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Computational Investigations of Iodine Oxides

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Isomers of IO_2, I_2O, and I_2O_2 have been characterized by ab initio methods. Vibrational frequencies and geometries were obtained at the MP2/6-31G(d) and MP2/6-311+G(3df) levels of theory, respectively. The thermochemistry was derived using approximate QCISD(T)/6-311+G(3df) (Gaussian-2) energies coupled with isodesmic reactions. Computed values of $\Delta_f H_{298}$ for these molecules are the following (in kJ mol^{-1}): OIO, 76.7; IOO, 96.6; IIO, 134.1; IOI, 92.4; IOOI, 156.8; IIO_2, 103.0; IOIO, 124.2; OIIO, 224.0. Uncertainties are discussed in the text. The results are compared with some previous empirical estimates and are employed in a QRRK analysis to interpret the IO + IO reaction: favorable products include I + OIO.

1. Introduction

Iodine oxides have been implicated in the atmospheric chemistry of iodine,[1,2] in the behavior of iodine−ozone mixtures,[3] and in the mechanism of oxygen−iodine lasers.[4] A recent review[5] has drawn attention to the lack of information about any gas-phase iodine oxides except the simplest, IO, which is now well-characterized, and OIO, whose electronic and vibrational spectra have been obtained both in the gas phase[6] and in a frozen argon matrix.[7] There are apparently no structural, vibrational, or thermochemical measurements available for other iodine oxides, and indeed the existence of some is speculative. The aim of the present work is to address this deficiency via ab initio analysis of the oxides IO_2, I_2O, and I_2O_2 and their isomers. The thermochemistry of eight oxides is presented, and all are found to be thermodynamically unstable with respect to the elements at 298 K. However, each molecule is stable with respect to breaking a single bond, and therefore, they may play roles as transient intermediates. The implications of some of the derived bond dissociation enthalpies for the kinetics of formation and loss of iodine oxides are assessed. The results should aid interpretation of the environmental fate of iodine. This has recently become of increasing interest, following the suggestion that iodine compounds may influence the lower stratosphere,[1,2] and in the light of the possible use of CF_3I and similar compounds as non global warming and ozone-friendly replacements for halon fire suppression agents[8] and perfluorocarbon plasma etchants for silicon wafers.[9,10]

2. Methodology

All computations were made with the Gaussian 94 program suite.[11] Gaussian-2 (G2) theory,[12] as extended to iodine-containing species by Glukhovstev et al.,[13] was applied to I_xO_y. All-electron basis sets were employed in non-relativistic calculations, and earlier good accord with experimental results suggests that relativistic effects are either small or cancel.[13] The first steps in standard G2 theory are to compute the geometry at the MP2=FULL/6-31G(d) and the frequencies at the HF/6-31G(d) levels of theory, respectively. Whereas such results are usually in good accord with experimental measurements, as we discussed earlier[14] this is clearly not the case for a test molecule, IO. We have employed MP2=FC/6-311+G(3df) calculations for the geometries because this level of theory gave better accord with the experimental IO bond length[15] than results obtained with smaller basis sets or other electron correlation treatments, including B3LYP and QCISD(T).[14] Frequency calculations at this level are too computationally demanding, and instead MP2=FC/6-31G(d) values scaled by a standard factor[16] of 0.9646 were employed.

Next, a series of calculations were carried out at each MP2=FC/6-311+G(3df)-optimized geometry to obtain the single-point energy at a high level of theory. Approximate QCISD(T)/6-311+G(3df) results were obtained via the G2-(ZPE=MP2) methodology of Curtiss et al.[16] Their procedure is modified here by the use of geometries obtained with a larger basis set and by the use of MP2=FC/6-31G(d) vibrational frequencies obtained with the frozen core approximation. The vibrational frequencies were also employed to calculate the enthalpy corrections, $H_{298} - H_0$, and other thermodynamic functions.

