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Theoretical Study of I_2O

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ABSTRACT: *We present high-level density functional calculations (DFT) on the unknown I_2O molecule. The results suggest that the compound may be sufficiently stable for detection and synthesis. Our results also suggest that the DFT method is a reliable and computationally cheap alternative to G2, for estimating thermodynamic properties. The trends in relative stabilities within the HOX and X_2O series are discussed (X = halogen).* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:383–385, 1998

INTRODUCTION

Bock et al. [1] have suggested that one could construct 1638 triatomic molecules from 13 nonmetallic elements (H, B, C, Si, N, P, O, S, F, Cl, Br, I, and Xe). Most of these compounds have already been characterized, but for a few exceptions. One such exception is I_2O, which provides an interesting sequel to our previous study of Br_2O [2]. The series of dihalogen oxides (X_2O; X = F,Cl,Br,I) comprises compounds of very different thermodynamic stabilities. The first two members of the series are sufficiently stable to have been well characterized experimentally, while Br_2O has been fully characterized only recently [3].

COMPUTATIONAL METHOD

We have used density functional theory (DFT) with a large basis set in order to estimate enthalpy of formation of I_2O. All the calculations were performed with the Gaussian 94 program package [4].

The use of DFT in high-accuracy thermodynamic calculations is new, but it appears to be a good (and cheap) alternative to the standard G2 method as has been shown recently [5]. DFT calculations were performed at the B3LYP/6-311++G(3df,3pd)//B3LYP/6-311G(2d,2p) level. The relativistic effective core potentials (ECP) for bromine and iodine were taken from the work of Bergner et al. [6a]. Glukhovtsev et al. [6b] demonstrated that these ECP are useful in high-level ab initio calculations of thermodynamic properties for bromine and iodine compounds. They also suggested a set of polarization and diffuse functions suitable for these ECP, which were used in this work. Each calculation converged to a genuine minimum on the potential energy surface, as indicated by the absence of imaginary vibrational frequencies.

RESULTS AND DISCUSSION

The results indicate that the I_2O molecule is bent, with I–O bond lengths of 2.0492 Å and an angle of 117.06°. In order to test the suitability of our approach for determining enthalpies, we have calculated [ΔH_f(g) at 298 K] values for the whole series of X_2O compounds using the isodesmic reaction

$$2\ HOX = X_2O + H_2O \quad (X = F, Cl, Br, I)$$

The [ΔH_f(g);298 K] HOX values were taken from Glukhovtsev et al. [7], ΔH_f(g) of water from the standard source [8], and total DFT energies included vibrational corrections.

The calculations gave ΔH_f(g) at 298 K for I_2O as 121.86 $kJmol^{-1}$. This is higher than the value of 107.6 ± 3.5 $kJmol^{-1}$ that was estimated for Br_2O [3],

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Dedicated to Prof. Dr. Heinrich Nöth on the occasion of his seventieth birthday.

and it indicates that I_2O is less stable than its bromine analog. The lower stability of I_2O can be expected from the known trends in the F_2O, Cl_2O, and Br_2O series, as well as those from the HOX series [7] (Figure 1). In both cases, the increase in the atomic number of halogen leads to an increase in enthalpy of formation.

The enthalpy results are summarized in Table 1, and they demonstrate several important points. The DFT method is useful for estimating thermodynamic properties as is shown by the good agreement between experimental and theoretical values for F_2O and Cl_2O. The DFT value for Br_2O is slightly higher than the experimental value [3], but it is lower than the value of 121.7 $kJmol^{-1}$ estimated by Lee [9] using high-level ab initio calculations. The experimental values for F_2O and Cl_2O were established by a combination of several types of measurements, and it is plausible that the Br_2O value should be remeasured (via different methods) in order to confirm its true value. Large experimental uncertainties in Table 1 demonstrate the difficulties involved in measurement of enthalpies of unstable compounds.

