCl. The ClOCIO isomer is predicted to be 11.4 kcal/mol above ClClO<sub>2</sub>.<sup>64</sup> Lower level B3LYP/DZP++ calculations<sup>66</sup> predict that the ClOOCl isomer is the most stable with the ClClO<sub>2</sub> and ClOCIO isomers much higher in energy, a result clearly contradicted by the current higher level CCSD(T)/CBS results.

Our calculated heats of formation of the Br<sub>2</sub>O<sub>2</sub> isomers are in good agreement with those from lower level (CCSD(T)/AREP/TZ(2df)) calculations,<sup>71</sup> and we prefer our more reliable calculations that should be good to  $\pm 1$  kcal/mol for all of the compounds except for XO with error bars of  $\pm 1.5$  kcal/mol. Compared to the Cl<sub>2</sub>O<sub>2</sub> isomers, the Br<sub>2</sub>O<sub>2</sub> isomers have a different stability pattern with BrOOBr predicted to be the most stable, BrBrO<sub>2</sub> the next most stable, 8.5 kcal/mol higher in energy, and BrOBrO the least stable isomer, 9.3 kcal/mol above BrOOBr.

The heats of formation of the IIO<sub>2</sub> isomers have been reported using G2 energies coupled with isodesmic reactions.<sup>76,77</sup> Our higher level CCSD(T)/CBS values differ largely by as much as 9 kcal/mol, and we prefer our more reliable calculations. For the I<sub>2</sub>O<sub>2</sub> isomers, IIO<sub>2</sub> is predicted to be the most stable isomer with IOIO 3.3 kcal/mol higher in energy and the peroxide isomer IOOI 9.4 kcal/mol above IIO<sub>2</sub>.

For the XXO<sub>2</sub> isomers (X = Cl, Br, and I), an additional isomer of the form OXXO should be considered. For X = Cl and Br, the complex dissociates to the respective XO diatomic molecules at the highest level of optimization performed (CCSD(T)/aVTZ). However for X = I, the OIIO isomer was predicted to be a metastable species with an I-I bond length of 2.921 Å at the CCSD(T)/aVTZ level. The  $r(\text{IO})$  distance in OIIO is predicted to be 0.044 Å shorter than that of IO (<sup>2</sup>Π) while the  $r(\text{II})$  distance is predicted to be 0.216 Å longer than that of I<sub>2</sub> (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) at the CCSD(T)/aVTZ level. OIIO is characterized by all real harmonic frequencies at the CCSD(T)/aVTZ

**TABLE 4: Relative Stabilities of the XXO<sub>2</sub> and XYO<sub>2</sub> (X, Y = Cl, Br, I) Isomers in kcal/mol at 298 K**

X, Y	XYO <sub>2</sub>	YXO <sub>2</sub>	XOOY	XOYO	YOXO
Cl, Cl <sup>a</sup>	0.0		3.1	11.5	
Cl, Br	4.7	1.6	0.0	9.8	8.3
Cl, I	0.0	32.2	23.3	20.6	30.0
Br, Br	8.5		0.0	9.3	
Br, I	0.0	35.2	18.6	14.3	26.4
I, I	0.0		9.3	3.3	

<sup>a</sup> Reference 64.

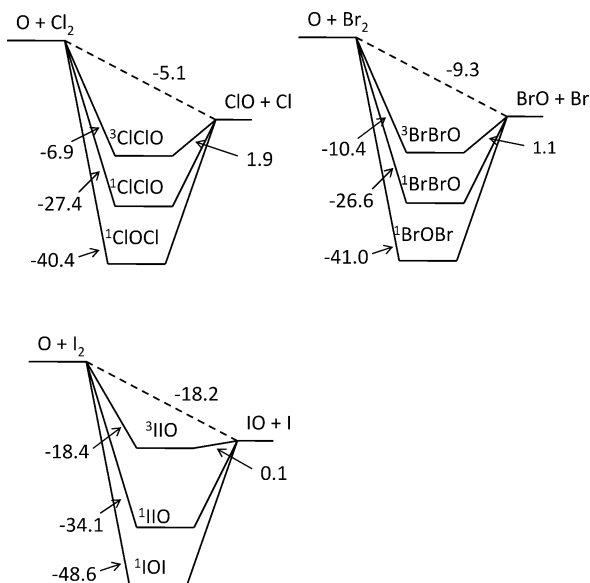
level. OIIO is predicted to be the least stable isomer lying 28.9 kcal/mol higher in energy than IIO<sub>2</sub>.

For the mixed halogen isomers, XYO<sub>2</sub>, we predict that ClOOBr is the most stable isomer for X = Cl, Y = Br with BrClO<sub>2</sub> only 1.6 kcal/mol higher in energy. The ClBrO<sub>2</sub> isomer is only 4.7 kcal/mol above ClOOBr. The BrOCIO and ClOBrO isomers are predicted to be the least stable isomers, 8.3 and 9.8 kcal/mol less stable than ClOOBr, respectively. Thus, the relative energies of these isomers are like that of Br<sub>2</sub>O<sub>2</sub>.

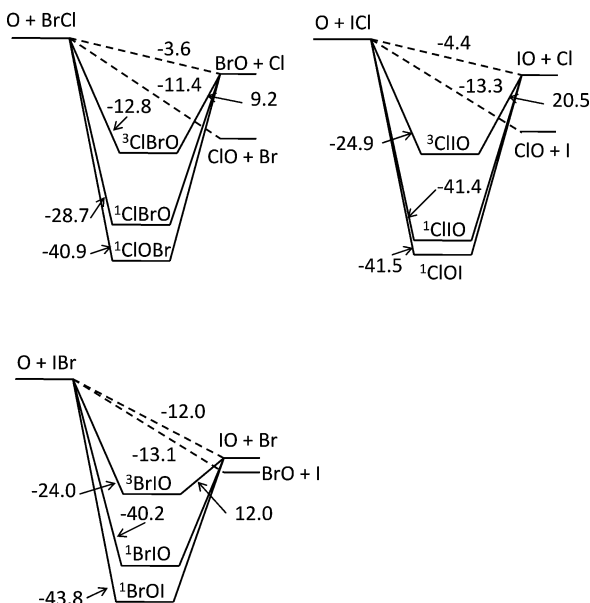
The heats of formation of the ICIO<sub>2</sub> isomers have been reported in the NASA tables,<sup>35</sup> and are actually “corrected” values based on the heats of formation of the I<sub>2</sub>O<sub>2</sub> isomers that were derived using an approximate QCISD(T)/6-311+G(3df) (G2) method coupled with isodesmic reactions.<sup>76</sup> Our CCSD(T)/CBS values differ largely from these “corrected” calculated values, and we prefer our more reliable calculations. The relative stabilities for the X = Cl, Y = I isomers are considerably different than those of the X = Cl, Y = Br isomers. ClIO<sub>2</sub> is the most stable isomer with the ICIO<sub>2</sub> isomer 32.2 kcal/mol higher in energy. Thus, the least electronegative I atom wants to be in the highest oxidation state position. The ClOIO, ClOOI, and IOClO isomers are 20.6, 23.3, and 30.0 kcal/mol higher in energy than ClIO<sub>2</sub>, respectively. The relative energy orderings of the BrIO<sub>2</sub> isomers are the same as those of the ClIO<sub>2</sub> isomers, except that the actual numerical values are different. BrIO<sub>2</sub> is predicted to be the most stable isomer with the BrOIO isomer lying 14.3 kcal/mol higher in energy as compared to the energy difference of 20.6 kcal/mol between ClIO<sub>2</sub> and ClOIO. For both the X = Cl, Y = I and X = Br, Y = I isomers, the next most stable isomer has the I atom in the highest oxidation state position, XOIO. Similarly as found for OIIO, OIBrO is predicted to be a metastable species with an I-Br bond length of 2.841 Å, 0.338 Å longer than that of IBr (<sup>1</sup>Σ<sup>+</sup>) at the CCSD(T)/aVTZ level. The  $r(\text{IO})$  and  $r(\text{BrO})$  distances are predicted to be 0.044 and 0.036 Å shorter than those of IO (<sup>2</sup>Π) and BrO (<sup>2</sup>Π) at the same level, respectively. OIBrO is characterized by all real harmonic frequencies at the CCSD(T)/aVTZ level. OIBrO is predicted to be the least stable isomer lying 44.1 kcal/mol higher in energy than BrIO<sub>2</sub>.