The enthalpy of formation of IOI was derived via the computed 0 K reaction enthalpy ΔH_0 for the isodesmic reaction

$$IOI + H_2O \rightarrow 2\ HOI \qquad (1)$$

coupled with the known $\Delta_f H_0$ of H_2O[15] and HOI (see below). $\Delta_f H_0$(IIO) was obtained from $\Delta_f H_0$(IOI) together with the G2 energy difference between the two isomers. $\Delta_f H_{298}$ values were obtained via the relation $\Delta_f H_{298} = \Delta_f H_0 + (H_{298} - H_0)_{\text{compound}} - (H_{298} - H_0)_{\text{elements}}$. Similarly, $\Delta_f H_0$(IOOI) was obtained via the isodesmic process

$$IOOI + 2H_2O \rightarrow 2HOI + H_2O_2 \qquad (2)$$

and the known $\Delta_f H_0$ of H_2O_2,[15] H_2O, and HOI. The formation enthalpies of other I_2O_2 isomers were assessed through G2 energies relative to IOOI. The thermochemistry of OIO was derived from its experimentally known electron affinity[17] combined with the enthalpy of formation of the anion OIO^-,

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TABLE 1: Comparison of Computed and Experimental Bond Lengths and Frequencies

	length/10^{-10} m		frequency/cm^{-1}	
bond	MP2=FC/ 6-311+G(3df)	obsd[a]	MP2=FC/ 6-31G(d)[b]	obsd[a]
I−I	2.680	2.665	217	213
I−O	1.888	1.868	724	673
O−O	1.219	1.208	1360	1556
HO−OH	1.444	1.464	896	875

[a] Reference 15. [b] Scaled by 0.9646.

evaluated via ΔH_0 for the congeneric reaction

$$\mathrm{OIO^-} + \mathrm{ClO} \rightarrow \mathrm{OClO^-} + \mathrm{IO} \tag{3}$$

extrapolated to 298 K via $H_{298} - H_0$ values. This procedure avoids the need for explicit calculation of the spin−orbit coupling term in OIO, which instead is included in its measured electron affinity. $\Delta_f H_{298}$ of IO,[18] ClO,[19] and OClO[19] were taken from the literature. The latter quantity, combined with the electron affinity of OClO,[17] yields $\Delta H_{298}(\mathrm{OClO^-})$. The "ion convention" was employed for the thermochemistry.[20]

IOO was found to be a very loose adduct of an I atom to O_2, and therefore its thermochemistry was assessed from the energy relative to I + O_2.

We expect errors in the isodesmic reactions arising from deficiencies in the vibrational frequencies, basis sets, and correlation corrections mostly to cancel, so that the largest contribution to the uncertainty of the resulting thermochemistry comes from the uncertainty in $\Delta_f H_0$(HOI). We have employed our estimated value[21] of −64.9 ± 5.4 kJ mol^{-1}, which compares well with a value of −55.2 ± 6.9 kJ mol^{-1} computed by Hassanzadeh and Irikura.[22] Propagation of its uncertainty through eqs 1−3 leads to an uncertainty of ±5.4 kJ mol^{-1} for OIO and ±10.8 kJ mol^{-1} for the molecules containing two iodine atoms. Uncertainties in other ancillary quantities are negligible. This is a lower limit, which does not include allowance for errors in the relative energies for isomers. More conservative limits of ±15 kJ mol^{-1} are suggested provisionally for all of the species until the accuracy of the calculations can be tested against experiment.

3. Results and Discussion

A comparison between experimental and computed results for I−O, I−I, and O−O bonds is given in Table 1, which indicates good accord for the known bond lengths and moderate accord for the frequencies at the theoretical levels employed. These frequencies are used to derive thermodynamic functions and zero-point energies, and an error of 100 cm^{-1} corresponds to only 0.6 kJ mol^{-1} in zero-point energy. Figures 1 and 2 show the computed geometries of the iodine oxides **1**−**8**, and the computed frequencies are listed in Table 2. It should be noted that the ab initio frequencies for the anions $\mathrm{OClO^-}$ and $\mathrm{OIO^-}$ are too high (by around 16%) by comparison with measured symmetric stretches of 774 ± 25 and 675 ± 25 cm^{-1}, respectively.[17] The computed energies and thermochemistry for iodine oxides and ancillary species are listed in Table 3.