I_2O appears to be only slightly less stable than Br_2O, which had been detected recently [10]. The procedure used for generation of Br_2O could perhaps be useful in searching for the presence of I_2O. In order to help in possible identification, we give in Table 2 its fundamental vibrational frequencies. The thermodynamic stabilities of both X_2O and HOX decrease with the increase in halogen's atomic number, but the decrease is much more prominent in the former series (Figure 1). The decrease in stability of

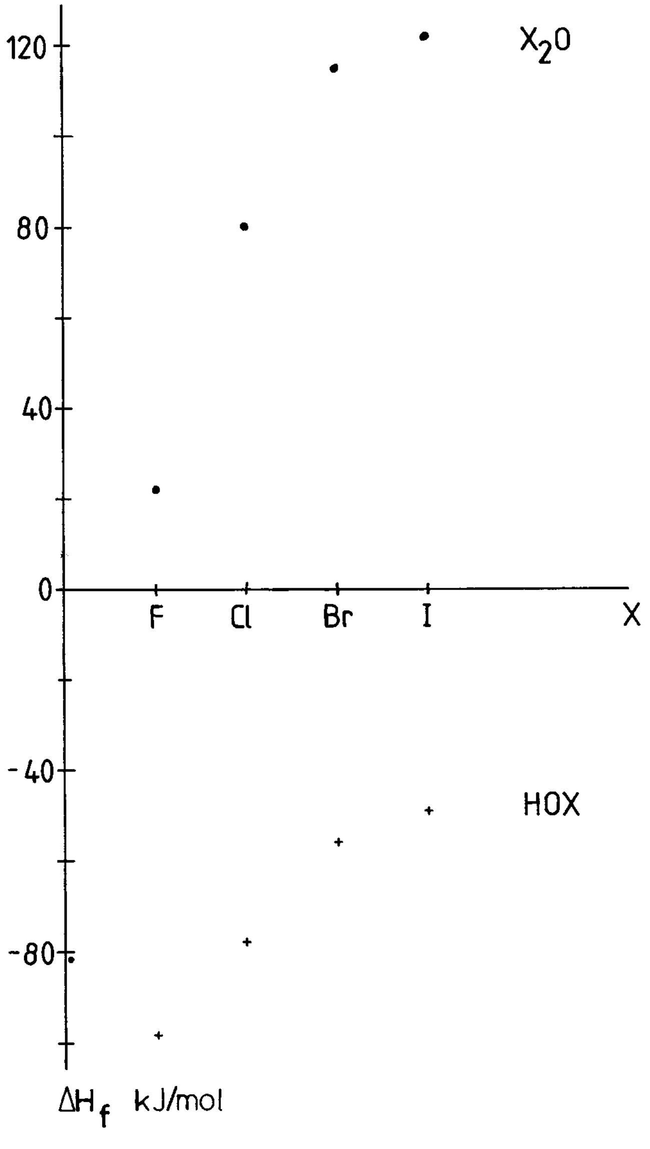

FIGURE 1 A comparison of thermodynamic stabilities ($\Delta H_f^\circ/kJmol^{-1}$; 298 K) for hypohalous acids [7] and dihalogen oxides [11]. Circles indicate oxides, and crosses, hypohalous acids.

TABLE 1 Comparison of Experimental and Theoretical ΔH_f° (g); 298 K for the X_2O Series

Compound	*$\Delta H_f^\circ/kJmol^{-1}$ (exp)*	*$\Delta H_f^\circ/kJmol^{-1}$ (DFT)*
F_2O	24.5 ± 1.6	21.99
Cl_2O	79 ± 10	79.9
Br_2O	107.6 ± 3.5	115.47
I_2O	119.5 ± 25[a]	121.86

Experimental values from ref. [11]
[a] Estimated value [11b].

TABLE 2 Vibrational Frequencies (scaled) for I_2O[a]

Mode	*Symmetry*	*Frequency/cm^{-1}*
Asym str.	b_2	530.8
Sym str.	a_1	416.4
Bend	a_1	121.9

[a] Scaling factors were taken from Ref. [12].

TABLE 3 Mulliken Population Analysis (Net Charges along the X–O Bond)

Compound	*$\delta(X)$*	*$\delta(O)$*
F_2O	−0.11	+0.22
Cl_2O	+0.07	−0.15
Br_2O	+0.18	−0.36
I_2O	+0.19	−0.38
HOF	−0.21	−0.34
HOCl	+0.02	−0.55
HOBr	+0.16	−0.70
HOI	+0.24	−0.76

X_2O can be rationalized (in the language of Frontier MO theory) by destabilizing *n–n* interactions between two occupied MOs. The larger the atomic number (and size) of the halogen atom, the stronger the interactions between two HOMO halogen np orbitals become, which leads to the overall destabilization along the X_2O series. However, in order to account for the relative decrease in stability of HOX vs. X_2O, we have performed a Mulliken population analysis (Table 3). The results suggest that the different variation of stability is related to the polarity of the X–O bond. The less polar the bond is, the faster will stability decrease with increasing atomic number of X.

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