**Bond Dissociation Energies (BDEs).** The adiabatic BDEs at 298 K are presented in Table 4, and the stability of various species is summarized in Figures 1–4. There is a proportional decrease in the BDEs of X<sub>2</sub> (X = Cl, Br, I) with a decrease in the electronegativity of the halogen down the group. Considering the XO (X = Cl, Br, I) diatomics, the Cl-O BDE is larger than that of Br-O by 7.8 kcal/mol, and that of I-O is larger and within 1 kcal/mol of that of Br-O. The BDE of ICl is slightly lower than that of Cl<sub>2</sub> by 8 kcal/mol, and that of IBr is essentially the same as that of Br<sub>2</sub>, indicating the effect of I on the respective BDEs.

The <sup>3</sup>A'' state of ClClO is 6.9 kcal/mol below the reactant O(<sup>3</sup>P) + Cl<sub>2</sub> and 1.9 kcal/mol below the product state ClO + Cl, consistent with the observation of a weak complex in



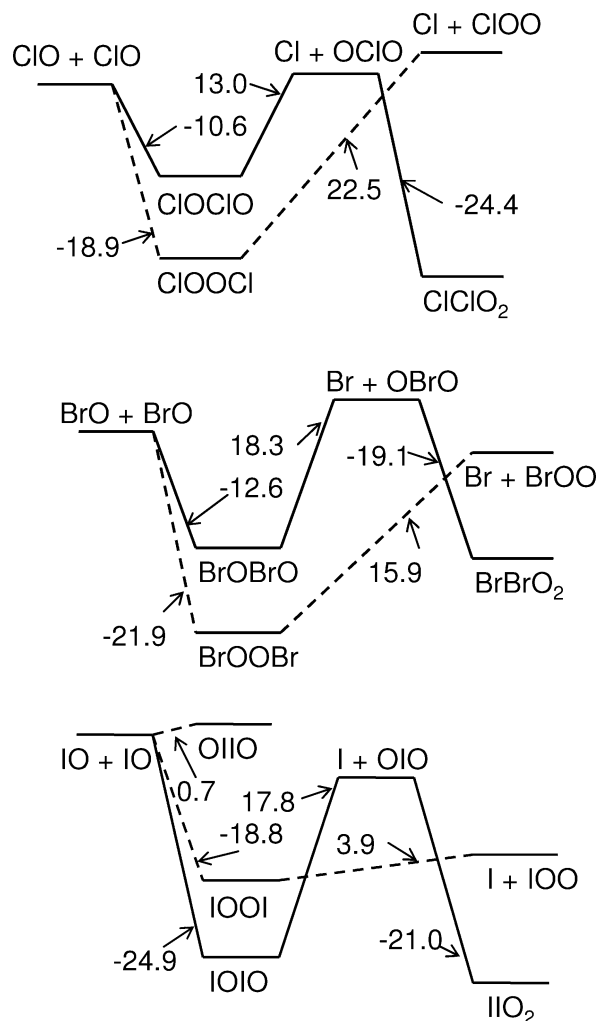
**Figure 1.** Energy profiles for the  $O + X_2$  ( $X = \text{Cl, Br, I}$ ) reactions in kcal/mol at 298 K. Energies are the energy differences between different species.



**Figure 2.** Energy profiles for the  $O + XY$  ( $X, Y = \text{Cl, Br, I}$ ) reactions in kcal/mol at 298 K. Energies are the energy differences between different species.

molecular beam scattering experiments.<sup>54,57</sup> The singlet state of ClCIO is predicted to have much higher BDEs. The  $^3A''$  states of BrBrO and IIO are 10.4 and 18.4 kcal/mol below the reactant  $O(^3P) + X_2$  ( $X = \text{Br, I}$ ) and 1.1 and 0.1 kcal/mol below the product state  $XO + X$  ( $X = \text{Br, I}$ ), respectively, similarly consistent with the observation of a weak complex in molecular beam scattering experiments<sup>55,56</sup> and as found for ClCIO. The singlet states of BrBrO and IIO also have much higher BDEs. The BrO–O BDEs are predicted to be 64.8 and 59.0 kcal/mol at the BP86/DZP++ and BLYP/DZP++ levels, respectively, in reasonable agreement with our CCSD(T)/CBS value.<sup>73</sup>

The  $^3A''$  state of ClBrO is the least stable isomer with respect to bond breaking and is 12.8 kcal/mol below the reactant  $O(^3P) + \text{BrCl}$  and 9.2 kcal/mol below the product state  $\text{BrO} + \text{Cl}$ . The  $^1A'$  state of ClBrO is predicted to have much higher BDEs than the triplet state. The lowest BDE in ClOBr is for breaking



**Figure 3.** Energy profiles for the  $XO + XO$  ( $X = \text{Cl, Br, I}$ ) reactions in kcal/mol at 298 K. Energies are the energy differences between different species.

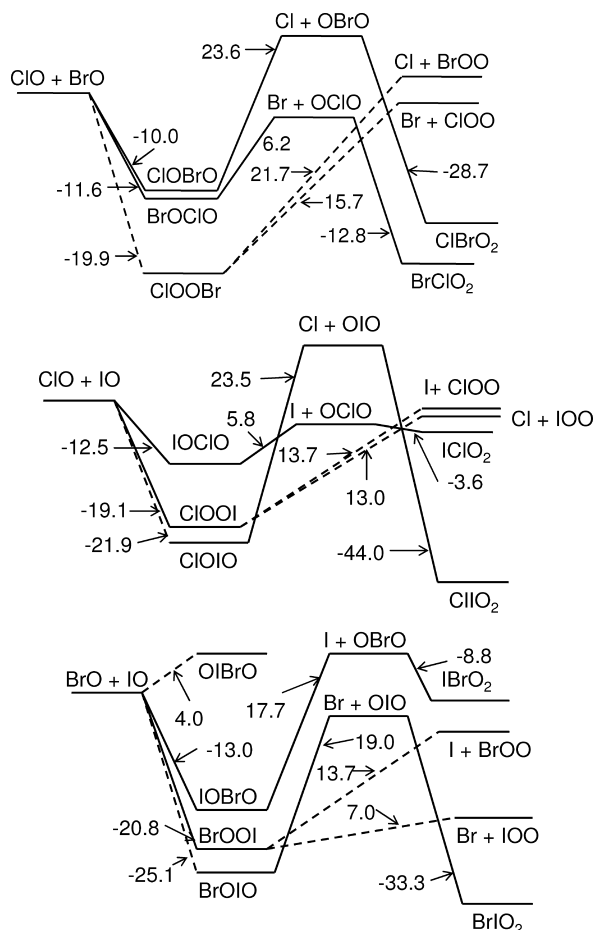
the O–Br bond with the  $\text{BrO} + \text{Cl}$  pathway lying 7.8 kcal/mol higher in energy. Compared to ClBrO ( $^1A'$ ), BrClO ( $^1A'$ ) is less stable with respect to bond breaking, indicating a preference for having the least electronegative halogen in the central bonding position.