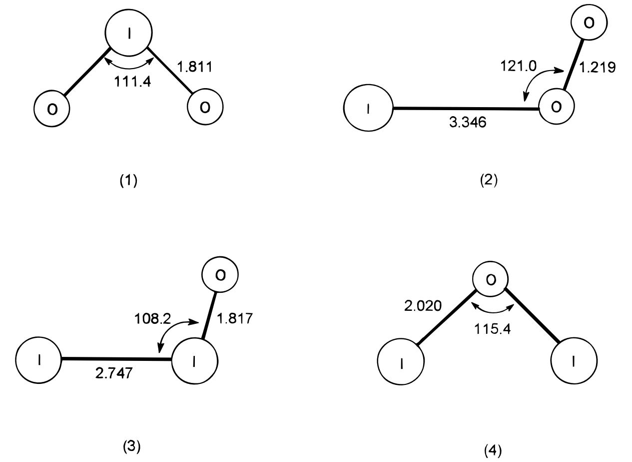

Figure 1. MP2=FC/6-311+G(3df) geometries of triatomic iodine oxides with bond lengths in 10^{-10} m and angles in degrees. (**1**) C_{2v} OIO, $^2B_1$. (**2**) C_S IOO, $^2A''$. (**3**) C_S IIO, $^1A'$. (**4**) C_{2v} IOI, $^1A_1$.

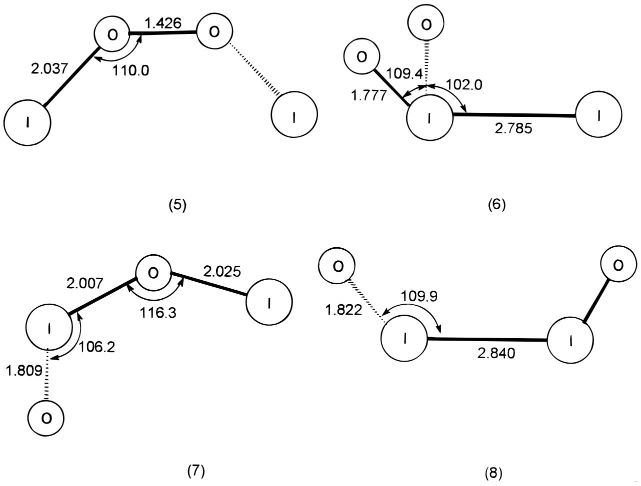

Figure 2. MP2=FC/6-311+G(3df) geometries of tetratomic iodine oxides with bond lengths in 10^{-10} m and angles in degrees. (**5**) C_2 IOOI, ^1A, dihedral 86.0°. (**6**) C_S IIO_2, $^1A'$. (**7**) C_1 IOIO, ^1A, dihedral 67.0°. (**8**) C_2 OIIO, ^1A, dihedral 90.1°.

TABLE 2: Frequencies at the MP2=FC/6-31G(d) Level (Scaled by 0.9646)

oxide	state	frequencies/cm^{-1} [a]
OIO	$^2B_1$	B_2 836 (273); A_1 797 (5), 251 (22)
IOO[b]	$^2A''$	A′ 1610 (115), 198 (0.1), 81 (0.2)
IIO	$^1A'$	A′ 909 (153), 178 (30), 131 (5)
IOI	$^1A_1$	B_2 597 (18); A_1 422 (2), 126 (0.3)
IOOI	^1A	A 714 (26), 519 (12), 505 (2), 303 (0.9), 195 (0.0), 58 (0.4)
IIO_2	$^1A'$	A″ 968 (122), 133 (2); A′ 950 (86), 290 (22), 213 (59), 134 (13)
IOIO	^1A	A 928 (84), 561 (80), 398 (35), 206 (12), 120 (4), 50 (6)
OIIO	^1A	B 901 (368), 116 (11); A 917 (39), 130 (1.1), 77 (0.4), 62 (10)
$\mathrm{OClO^-}$	$^1A_1$	B_2 915 (21); A_1 853 (18), 361 (18)
$\mathrm{OIO^-}$	$^1A_1$	B_2 770 (182); A_1 760 (47), 244 (26)

[a] Frequencies grouped by symmetry and IR intensities, in km mol^{-1}, given in parentheses. [b] Unscaled B3LYP/6-311G(d,p) values.

3.1. IO_2 Species. The IO_2 system has been studied recently by matrix isolation methods. Condensation of flash-pyrolyzed iodine−oxygen mixtures by Maier and Bothur led to a species with a peak UV absorbance of about 250 nm, attributed to IOO, which reversibly photoisomerized to a species attributed to OIO.[7] The IR spectrum of OIO showed peaks for asymmetric and symmetric stretching of 800 and 768 cm^{-1}, respectively. Earlier gas-phase assignments derived via photoelectron spectroscopy of $\mathrm{OIO^-}$ by Gilles et al.[17] are 765 cm^{-1} for the symmetric stretch and 192 cm^{-1} for bending, while Himmelmann et al.[6] recently obtained 631 and 177 cm^{-1} from the visible spectrum. The computed values (Table 2) are in fair accord with these measurements and are consistent with an uncertainty in the computed frequencies of up to 200 cm^{-1}. No bound IOO

TABLE 3: Energies of I_xO_y Isomers and Ancillary Species

species	G2(ZPE=MP2)/au[a]	$\Delta_f H_0$/kJ mol^{-1}	$\Delta_f H_{298}$/kJ mol^{-1}	$H_{298} - H_0$/kJ mol^{-1}	$C_{p,298}$/J K^{-1} mol^{-1}	S_{298}/J K^{-1} mol^{-1}
OIO	−7067.153 93	80.4	76.7	11.6	45.9	279.9
IOO	−7067.141 74[b]	104.1	96.6	13.4	49.4	308.4
IIO	−13909.094 78	138.2	134.1	13.4	51.2	317.8
IOI	−13909.110 48	97.0	92.4	12.9	51.6	306.5
IOOI	−13984.162 87	162.7	156.8	16.1	69.8	337.0
IIO_2	−13984.183 41	108.7	103.0	16.2	67.6	339.9
IOIO	−13984.175 57	129.3	124.2	16.8	70.1	349.7
OIIO	−13984.138 04	227.8	224.0	18.0	70.0	356.3
OIO^- [c]	−7067.249 06		−171.9	11.7		
$OClO^-$ [d]	−609.916 34		−111.9[e]	11.1		
IO[f]	−6992.058 05	117.8[g]	115.9[g]	9.0[h]		239.6[h]
ClO[i]	−534.757 90		102.1[j]	9.5[h]		
H_2O_2	−151.369 17	−129.9[h]				
H_2O	−76.333 27	−238.9[h]				
HOI	−6992.719 57	−64.9[k]				

[a] 1 au ≈ 2625 kJ mol^{-1}. Calculated at MP2=FC/6-311+G(3df,2p) geometries with zero-point energies at MP2=FC/6-31G(d). [b] Unscaled B3LYP/6-311G(d) frequencies used. [c] Bond length 1.858×10^{-10} m and angle 109.4°. Ion convention used for thermochemistry. [d] Bond length 1.549×10^{-10} m and angle 113.8°. Ion convention used for thermochemistry. [e] References 17 and 19. [f] Bond length 1.888×10^{-10} m, frequency 724 cm^{-1} and includes an empirical spin−orbit correction of −0.00476 au (half the experimental $^2\Pi_{3/2} - {}^2\Pi_{1/2}$ splitting). [g] Reference 18. [h] Reference 15. [i] Bond length 1.549×10^{-10} m, frequency 825 cm^{-1} and includes an empirical spin−orbit correction of −0.00072 au (half the experimental $^2\Pi_{3/2} - {}^2\Pi_{1/2}$ splitting). [j] Reference 19. [k] Reference 14.

species was located at the MP2=FULL/6-31G(d) level of theory, although a very loose adduct with $r(I-O) = 2.870 \times 10^{-10}$ m was found using density functional theory (B3LYP/6-311G(d)). As seen on Figure 1, use of MP2=FC/6-311+G(3df) theory led to an even greater I−O distance, and at the G2 level IOO appears to be bound by only 3.1 kJ mol^{-1} relative to I + O_2 at 0 K. This binding energy is probably not very accurate. There is significant spin contamination ($\langle S^2 \rangle = 1.60$) in the IOO wavefunction and a possibility of basis set superposition error. A crude estimate of the latter effect was obtained via the counterpoise method at the HF/6-311+G(3df,2p) level, where it was found that the I and O_2 fragments were stabilized by 1.6 kJ mol^{-1} when their energies were evaluated with the combined IOO basis functions. Clearly the interaction between I and O_2 is weak. The I−O distance approximately equals the sum of the I and O van der Waals radii and is consistent with the speculation by Maier and Bothur that IOO might be described as a complex between I and O_2.[7] However, it is not clear that such a weak interaction could perturb the I and O_2 orbitals sufficiently to yield the observed UV spectrum. Another, as yet unidentified, species may be involved. Further evidence that I and O_2 do not bond strongly comes from the kinetics of I atom recombination in the presence of various buffer gases, M. If I and O_2 bonded readily at room temperature, as do I and NO, then the rate of recombination would be dramatically enhanced via the radical complex mechanism