ClCIO ( $^1A'$ ) is the least stable isomer with respect to bond breaking and is expected to fragment by breaking the I–Cl bond. The  $^3A''$  state of ClIO is 24.9 kcal/mol below the reactant  $O(^3P) + \text{ICl}$  and 20.5 kcal/mol below the product state  $\text{IO} + \text{Cl}$ . The  $^1A'$  state of ClIO has much higher BDEs. Similarly as found for ClOBr, the lowest BDE of ClOI is for breaking the O–I bond with the  $\text{IO} + \text{Cl}$  pathway 8.9 kcal/mol higher in energy.

Similarly as found for the chlorine–iodine triatomic isomers, IBrO ( $^1A'$ ) is the least stable with respect to bond breaking followed by the  $^3A''$  state of BrIO. The  $^3A''$  state of BrIO is 24.0 kcal/mol below the reactant  $O(^3P) + \text{IBr}$  and 13.7 kcal/mol below the product state  $\text{IO} + \text{Br}$ . The singlet state of BrIO has much higher BDEs. For BrOI, the lowest BDE is for breaking the O–Br bond with the O–I BDE being slightly higher in energy by 1 kcal/mol.

The BDEs show that ClCIO<sub>2</sub> is more stable with respect to bond breaking than ClOOCl. In ClOOCl, the lowest BDE is the central O–O bond whereas in ClCIO<sub>2</sub>, the weakest BDE is for the Cl–Cl bond. The Cl–O BDE in ClOOCl is slightly higher than the O–O BDE. ClOCIO is expected to fragment by breaking the central O–Cl bond.





**Figure 4.** Energy profiles for the  $XO + YO$  ( $X, Y = \text{Cl, Br, I}$ ) reactions in kcal/mol at 298 K. Energies are the energy differences between different species.

Similarly as found for the analogous chlorine isomers, the BDEs show that  $\text{BrBrO}_2$  and  $\text{IIO}_2$  are more stable with respect to bond breaking than  $\text{BrOOBr}$  and  $\text{IOOI}$ , respectively. However, unlike  $\text{ClOOCl}$ , the lowest BDE in  $\text{BrOOBr}$  and  $\text{IOOI}$  is for breaking the terminal  $\text{O}-\text{X}$  ( $X = \text{Br, I}$ ) bond as opposed to the central  $\text{O}-\text{O}$  bond. The  $\text{BrO}-\text{OBr}$  BDE was predicted<sup>72</sup> using several DFT functionals with a DZP++ basis set, and the B3LYP value of 20.7 kcal/mol shows the best agreement with our CCSD(T)/CBS value.  $\text{BrOBrO}$  is expected to fragment by breaking the central  $\text{O}-\text{Br}$  bond as found for  $\text{ClOCIO}$  while for  $\text{IOIO}$ , fragmentation is expected to occur by breaking the terminal  $\text{O}-\text{I}$  bond with the pathway for breaking the central  $\text{O}-\text{I}$  bond lying 5.9 kcal/mol higher in energy. For  $\text{OIIO}$ , fragmentation is expected to occur by breaking the central  $\text{I}-\text{I}$  bond with  $\text{OIIO}$  predicted to be above the products  $\text{IO} + \text{IO}$  by 0.7 kcal/mol so  $\text{OIIO}$  is a metastable species. The other pathway for breaking the terminal  $\text{I}-\text{O}$  bond and producing  $\text{IIO} (^1\text{A}') + \text{O}$  is predicted to be 36.1 kcal/mol higher in energy.

We now consider the BDEs of the mixed halogen isomers. The BDEs show that  $\text{ClBrO}_2$  is more stable with respect to bond breaking than is  $\text{ClOOBr}$  and  $\text{BrClO}_2$ . In  $\text{ClOOBr}$ , the weakest BDE is not for breaking the central  $\text{O}-\text{O}$  bond, as found in  $\text{ClOOCl}$ , but for breaking the terminal  $\text{O}-\text{Br}$  bond, as found in  $\text{BrOOBr}$ . The  $\text{ClOO} + \text{Br}$  pathway is favored by 4.2 kcal/mol compared to the  $\text{ClO} + \text{BrO}$  pathway. In  $\text{ClOBrO}$ , the lowest BDE is for breaking the central  $\text{O}-\text{Br}$  bond followed by the terminal  $\text{O}-\text{Cl}$  bond, which is 13.5 kcal/mol higher in energy. Unlike  $\text{ClOBrO}$ , the lowest BDE in  $\text{BrOCIO}$  is for breaking the terminal  $\text{O}-\text{Br}$  bond and forming  $\text{OCIO}$  with the

$\text{ClO} + \text{BrO}$  pathway lying 5.4 kcal/mol higher in energy. On comparison of  $\text{ClBrO}_2$  versus  $\text{BrClO}_2$  and  $\text{ClOBrO}$  versus  $\text{BrOCIO}$ , the most stable isomer with respect to bond breaking has the least electronegative element as the central atom.

Considering the mixed chlorine–iodine systems, the BDEs show that  $\text{ClIO}_2$  is the most stable isomer with respect to bond breaking whereas  $\text{IClO}_2$  is the least stable. In  $\text{ClOOI}$ , the weakest BDE is for breaking the  $\text{O}-\text{Cl}$  bond leading to the  $\text{IOO}$  product with the  $\text{ClOO} + \text{I}$  pathway lying less than a kcal/mol higher in energy. Similarly as found for  $\text{ClOOBr}$ , the most stable pathway is for breaking the central  $\text{O}-\text{O}$  bond and forming  $\text{ClO} + \text{IO}$ . In  $\text{ClOIO}$ , the lowest BDE is for breaking the central  $\text{O}-\text{I}$  bond with the terminal  $\text{O}-\text{Cl}$  BDE predicted to be 1.8 kcal/mol higher in energy. Similarly as found for  $\text{BrOCIO}$ , the lowest BDE of  $\text{IOClO}$  is for forming  $\text{OCIO}$  and breaking the terminal  $\text{O}-\text{I}$  bond. The pathway forming  $\text{ClO} + \text{IO}$  is predicted to be higher in energy by 6.5 kcal/mol.

Considering the bromine–iodine mixed systems, the BDEs show that  $\text{BrIO}_2$  is the most stable isomer with respect to bond breaking followed by  $\text{BrOIO}$ , whereas  $\text{BrOOI}$  and  $\text{OIBrO}$  are the least stable isomers. In  $\text{BrOOI}$ , the weakest BDE is for breaking the terminal  $\text{O}-\text{Br}$  followed by the terminal  $\text{O}-\text{I}$  bond, which is predicted to be 6.7 kcal/mol higher in energy. Similarly as found in  $\text{ClOOI}$ , the most stable bond in  $\text{BrOOI}$  is the central  $\text{O}-\text{O}$  bond. In  $\text{BrOIO}$ , the lowest BDE is for breaking the terminal  $\text{O}-\text{Br}$  bond with the pathway forming  $\text{BrO} + \text{IO}$  predicted to be 6.1 kcal/mol higher in energy. The  $\text{IOBrO}$  isomer is less stable with respect to bond breaking compared to the  $\text{BrOIO}$  isomer. However unlike  $\text{BrOCIO}$  and  $\text{IOClO}$ , the lowest BDE in  $\text{IOBrO}$  is for breaking the central  $\text{O}-\text{Br}$  bond forming  $\text{BrO} + \text{IO}$  as opposed to the terminal  $\text{O}-\text{I}$  bond. The pathway forming  $\text{OBrO} + \text{I}$  is 4.7 kcal/mol higher in energy. Fragmentation of  $\text{OIBrO}$  is expected to occur by breaking the central  $\text{I}-\text{Br}$  bond with  $\text{OIBrO}$  predicted to be above the products  $\text{IO} + \text{BrO}$  by 4.7 kcal/mol so  $\text{OIBrO}$  is also a metastable species. The pathways for breaking the terminal  $\text{I}-\text{O}$  and  $\text{Br}-\text{O}$  bonds are essentially the same, within 1 kcal/mol, and are  $\sim 44$  kcal/mol higher in energy.