$$I + M \rightleftharpoons IM$$

$$I + IM \rightarrow I_2 + M$$

At room temperature, the collision efficiencies for I atom recombination in the presence of M = Ar, O_2, and NO are in the approximate ratio $1:2:10^4$,[23] indicating no special enhancement by oxygen (unlike NO), and thus that IOO is not easily formed. The NIST-JANAF empirically estimated $\Delta_f H_{298}$ for IOO is 116.5 ± 40 kJ mol^{-1},[5] in accord with but 20 kJ mol^{-1} more positive than our estimate in Table 3. For OIO the empirical NIST-JANAF[5] $\Delta_f H_{298}$ of 159.3 ± 25 kJ mol^{-1} lies 80 kJ mol^{-1} above our ab initio value, which we believe to be more accurate. In particular, our calculations show that OIO is stable with respect to I + O_2. The $\langle S^2 \rangle$ values for ClO and IO were 0.77 and 0.78, respectively, so that spin contamination has a negligible impact on the energy of reaction 3.

The OI−O bond dissociation enthalpy at 298 K derived via $\Delta_f H_{298}(IO)$[18] is 288 kJ mol^{-1}, a value which implies that OIO could be formed exothermically by abstraction reactions of IO with several atmospheric oxidants including O_3, HO_2, N_2O, and NO_3. Such reactions may have significant barriers, and it is noted that the reactions of IO with O_3 and N_2O are very slow.[24] Oxygen atom abstraction from NO_2 is endothermic by 18 kJ mol^{-1} at 298 K.

3.2. I_2O Species.

Two isomers are illustrated in Figure 1. Because I−O bonds are stronger than I−I bonds, the IOI isomer is more stable than the IIO configuration. There are no measurements on these molecules to compare with our calculations, although the NIST-JANAF tables contain empirical estimates.[5] The frequencies and geometry are close to our computed values, while the ab initio values of $\Delta_f H_{298}$ for IOI and IIO (Table 3) lie near the lower and upper limits of the empirical estimates of 119.5 ± 25 and 106.7 ± 40 kJ mol^{-1}, respectively.[5] The NIST-JANAF tables assign the ground state of IIO as a triplet,[5] in disagreement with our calculations. At the singlet A′ IIO geometry, the lowest lying triplet state, A″, is found at the QCISD(T)/6-311G(d) level to lie 124 kJ mol^{-1} above the singlet state. This discrepancy accounts for much of the 13 J K^{-1} mol^{-1} difference between our entropy (Table 3) and the published value.[5] We were unable to locate a $^3A''$ minimum at the HF/6-31G(d) level, and this state may not be bound.

3.3. I_2O_2 Species.

Four bound isomers are illustrated in Figure 2, and the relative stabilities are shown in Figure 3. The most stable isomer is IIO_2, which has a pair of the shortest I−O bonds found in this study, $r(I-O) = 1.78 \times 10^{-10}$ m, and the highest I−O stretching frequencies of about 960 cm^{-1}, suggesting that these may be double bonds. The iodinated analog of hydrogen peroxide, IOOI, presumably has single I−O bonds, and $r(I-O) = 2.04 \times 10^{-10}$ m with lower I−O stretching frequencies of about 510 cm^{-1}. Many of the I−O bond lengths and frequencies here fall between these limits, suggesting partial multiple bond character in these iodine oxides.

There appear to be no literature data for these oxides, although they have been discussed in the context of the kinetics of the IO + IO self reaction

$$IO + IO \rightarrow \text{products} \tag{4}$$

which have been measured several times, with IO generation

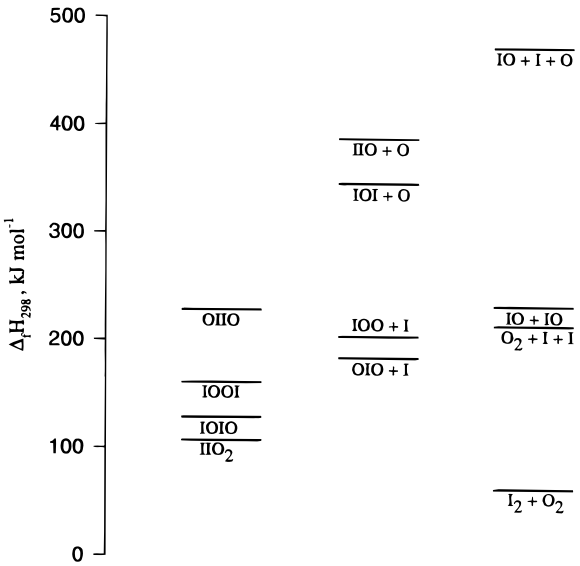

Figure 3. Enthalpies of formation of combinations of two oxygen and two iodine atoms at 298 K.