Of additional interest is a comparison of the  $\text{O}-\text{O}$  and  $\text{X}-\text{O}(\text{Y}-\text{O})$  BDEs in  $\text{XOOY}$ . The  $\text{O}-\text{O}$  BDEs are approximately 20 kcal/mol, ranging from 18 to 22 kcal/mol with the BDE for  $\text{BrOOBr}$  being the largest and that for  $\text{ClOOCl}$  being the lowest. Except for  $\text{ClOOCl}$ , the  $\text{O}-\text{O}$  BDEs are greater than the  $\text{X}-\text{O}(\text{Y}-\text{O})$  BDEs in these compounds. The  $\text{X}-\text{O}(\text{Y}-\text{O})$  BDEs show a larger variation from a low of 5 kcal/mol for  $\text{IOOI}$  to a high of 22 kcal/mol for  $\text{ClOOCl}$ . The remaining  $\text{X}-\text{O}$  BDEs fall in between these two values, and it does not always follow that the  $\text{X}$  with the highest atomic number has the weakest BDE as the  $\text{I}-\text{O}$  BDE in  $\text{IOOBr}$  is greater than the  $\text{Br}-\text{O}$  BDE and in  $\text{IOOCl}$  the  $\text{I}-\text{O}$  BDE is just above the  $\text{Cl}-\text{O}$  BDE. In the upper atmosphere, these  $\text{XOOY}$  compounds can be photolyzed leading to bond breaking and radical formation. The absorption spectra<sup>35</sup> for these compounds are of substantially higher energy than the BDEs, so dynamical processes<sup>132</sup> play an important role in determining which radicals are formed under atmospheric photolysis conditions and one cannot just examine the relative bond energies to determine if  $\text{X}$  or  $\text{OX}$  radicals are predominantly formed. In fact, for  $\text{ClOOCl}$ , experimental results show that the stronger  $\text{Cl}-\text{O}$  bond is preferentially photolyzed.<sup>132,133</sup>

**Insight into Halogen Oxide Self-Reactions.** The self-reactions of halogen oxides are interesting reactions not only from the standpoint of their significant role in ozone depletion reactions but also from the fundamental perspective that these

**TABLE 5: Adiabatic Bond Dissociation Energies (BDE) in kcal/mol at 298 K**

molecule	product	BDE	molecule	product	BDE
Cl <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	Cl + Cl	58.0 <sup>a</sup>		ClOCl + O	38.6 <sup>a</sup>
Br <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	Br + Br	46.2	ClClO <sub>2</sub> ( <sup>1</sup> A')	OCIO + Cl	24.4 <sup>a</sup>
I <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	I + I	36.2		ClClO + O	63.0 <sup>a</sup>
ClO ( <sup>2</sup> Π)	Cl + O	63.5 <sup>a</sup>	BrOOBr ( <sup>1</sup> A)	BrO + BrO	21.9
BrO ( <sup>2</sup> Π)	Br + O	55.5		BrOO + Br	15.9
IO ( <sup>2</sup> Π)	I + O	54.4	BrOBrO ( <sup>1</sup> A)	BrO + BrO	12.6
BrCl ( <sup>1</sup> Σ <sup>+</sup> )	Br + Cl	51.9		OBrO + Br	18.3
ICl ( <sup>1</sup> Σ <sup>+</sup> )	I + Cl	50.0		BrOBr + O	36.4
IBr ( <sup>1</sup> Σ <sup>+</sup> )	I + Br	45.9	BrBrO <sub>2</sub> ( <sup>1</sup> A')	OBrO + Br	19.1
ClOO ( <sup>2</sup> A'')	Cl + O <sub>2</sub>	3.9		BrBrO + O	51.6
	ClO + O	59.2	IOOI ( <sup>1</sup> A)	IO + IO	18.8
OCIO ( <sup>2</sup> B <sub>1</sub> )	ClO + O	60.4 <sup>a</sup>		IOO + I	5.2
ClOCl ( <sup>1</sup> A <sub>1</sub> )	ClO + Cl	34.9 <sup>a</sup>	IOIO ( <sup>1</sup> A)	IO + IO	24.9
ClClO ( <sup>1</sup> A')	Cl <sub>2</sub> + O	27.6 <sup>a</sup>		OIO + I	19.0
	ClO + Cl	21.9 <sup>a</sup>		IOI + O	48.9
ClClO ( <sup>3</sup> A'')	Cl <sub>2</sub> + O	7.2 <sup>a</sup>	IIO <sub>2</sub> ( <sup>1</sup> A')	OIO + I	22.2
	ClO + Cl	1.4 <sup>a</sup>		IIO + O	64.2
BrOO ( <sup>2</sup> A'')	Br + O <sub>2</sub>	-2.1	OIIO ( <sup>1</sup> A)	IIO + O	35.4
	BrO + O	61.5		IO + IO	-0.7
OBrO ( <sup>2</sup> B <sub>1</sub> )	O + BrO	49.7	ClOOBr ( <sup>1</sup> A)	ClO + BrO	19.9
BrOBr ( <sup>1</sup> A <sub>1</sub> )	BrO + Br	31.7		BrOO + Cl	21.7
BrBrO ( <sup>1</sup> A')	Br <sub>2</sub> + O	26.6		ClOO + Br	15.7
	BrO + Br	17.3	ClOBrO ( <sup>1</sup> A)	ClO + BrO	10.1
BrBrO ( <sup>3</sup> A'')	Br <sub>2</sub> + O	10.4		OBrO + Cl	23.6
	BrO + Br	1.1		ClOBr + O	36.1
IOO ( <sup>2</sup> A'')	O <sub>2</sub> + I	4.6	BrOCIO ( <sup>1</sup> A)	ClO + BrO	11.6
	IO + O	69.3		OCIO + Br	6.2
OIO ( <sup>2</sup> B <sub>1</sub> )	IO + O	61.5		ClOBr + O	37.6
IOI ( <sup>1</sup> A <sub>1</sub> )	IO + I	30.4	ClBrO <sub>2</sub> ( <sup>1</sup> A')	OBrO + Cl	28.7
IIO ( <sup>1</sup> A')	I <sub>2</sub> + O	36.6		ClBrO + O	53.4
	IO + I	18.4	BrClO <sub>2</sub> ( <sup>1</sup> A')	OCIO + Br	12.8
IIO ( <sup>3</sup> Σ <sup>-</sup> )	I <sub>2</sub> + O	18.4		BrClO + O	59.9
	I + IO	0.1	ClOOI ( <sup>1</sup> A)	ClO + IO	19.0
ClOBr ( <sup>1</sup> A')	ClO + Br	29.5		IOO + Cl	13.0
	BrO + Cl	37.3		ClOO + I	13.7
ClBrO ( <sup>1</sup> A')	BrCl + O	28.6	ClOIO ( <sup>1</sup> A)	ClO + IO	21.7
	BrO + Cl	25.1		OIO + Cl	23.5
ClBrO ( <sup>3</sup> A'')	BrCl + O	12.8		ClOI + O	47.9
	BrO + Cl	9.2	IOCIO ( <sup>1</sup> A)	ClO + IO	12.3
BrClO ( <sup>1</sup> A')	BrCl + O	25.2		OCIO + I	5.8
	ClO + Br	13.9	ClIO <sub>2</sub> ( <sup>1</sup> A')	ClOI + O	38.5
ClOI ( <sup>1</sup> A')	ClO + I	28.2		OIO + Cl	44.1
	IO + Cl	37.1	IClO <sub>2</sub> ( <sup>1</sup> A')	ClIO + O	68.6
ClIO ( <sup>1</sup> A')	ICl + O	41.4		OCIO + I	3.6
	IO + Cl	37.0		ICIO + O	56.9
ClIO ( <sup>3</sup> A'')	ICl + O	24.9	BrOOI ( <sup>1</sup> A)	BrO + IO	20.8
	IO + Cl	20.5		IOO + Br	7.0
IClO ( <sup>1</sup> A')	ICl + O	20.9		BrOO + I	13.7
	ClO + I	7.6	BrOIO ( <sup>1</sup> A)	BrO + IO	25.1
BrOI ( <sup>1</sup> A')	BrO + I	31.7		OIO + Br	19.0
	IO + Br	30.7		BrOI + O	48.8
BrIO ( <sup>1</sup> A')	IBr + O	40.2	IOBrO ( <sup>1</sup> A)	BrO + IO	13.0
	IO + Br	28.2		OBrO + I	17.7
BrIO ( <sup>3</sup> A'')	IBr + O	24.0		BrOI + O	36.8
	IO + Br	13.7	BrIO <sub>2</sub> ( <sup>1</sup> A')	OIO + Br	33.3
IBrO ( <sup>1</sup> A')	IBr + O	23.4		BrIO + O	66.7
	BrO + I	10.3	IBrO <sub>2</sub> ( <sup>1</sup> A')	OBrO + I	8.9
ClOOCl ( <sup>1</sup> A)	ClO + ClO	18.0 <sup>a</sup>		IBrO + O	48.3
	ClOO + Cl	22.5 <sup>a</sup>	OIBrO ( <sup>1</sup> A)	IBrO + O	40.1
ClOCIO ( <sup>1</sup> A)	ClO + ClO	9.7 <sup>a</sup>		BrIO + O	39.5
	OCIO + Cl	13.0 <sup>a</sup>		BrO + IO	-4.0

<sup>a</sup> Reference 64.

reactions may proceed through long-lived collision complexes on complex potential energy surfaces. The rates of halogen oxide self-reactions will be governed by the rates at which complexes are formed and by the stabilities and rates of their decomposition. These subtleties are manifested experimentally in the rate coefficients that exhibit significant pressure dependences, nega-

tive temperature dependences, and product distributions, which also depend on the pressure.

In the case of the ClO + ClO self-reaction, all three isomers have been experimentally isolated. In the case of BrO and IO, little is known experimentally about the complexes. Figure 3 shows that BrO self-reaction is very similar to its chlorine

analogue, in that the two important stable complexes are BrOOBr and BrOBrO that the reaction proceeds through. The BrOOBr is less stable than ClOOCl, and the favorable decomposition channel is the formation of Br + BrOO. The iodine oxide, IO, self-reaction favors the formation of the IOIO complex, which is the least stable complex for the ClO and BrO self-reactions. However, given that the IO self-reaction also favors the formation of IOOI, the branching ratios for the formation of the complexes are going to be important in establishing the partitioning between iodine-containing species in the reaction. Unlike the ClO and BrO self-reaction decomposition channels, in which the major stable products are halogen atoms (Cl or Br atoms) and molecular oxygen, the IO self-reaction potential energy surface in Figure 3 suggests that OIO, iodine atoms, and molecular oxygen are going to be major stable products. This is consistent with experimental studies on the IO self-reaction that showed the formation of gas phase OIO.<sup>127</sup>

Not surprisingly, little is known about the cross halogen oxide reactions, i.e., ClO + BrO, ClO + IO, and BrO + IO. Experimentally, these reactions are quite complex to study, and the determination of the channels leading to any observe stable products let alone their branching ratios because of the multiplicity of channels is difficult. Figure 4 illustrates the complexity of these cross halogen oxide reactions. There are some interesting observations for future experimental studies in regards to the speciation from the cross halogen oxide reactions. For example, in the ClO + BrO cross reaction, OClO is expected to be a major product, but OBrO is expected to be negligible. In the ClO + IO cross reaction, OClO could be formed but little OIO is expected, whereas in the case of the BrO + IO cross reaction, the OIO species is expected to be a major product. Indeed, in the experiments of Rowley et al. who studied the BrO + IO reaction, only OIO is observed and no evidence of OBrO is found in the experiments.<sup>134</sup> From the discharge flow mass spectroscopic experimental studies on ClO + IO from Bedjanian et al.,<sup>135</sup> only OClO is observed and not OIO, consistent with the predictions from the potential energy surface in Figure 4. These authors also observed Cl atoms and ICl, and these products can be explained by the channels giving Cl + IOO and I + ClOO. Both the IOO and ClOO are weakly bound and will produce Cl and I atoms, respectively. The recombination of Cl and I atoms to give ICl is consistent with the experimental results.

## Conclusion

High level CCSD(T)/CBS level plus additional corrections have been made for the thermodynamics of the BrBrO<sub>2</sub>, IIO<sub>2</sub>, ClBrO<sub>2</sub>, ClIO<sub>2</sub>, and BrIO<sub>2</sub> isomers, as well as various molecules involved in the bond dissociation processes. Of the BrBrO<sub>2</sub> isomers, BrOOBr is predicted to be the most stable by 8.5 and 9.3 kcal/mol compared to BrBrO<sub>2</sub> and BrOBrO at 298 K, respectively. The weakest bond in BrOOBr is the O–Br bond with a bond dissociation energy (BDE) of 15.3 kcal/mol, and in BrBrO<sub>2</sub>, it is the Br–Br bond of 19.1 kcal/mol. The smallest BDE in BrOBrO is for the central O–Br bond with a BDE of 12.6 kcal/mol. Of the IIO<sub>2</sub> isomers, IIO<sub>2</sub> is predicted to be the most stable by 3.3, 9.4, and 28.9 kcal/mol compared to IOIO, IOOI, and OIIO at 298 K, respectively. The weakest bond in IIO<sub>2</sub> is the I–I bond with a BDE of 22.2 kcal/mol. The smallest BDEs in IOIO and IOOI are the terminal O–I bonds with values of 19.0 and 5.2 kcal/mol, respectively.

**Acknowledgment.** We thank the U.S. Department of Energy, Office of Basic Energy Sciences, and the National Science

Foundation for funding. D.A.D. thanks the Robert Ramsay Fund at the University of Alabama for partial support.