TABLE 4: Estimated Arrhenius Parameters for Dissociation Reactions at the High-Pressure Limit at 298 K

reaction	A/s^{-1}	E_a/kJ mol^{-1}
$IOIO \rightarrow 2\ IO$	3.8×10^{16}	110.1
$IOIO \rightarrow I + OIO$	4.2×10^{15}	61.8
$IIO_2 \rightarrow I + OIO$	1.4×10^{16}	77.3

from the reactions $I + O_3$, $O + I_2$, and $O + CF_3I$.[3,25–30] The possible products $I_2 + O_2$ and $I + I + O_2$ are thermodynamically accessible but their contributions have been found to be small.[3,28] As seen in Figure 3, the four I_2O_2 isomers are thermodynamically plausible products of reaction 4. Formation of IIO_2 would require extensive bond rearrangement, but the next most stable species, IOIO, can be formed in an initially excited state by direct IO + IO addition. Excited IOIO* may either be stabilized by collision with the bath gas M, or may fragment, and the most stable fragmentation products are OIO + I:

$$IO + IO \rightleftharpoons IOIO^* \rightarrow OIO + I$$

$$(+M) \rightarrow IOIO\ (+\ M)$$

A QRRK analysis[31,32] of these competing pathways was carried out with assumed Lennard–Jones parameters for IOIO of $\sigma = 5 \times 10^{-10}$ m and $\epsilon/k_B = 500$ K. A rate constant for radical + radical reactions forming excited intermediates (i.e., the high-pressure limiting value) of 10^{-10} molecule^{-1} cm^3 s^{-1} was employed, which is roughly equal to the rate constants measured for IO + IO, O + IO, and $O + I_2$.[28] The Arrhenius parameters employed for the unimolecular dissociation steps at 298 K are listed in Table 4 and were derived as follows. Activation energies for dissociation steps were set equal to the endothermicity plus RT, and the pre-exponential factors were derived from microscopic reversibility and equilibrium constants on the basis of our computed enthalpy and entropy changes. The QRRK analysis indicates that, for pressures of up to 1 bar of N_2 bath gas, the dominant channel at 298 K will be the pressure-independent formation of OIO + I, unless there is a significant barrier to fragmentation of IOIO beyond the endothermicity. Preliminary searches of the B3LYP/6-31G(d) potential energy surface did not reveal such a barrier.

The species IOOI and OIIO are also possible products, but are less tightly bound than IOIO because of their weak central bonds, and at room temperature are not stable sinks for IO + IO. Any initially excited IOOI formed from IO + IO recombination is likely to decompose immediately to I + IOO and, as indicated above, IOO is weakly bound, so that IOOI might provide a path for a $2I + O_2$ product channel.

IOIO could be formed via

$$OIO + I + N_2 \rightarrow IOIO + N_2 \qquad (5)$$

The predicted kinetics are close to third order for up to 1 bar of N_2 at 298 K, and the predicted rate constant is 7.6×10^{-32} molecule^{-2} cm^6 s^{-1}. Changing the I–OIO bond strength at 298 K of 59 kJ mol^{-1} by ±15 kJ mol^{-1} changes k_5 by about a factor of 3, which is an approximate measure of the uncertainty in this rate constant arising from the thermochemistry. At 1 bar of N_2 the lifetime of IOIO with respect to dissociation to OIO + I is predicted to be about 1 ms, so IOIO is hardly stable at ambient conditions, although of course its lifetime will increase at lower temperatures and lower pressures. The channel

$$IOIO + N_2 \rightarrow IO + IO + N_2 \qquad (6)$$

is predicted to show second-order kinetics for N_2 of up to 1 bar, with $k_6 = 2.1 \times 10^{-24}$ molecule^{-1} cm^3 s^{-1}. Variation of the IO–IO bond strength of 108 kJ mol^{-1} by ±15 kJ mol^{-1} leads to changes of a factor of 2 in k_6. The corresponding reverse rate constant k_{-6} is 1.1×10^{-31} molecule^{-2} cm^6 s^{-1}. This compares reasonably with the apparent low-pressure limiting recombination rate constant obtained by Jenkin and Cox[27] of about $(4 \pm 2) \times 10^{-31}$ molecule^{-2} cm^6 s^{-1}. However, they observed significant fall-off at 0.5 bar, not reproduced in our calculations.