**Supporting Information Available:** Calculated geometry parameters for the XY (X, Y = O, Cl, Br, and I) diatomics as a function of basis set, for the OXO and XOY (X, Y = Cl, Br, and I) triatomics as a function of basis set, for the XYO (X, Y = Cl, Br, and I) triatomics as a function of basis set, for the XOY (X, Y = Cl, Br, and I) tetraatomics as a function of basis set, and for the XYO<sub>2</sub> (X, Y = Cl, Br, and I) tetraatomics as a function of basis set, calculated CCSD(T)/aVTZ frequencies, CCSD(T) total energies ( $E_h$ ) as a function of the basis set, and calculated  $T_1$  diagnostics at the CCSD(T)/aVQZ level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Molina, M. J.; Rowland, F. S. *Nature* **1974**, *249*, 810.
- (2) von Hobe, M.; Salawitch, R. J.; Canty, T.; Keller-Rudek, H.; Moortgat, G. K.; Grooss, J.-U.; Muller, R.; Strohm, F. *Atmos. Chem. Phys.* **2007**, *7*, 3055.
- (3) von Hobe, M. *Science* **2007**, *318*, 1878.
- (4) Yagi, K.; Williams, J.; Wang, N. -Y.; Cicerone, R. J. *Science* **1995**, *267*, 1979.
- (5) WMO Global Ozone Research and Monitoring Project; Report No. 44, Scientific Assessment of Ozone Depletion; World Meteorological Organization, Geneva, 1999.
- (6) Barrie, L. A.; Bottenheim, J. W.; Hart, W. R. *J. Geophys. Res.* **1994**, *25*, 313.
- (7) LeBras, G.; Platt, U. *Geophys. Res. Lett.* **1995**, *29*, 2677.
- (8) Anderson, J. G.; Toohey, D. W.; Brune, W. H. *Science* **1991**, *251*, 39.
- (9) Salawitch, R. J.; McElroy, M. B.; Yatteau, J. H.; Wofsky, S. C.; Schoeberl, M. R.; Lait, L. R.; Newman, P. A.; Chan, K. R.; Loewenstein, M.; Podolske, J. R.; Strahan, S. E.; Proffitt, M. H. *Geophys. Res. Lett.* **1990**, *17*, 561.
- (10) Clyne, M. A. A.; Watson, J. W.; Hart, W. R. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 336.
- (11) Sander, S. P.; Watson, R. T. *J. Phys. Chem.* **1981**, *85*, 4000.
- (12) Cox, R. A.; Sheppard, D. W.; Stevens, M. P. *J. Photochem.* **1982**, *19*, 189.
- (13) Turnipseed, A. A.; Birks, J. W.; Calvert, J. G. *J. Phys. Chem.* **1990**, *94*, 7477.
- (14) Lencar, I. T.; Laverdet, G.; Bras, G. L.; Poulet, G. *Int. J. Chem. Kinet.* **1991**, *23*, 47.
- (15) Bridir, I.; Veyret, B.; Lesclaux, R. *Chem. Phys. Lett.* **1993**, *201*, 563.
- (16) Mauldin, R. L., III; Wahner, A.; Ravishankara, A. P. *J. Phys. Chem.* **1993**, *97*, 7585.
- (17) Rowley, D. M.; Harwood, M. H.; Freshwater, R. A.; Jones, R. L. *J. Phys. Chem.* **1996**, *100*, 3020.
- (18) Harwood, M. H.; Rowley, D. M.; Cox, R. A.; Jones, R. L. *J. Phys. Chem. A* **1998**, *102*, 1790.
- (19) Butkovskaya, N. I.; Morozov, I. I.; Tal'rose, V. L.; Vasiliev, E. S. *Chem. Phys.* **1983**, *79*, 21.
- (20) Rattigan, O. V.; Jones, R. L.; Cox, R. A. *Chem. Phys. Lett.* **1994**, *230*, 121.
- (21) Rattigan, O. V.; Cox, R. A.; Jones, R. L. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4189.
- (22) Li, Z.; Freidl, R. R.; Sander, S. P. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2683.
- (23) Li, Z. *J. Phys. Chem. A* **1999**, *103*, 1206.
- (24) Chameides, W. L.; Davis, D. D. *J. Geophys. Res., [Atmos.]* **1980**, *85*, 7383.
- (25) Jenkin, M. E.; Cox, R. A.; Candeland, D. E. *J. Geophys. Res., [Atmos.]* **1985**, *2*, 359.
- (26) Davis, D. J.; Crawford, J.; Liu, S.; McKeen, S.; Bandy, A.; Thornton, D.; Rowland, F.; Blake, D. *J. Geophys. Res., [Atmos.]* **1996**, *101*, 2135.
- (27) Vogt, R.; Sander, R.; Glasow, V.; Crutzen, P. J. *J. Geophys. Res., [Atmos.]* **1999**, *32*, 375.
- (28) Allan, B. J.; McFiggans, G.; Plane, J. M. C. P.; Coe, H. *J. Geophys. Res., [Atmos.]* **2000**, *105*, 14363.
- (29) McFiggans, G.; Plane, J. M. C.; Allan, B. J.; Carpenter, L. J.; Coe, H.; O'Dowd, C. *J. Geophys. Res., [Atmos.]* **2000**, *105*, 14371.
- (30) Calvert, J. G.; Lindberg, S. E. *Atmos. Environ.* **2004**, *38*, 5087.