Our analysis of reaction 4 suggests that k_4 should be pressure-independent and that significant products are I + OIO. Consistent with these products, Vipond and Wayne have found high yields of I atoms (around 0.5–0.8) from IO + IO chemistry in a flow tube at about 2.6 mbar pressure.[33] Such low pressures tend to favor dissociation over adduct stabilization. The predicted pressure-independence is consistent with the measurements by Laszlo et al.[28] and Harwood et al.[29] obtained in the absence of ozone. If IOIO was a major product, then k_4 would be pressure-dependent. The situation is more complicated in the presence of ozone. Himmelmann et al.[6] observed OIO following the generation of I atoms in the presence of O_3, which will react to form $IO + O_2$, and noted that OIO might be formed by reaction 4 or by the reaction

$$IO + O_3 \rightarrow OIO + O_2 \qquad (7)$$

Harwood et al.[29] suggested that k_7 is small, as observed by Gilles,[24] which would support our proposal that reaction 4 is a source of OIO. A pressure dependence of k_4 in ozone-containing systems has been attributed to formation of a stabilized I_2O_2 adduct.[3,27] If instead I + OIO were the main products of reaction 4, then reaction of I with O_3 would be expected to cycle the I atoms back to IO, so that the observed k_4 would be halved in the presence of excess O_3. The ratio observed by Sander[3] was around 0.56–0.83, depending on the pressure, very roughly in line with our expectations. We cannot explain the pressure dependence observed in the presence of ozone, but we do note that Laszlo et al.[28] observed complex kinetics under such conditions, and we speculate that in the presence of ozone there may be secondary chemistry which is not yet understood.

Our interpretation of the IO self-reaction can be contrasted to measurements for ClO + ClO. In the latter case termolecular recombination dominates over bimolecular processes at pressures above 13 mbar,[19] which reflects the different thermochemistry: disproportionation to Cl + OClO is endothermic by 11.3 ± 4.2 kJ mol^{-1},[19] rather than exothermic as proposed here for IO + IO → I + OIO.

We point out that an alternative to reaction 5 for the reaction of I with OIO is

$$\mathrm{OIO} + \mathrm{I} + \mathrm{N_2} \rightarrow \mathrm{IIO_2} + \mathrm{N_2} \qquad (8)$$

The higher frequencies of IIO_2 lead to smaller densities of states at a given energy than for IOIO, which more than offsets the greater $\mathrm{I{-}IO_2}$ adduct formation enthalpy of 75 kJ mol^{-1}, so that k_8 is predicted to be about half k_5, at 4.0×10^{-32} molecule^{-2} cm^6 s^{-1}. Changing the $\mathrm{I{-}IO_2}$ bond strength by ±15 kJ mol^{-1} changes k_8 by a factor of 3. The lifetime of IIO_2 with respect to the reverse of reaction 8 is predicted to be around 4 s at ambient conditions. This is the most stable of the I_2O_2 isomers, but is still only barely so under ambient conditions. In experiments with significant concentrations of atomic I, molecular iodine might be formed via the abstraction reactions

$$\mathrm{I} + \mathrm{IOIO} \rightarrow \mathrm{I_2} + \mathrm{OIO}$$

$$\mathrm{I} + \mathrm{IIO_2} \rightarrow \mathrm{I_2} + \mathrm{OIO}$$

These processes potentially complete pathways for reformation of I_2 from I,[34] and our thermochemistry indicates that both are exothermic.

Conclusions

Isomers of IO_2, I_2O, and I_2O_2 have been characterized by ab initio methods. For the first time, structural information is presented for these species, as well as vibrational frequencies, and their thermochemistry has been derived using G2 energies coupled with isodesmic reactions. There are no measurements of the heats of formation for these molecules, and the present work exhibits some significant differences from recent empirical estimates. The results are employed to interpret the kinetics of the IO + IO reaction, and OIO is likely to be a significant product. Potential further reactions of I with OIO are also discussed.

Note Added in Proof. Cox and co-workers have recently investigated the IO + IO reaction by time-resolved UV absorption spectroscopy and found that OIO is a significant product, with no evidence for formation of a stabilized I_2O_2 adduct.[35]

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References and Notes

(1) Solomon, S.; Garcia, R. R.; Ravishankara, A. R. *J. Geophys. Res. D* **1994**, *99*, 20491.