- (31) Saiz-Lopez, A.; Mahajan, A. S.; Salmon, R. A.; Bauguittie, S. J. B.; Jones, A. E.; Roscoe, H. E.; Plane, J. M. C. *Science* **2007**, *317*, 348.
- (32) Bloss, W. J.; Lee, J. D.; Johnson, G. P.; Sommariva, R.; Heard, D. E.; Saiz-Lopez, A.; Plane, J. M. C.; McFiggans, G.; Coe, H.; Flynn, M.; Williams, P.; Rickard, A. R.; Flemming, Z. L. *Geophys. Res. Lett.* **2003**, *32*.
- (33) McFiggans, G.; Cox, R. A.; Mossinger, J. C.; Allan, B. J.; Plane, J. M. C. *J. Geophys. Res., [Atmos.]* **2002**, *107*, 4271.
- (34) Carpenter, L. J.; Liss, P. S.; Penkett, S. A. *J. Geophys. Res., [Atmos.]* **2003**, *108*, 4256.
- (35) Sander, S. P.; Friedl, R. R.; Ravishankara, A. R.; Golden, D. M.; Kolb, C. E.; Kurylo, M. J.; Huie, R. E.; Orkin, V. L.; Molina, M. J.; Moortgat, G. K.; Finlayson-Pitts, B. J. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies: Evaluation Number 14*; JPL Publication 02-25; National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology: Pasadena, CA, 2003; [http://jpldataeval.jpl.nasa.gov/pdf/JPL\\_02-25\\_rev02.pdf](http://jpldataeval.jpl.nasa.gov/pdf/JPL_02-25_rev02.pdf).
- (36) Chase, M. W. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1069.
- (37) Chase, M. W., Jr. *J. Phys. Chem. Ref. Data* **1998**, Monograph 9, NIST-JANAF Thermochemical Tables, 4th ed., Suppl. 1.
- (38) Coxon, J. A.; Ramsay, D. A. *Can. J. Phys.* **1976**, *54*, 1034.
- (39) Kim, H.; Dooley, K. S.; Johnson, E. R.; North, S. W. *J. Chem. Phys.* **2006**, *124*, 134304.
- (40) Wilmouth, D. M.; Hanisco, T. F.; Donahue, N. M.; Anderson, J. G. *J. Phys. Chem. A* **1999**, *103*, 8935.
- (41) Radlein, D. S. A. G.; Whitehead, J. C.; Grice, R. *Nature* **1975**, *253*, 37.
- (42) Buss, R. J.; Sibener, S. J.; Lee, Y. T. *J. Phys. Chem.* **1983**, *87*, 4840.
- (43) Bedjanian, Y.; Le Bras, G.; Poutlet, G. *J. Phys. Chem. A* **1997**, *101*, 4088.
- (44) Dooley, K. S.; Geidosch, J. N.; North, S. W. *Chem. Phys. Lett.* **2008**, *457*, 303.
- (45) (a) Nicovich, J. M.; Kreutter, K. D.; Shackelford, C. J.; Wine, P. H. *Chem. Phys. Lett.* **1991**, *179*, 367. (b) Baer, S.; Hippler, H.; Rahn, R.; Siefke, M.; Seitzinger, N.; Troe, J. *J. Chem. Phys.* **1991**, *95*, 6463. (c) Maudlin, R. L., III; Burkholder, J. B.; Ravishankara, A. R. *J. Phys. Chem.* **1992**, *96*, 2582.
- (46) Davis, H. F.; Lee, Y. T. *J. Chem. Phys.* **1996**, *105*, 8142.
- (47) Plenge, J.; Kühl, S.; Vogel, B.; Müller, R.; Stroh, F.; von Hobe, M.; Flesch, R.; Rühl, E. *J. Phys. Chem. A* **2005**, *109*, 6730.
- (48) Thorn, R. P., Jr.; Monks, P. S.; Stief, L. J.; Kuo, S.-C.; Zhang, Z.; Klemm, R. B. *J. Phys. Chem.* **1996**, *100*, 12199.
- (49) Klemm, R. B.; Thorn, R. P., Jr.; Stief, L. J.; Buckley, T. J.; Johnson, R. D., III *J. Phys. Chem. A* **2001**, *105*, 1638.
- (50) Blake, J. A.; Browne, R. J.; Burns, G. J. *Chem. Phys.* **1970**, *53*, 3320.
- (51) Butkovskaya, N. I.; Morozov, I. I.; Talrose, V. L.; Vasiliev, E. *Chem. Phys.* **1990**, *79*, 21.
- (52) Rattigan, O. V.; Cox, R. A.; Jones, R. L. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4189.
- (53) Rattigan, O. V.; Jones, R. L.; Cox, R. A. *Chem. Phys. Lett.* **1994**, *230*, 121.
- (54) (a) Parrish, D. D.; Herschbach, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 6133. (b) Dixon, D. A.; Parrish, D. D.; Herschbach, D. R. *Faraday Discuss. Chem. Soc.* **1973**, *55*, 385.
- (55) Grice, P. *Acc. Chem. Res.* **1981**, *14*, 37.
- (56) Clough, P. N.; O'Neil, G. M.; Geddes, J. *J. Chem. Phys.* **1978**, *69*, 3128.
- (57) Gorby, P. A.; Nowikow, C. V.; Grice, R. *Mol. Phys.* **1979**, *37*, 347.
- (58) Bartlett, R. J.; Musial, M. *Rev. Mod. Phys.* **2007**, *79*, 291.
- (59) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803.
- (60) (a) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- (61) (a) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484. (b) Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727. (c) Dixon, D. A.; Feller, D.; Peterson, K. A. *J. Chem. Phys.* **2001**, *115*, 2576. Pollack, L.; Windus, T. L.; de Jong, W. A.; Dixon, D. A. *J. Phys. Chem. A* **2005**, *109*, 6934.
- (62) Peterson, K. A.; Shepler, B. C.; Figgen, D.; Stoll, H. *J. Phys. Chem. A* **2006**, *110*, 13877.
- (63) Feller, D.; Peterson, K. A.; Dixon, D. A. *J. Chem. Phys.* **2008**, *129*, 204015.
- (64) Matus, M. H.; Nguyen, M. T.; Peterson, K. A.; Francisco, J. S.; Dixon, D. A. *J. Phys. Chem. A* **2008**, *112*, 9623.
- (65) Karton, A.; Parthiban, S.; Martin, J. M. L. *J. Phys. Chem. A* **2009**, *113*, 4802.
- (66) Li, Q.; Lu, S.; Xie, Y.; Schleyer, P. V. R.; Schaefer, H. F., III *Int. J. Quantum Chem.* **2003**, *95*, 731.
- (67) Lee, T. J.; Rohlfing, C. M.; Rice, J. E. *J. Chem. Phys.* **1992**, *97*, 6593.
- (68) Lee, S. Y. *J. Phys. Chem. A* **2004**, *108*, 10754.
- (69) Peterson, K. A. *J. Chem. Phys.* **1998**, *109*, 8864.
- (70) Lee, T. J. *J. Phys. Chem.* **1995**, *99*, 15074.
- (71) Pacios, L. F.; Gümez, P. C. *J. Molec. Struct.: THEOCHEM* **1999**, *467*, 223.
- (72) Pak, C.; Xie, Y.; Schaefer, H. F., III *Mol. Phys.* **2003**, *101*, 211.
- (73) Xie, Y.; Schaefer, H. F., III; Wang, Y.; Fu, X. -Y.; Liu, R. -Z. *Mol. Phys.* **2000**, *98*, 879.
- (74) Li, Z.; Jeong, G.-R. *Chem. Phys. Lett.* **2001**, *340*, 194.
- (75) Francisco, J. *Chem. Phys. Lett.* **1998**, *288*, 307.
- (76) Misra, A.; Marshall, P. J. *J. Phys. Chem. A* **1998**, *102*, 9056.
- (77) Kaltsoyannis, N.; Plane, J. M. C. *J. Phys. Chem. Chem. Phys.* **2008**, *10*, 1723.
- (78) Peterson, K. A. *Mol. Phys.*, in press, 2010.
- (79) (a) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219. (b) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.
- (80) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.
- (81) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548.
- (82) DeYonker, N. J.; Peterson, K. A.; Wilson, A. K. *J. Phys. Chem. A* **2007**, *111*, 11383.
- (83) Peterson, K. A.; Yousaf, K. E. Manuscript in preparation.
- (84) Dixon, D. A.; Grant, D. J.; Christe, K. O.; Peterson, K. A. *Inorg. Chem.* **2008**, *47*, 5485.
- (85) (a) Peterson, K. A. *J. Chem. Phys.* **2003**, *119*, 11099. (b) Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2003**, *119*, 11113.
- (86) Dunham, J. L. *Phys. Rev.* **1932**, *41*, 721.
- (87) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410.
- (88) (a) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89. (b) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756. (c) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742. (d) de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48 EMSL basis set library. <http://www.emsl.pnl.gov/forms/basisform.html>.
- (89) Davidson, E. R.; Ishikawa, Y.; Malli, G. L. *Chem. Phys. Lett.* **1981**, *84*, 226.
- (90) Dixon, D. A.; de Jong, W. A.; Peterson, K. A.; Christe, K. O.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **2005**, *127*, 8627.
- (91) Dixon, D. A.; Grant, D. J.; Peterson, K. A.; Christe, K. O.; Schrobilgen, G. J. *Inorg. Chem.* **2008**, *47*, 5485.
- (92) Grant, D. J.; Dixon, D. A.; Francisco, J. S.; Feller, D.; Peterson, K. A. *J. Phys. Chem. A* **2009**, *113*, 11343.
- (93) Feller, D.; Peterson, K. A.; Dixon, D. A. *J. Phys. Chem. A* **2010**, *114*, 613.
- (94) Lyman, J. L.; Holland, R. *J. Phys. Chem.* **1988**, *92*, 7232.
- (95) Pagsberg, P.; Ratajczak, E.; Sillescu, A.; Jodkowski, J. T. *Chem. Phys. Lett.* **1987**, *141*, 88.
- (96) Moore, C. E. *Atomic energy levels as derived from the analysis of optical spectra, Volume 1, H to V*; U.S. National Bureau of Standards Circular 467, COM-72-50282; U.S. Department of Commerce, National Technical Information Service: Washington, DC, 1949. The atomic spin-orbit corrections are  $\Delta E_{\text{SO}}(\text{O}) = 0.22$  kcal/mol,  $\Delta E_{\text{SO}}(\text{F}) = 0.39$  kcal/mol,  $\Delta E_{\text{SO}}(\text{Cl}) = 0.84$  kcal/mol,  $\Delta E_{\text{SO}}(\text{Br}) = 3.50$  kcal/mol, and  $\Delta E_{\text{SO}}(\text{I}) = 7.24$  kcal/mol.
- (97) Peterson, K. A.; Shepler, B. C.; Figgen, D.; Stoll, H. *J. Phys. Chem. A* **2006**, *110*, 13877.
- (98) Shepler, B. C.; Balabanov, N. B.; Peterson, K. A. *J. Phys. Chem. A* **2005**, *109*, 11363.
- (99) Feller, D.; Peterson, K. A.; de Jong, W. A.; Dixon, D. A. *J. Chem. Phys.* **2003**, *118*, 3510.
- (100) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (101) (a) Nash, C. S.; Bursten, B. E.; Ermler, W. C. *J. Chem. Phys.* **1997**, *106*, 5133. (b) Ross, R. B.; Gayen, S.; Ermler, W. C. *J. Chem. Phys.* **1994**, *100*, 8145. (c) Lajohn, L.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. *J. Chem. Phys.* **1987**, *87*, 2812. (d) Hurley, M.; Pacios, L. F.; Christiansen, P. A.; Ross, R. B.; Ermler, W. C. *J. Chem. Phys.* **1986**, *84*, 6840. (e) Ross, R. B.; Ermler, W. C.; Christiansen, P. A. *J. Chem. Phys.* **1986**, *84*, 3297.
- (102) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.
- (103) *MOLPRO a package of ab initio programs designed by Werner, H.-J.; and Knowles, P. J.* version 2006.2, Universität Stuttgart, Stuttgart, Germany, University of Birmingham, Birmingham, United Kingdom. Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, G.; Hetzer, G.; Knowles, P. J.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.,