(2) Solomon, S.; Burkholder, J. B.; Ravishankara, A. R.; Garcia, R. R. *J. Geophys. Res. D* **1994**, *99*, 20929.

(3) Sander, S. P. *J. Phys. Chem.* **1986**, *90*, 2194.

(4) Zolotarev, V. A.; Ishkov, D. V.; Podmar'kov, Y. P.; Frolov, M. P.; Yuryshev, N. N. *Sov. J. Quantum Electron.* **1991**, *21*, 826.

(5) Chase, M. W. *J. Phys. Chem. Ref Data* **1996**, *25*, 1297.

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

(7) Maier, G.; Bothur, A. *Chem. Ber./Recueil* **1997**, *130*, 179.

(8) Tapscott, R. E.; Skaggs, S. R.; Dierdorf, D. In *Halon Replacements: Technology and Science*; Tsang, W.; Miziolek, A. W., Eds.; ACS Symp. Ser. 611; American Chemical Society: Washington, DC, 1995; Chapter 14.

(9) Misra, A.; Sees, J.; Hall, L.; Levy, R. A.; Zaitsev, V. B.; Aryusook, K.; Ravindranath, C.; Sigal, V.; Kesari, S.; Rufin, D. *Mater. Lett.* **1998**, *34*, 415.

(10) Fracassi F.; d'Augustino, R.; Stenardo, M.; Atzei, L. R.; Illuzi, F. Environmental Impact of Fluorocarbon and Iodofluorocarbon Containing Glow Discharges for SiO_2 Etching. *Proceedings of the Fourth International ESH Conference*; Milan, Italy, 1997; Vol. 1.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(12) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(13) Glukhovtsev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. *J. Chem Phys.* **1995**, *103*, 1878.

(14) Misra, A.; Marshall, P. *J. Chem Soc., Faraday Trans.* **1997**, *93*, 3301.

(15) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B., Eds. *Thermodynamic Properties of Individual Substances Vol. I*, 4th ed.; Hemisphere: New York, 1989.

(16) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1995**, *103*, 4192.

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

(18) Bedjanian, Y.; Le Bras, G.; Poulet, G. *J. Phys. Chem. A* **1997**, *101*, 4088.

(19) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation Number 12, JPL Publication 97-4; Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 1997.

(20) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref Data* **1988**, *17;* Suppl. 1, *Gas-Phase Ion and Neutral Thermochemistry*.

(21) Berry, R. J.; Yuan, J.; Misra, A.; Marshall, P. *J. Phys. Chem. A* **1998**, *102*, 5182.

(22) Hassanzadeh, P.; Irikura, K. K. *J. Phys. Chem. A.* **1997**, *101*, 1580.

(23) Baulch, D. L.; Duxbury, J.; Grant, S. J.; Montague, D. C. *J. Phys. Chem. Ref. Data* **1981**, *10*; Suppl. 1, *Evaluated Kinetic Data for High-Temperature Reactions Vol. 4.*

(24) Gilles, M. K. Personal communication, 1998.

(25) Clyne, M. A. A.; Cruse, H. W. *Trans. Faraday Soc.* **1970**, *66,* 2227.

(26) Cox, R. A.; Coker, G. B. *J. Phys. Chem.* **1983**, *87,* 4478.

(27) Jenkin, M. E.; Cox, R. A. *J. Phys. Chem.* **1985**, *89,* 192.

(28) Laszlo, B.; Kurylo, M. J.; Huie, R. E. *J. Phys. Chem.* **1995**, *99*, 11701.

(29) Harwood, M. H.; Burkholder, J. B.; Hunter, M.; Fox, R. W.; Ravishankara, A. R. *J. Phys. Chem. A.* **1997**, *101*, 853.

(30) Stickel, R. E.; Hynes, A. J.; Bradshaw, J. D.; Chameides, W. L.; Davis, D. D. *J. Phys. Chem.* **1988**, *92*, 1862.

(31) Dean, A. M. *J. Phys. Chem.* **1985**, *89,* 4600.

(32) Westmoreland, P. R. BI_QRRK computer program, 1993.

(33) Vipond, A. Personal communication, 1998.

(34) Spietz, P. Personal communication, 1998.

(35) Bloss, W. J.; Rowley, D. M.; Cox, R. A.; Jones, R. L. Kinetic Studies of Iodine Oxide Reactions of Atmospheric Importance. *15th International Symposium on Gas Kinetics*, Bilbao, Spain, 1998; Posters A45/A46.