Schütz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Werner, H.-J.

(104) (a) Apra, E.; Bylaska, E. J.; Jong, W. d.; Hackler, M. T.; Hirata, S.; Pollack, L.; Smith, D.; Straatsma, T. P.; Windus, T. L.; Harrison, R. J.; Nieplocha, J.; Tipparaju, V.; Kumar, M.; Brown, E.; Cisneros, G.; Dupuis, M.; Fann, G. I.; Fruchtl, H.; Garza, J.; Hirao, K.; Kendall, R.; Nichols, J. A.; Tsemekhman, T.; Valiev, M.; Wolinski, K.; Anchell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachsel, H.; Deegan, M.; Dyall, K.; Elwood, D.; Glendening, E.; Gutowski, M.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kobayashi, R.; Kuttel, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nakajima, T.; Niu, S.; Rosing, M.; Sandrone, G.; Stave, M.; Taylor, H.; Thomas, G.; Lenthe, J. v.; Wong, A.; Zhang, Z. *NWChem*; William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory: Richland, WA, 2003. (b) Kendall, R. A.; Apra, E.; Bernholdt, D. E.; Bylaska, E. J.; Dupuis, M.; Fann, G. I.; Harrison, R. J.; Ju, J.; Nichols, J. A.; Nieplocha, J.; Straatsma, T. P.; Windus, T. L.; Wong, A. T. *Comput. Phys. Commun.* **2000**, *128*, 260.

(105) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision E.01*; Gaussian, Inc.: Wallingford, CT, 2004.

(106) Müller, H. S. P.; Miller, C. E.; Cohen, E. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2129.

(107) Miller, C. E.; Nicolaisen, S. L.; Francisco, J. S.; Sander, S. P. *J. Chem. Phys.* **1997**, *107*, 2300.

(108) Müller, H. S. P.; Cohen, E. A. *J. Chem. Phys.* **1997**, *106*, 8344.

(109) Jacobs, J.; Kronberg, M.; Müller, H. S. P.; Willner, H. *J. Am. Chem. Soc.* **1994**, *116*, 1106.

(110) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules. Molecular Spectra and Molecular Structure*, Van Nostrand: Princeton, NJ, 1979; Vol. IV.

(111) Tevault, D. E.; Walker, R. R.; Fox, W. B. *J. Phys. Chem.* **1978**, *82*, 2733.

(112) (a) Drouin, B. J.; Miller, C. E.; Cohen, E. A.; Wagner, G.; Birk, M. *J. Mol. Spectrosc.* **2001**, *207*, 4. (b) Drouin, B. J.; Miller, C. E.; Müller, H. S. P.; Cohen, E. A. *J. Mol. Spectrosc.* **2001**, *205*, 128.

(113) Miller, C. E.; Cohen, E. A. *J. Chem. Phys.* **2001**, *115*, 6459.

(114) Lee, Y.-C.; Lee, Y.-P. *J. Phys. Chem. A* **2000**, *104*, 6951.

(115) Kolm, J.; Engdahl, A.; Schrems, O.; Nelander, B. *Chem. Phys.* **1997**, *214*, 313.

(116) Tevault, D. E.; Walker, R.; Smardzewski, R. R.; Fox, W. B. *J. Phys. Chem.* **1978**, *82*, 2733.

(117) Fleischmann, O. C.; Meyer-Arneck, J.; Burrows, J. P.; Orphal, J. *J. Phys. Chem. A* **2005**, *109*, 5093.

(118) Kolm, J.; Engdahl, A.; Schrems, O.; Nelander, B. *Chem. Phys.* **1997**, *214*, 313.

(119) Chu, L. T.; Li, Z. *Chem. Phys. Lett.* **2000**, *330*, 68.

(120) Kolm, J.; Schrems, O.; Beichert, P. *J. Phys. Chem. A* **1998**, *102*, 1083.

(121) Levason, W.; Ogden, J. S.; Spicer, M. D.; Young, N. A. *J. Am. Chem. Soc.* **1990**, *112*, 1019.

(122) Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *J. Chem. Phys.* **1992**, *96*, 8012.

(123) Maier, G.; Bothur, A. *Chem. Ber.* **1997**, *130*, 179.

(124) Bahou, M.; Schriver-Mazzuoli, L.; Schriver, A.; Chaquin, P. *Chem. Phys.* **1997**, *216*, 105.

(125) Hawkins, M.; Andrews, L.; Downs, A. J.; Drury, D. J. *J. Am. Chem. Soc.* **1984**, *106*, 3076.

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

(127) Himmelmann, S.; Orphal, J.; Bovensmann, H.; Richter, A.; Ladstätter-Weissenmayer, A.; Burrows, J. P. *Chem. Phys. Lett.* **1996**, *251*, 330.

(128) Gómez Martin, J. C.; Plane, J. M. C. *Chem. Phys. Lett.* **2009**, *474*, 79 These authors reported a value of  $D_0(\text{O}-\text{IO}) = 59.46 \pm 0.24$  kcal/mol from the photofragment excitation spectrum. Combining this value with other experimental data and our 0 to 298 K calculated temperature correction gives  $\Delta H_f^{298}(\text{OIO})$ .

(129) Cox, R. A.; Hayman, G. D. *Nature* **1988**, *332*, 796.

(130) Plenge, J.; Kühl, S.; Vogel, B.; Müller, R.; Stroh, F.; von Hobe, M.; Flesch, R.; Rühl, E. *J. Phys. Chem. A* **2005**, *109*, 6730.

(131) Nickolaisen, S. L.; Friedl, R. R.; Sander, S. P. *J. Phys. Chem.* **1994**, *98*, 155.

(132) Moore, T. A.; Okumura, M.; Seale, J. W.; Minton, T. K. *J. Phys. Chem. A* **1999**, *103*, 1691.

(133) (a) Cox, R. A.; Hayman, G. D. *Nature* **1988**, *332*, 796. (b) Molina, M. J.; Colussi, A. J.; Molina, L. T.; Schindler, R. N.; Tso, T.-L. *Chem. Phys. Lett.* **1990**, *173*, 310.

(134) Rowley, D. W.; Bloss, W. J.; Cox, R. A.; Jones, R. L. *J. Phys. Chem. A* **2001**, *105*, 7855.

(135) Bedjanian, Y.; LeBras, G.; Poulet, G. *J. Phys. Chem. A* **1997**, *101*, 4088.

JP911320P