Computational studies of the isomers of ClIO and ClIO₂

Implications for the stratospheric chemistry of iodine

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The geometries of three ClIO isomers and five ClIO₂ isomers have been computed at the MP2 = fc/6-311 + G(3df) level of theory. MP2 = full/6-31G(d) vibrational frequencies were computed. Gaussian-2 energies and isodesmic reactions were employed to derive $\Delta_f H_{298}$ for ClIO, ClOI, ICIO, ClIO₂, ClOIO, ClOOI, IOClO and ICIO₂ of 74.7, 82.5, 172.4, 17.0, 113.5, 132.0, 159.9 and 189.8 kJ mol⁻¹, respectively. These results were used to assess likely products of the IO + ClO reaction: there are both indirect pathways to I + ClO₂ *via* bound intermediates, and a direct path *via* abstraction. The other products which are exothermic and capable of being formed without complex rearrangements are ClOIO, ClOOI and OClOI.

Introduction

Iodine compounds, such as iodomethane, are thought to be emitted into the atmosphere from several natural sources, including oceanic plankton¹ and combustion of terrestrial biomass.² There are also potential anthropogenic sources of iodine that reflect the growing interest in the use of iodofluorocarbons as ozone-friendly, non-global-warming substitutes for other halocarbons. Two applications are as possible replacements for CF₃Br as a fire extinguishing agent,³ and as a replacement for CF₄ and C₂F₆ in plasma etching and chamber cleaning during the processing of silicon wafers.^{4,5}

Platt and Janssen recently reviewed the tropospheric chemistry of iodine and other halogens,⁶ while Ravishankara and co-workers analyzed the stratospheric chemistry of iodine.^{2,7} The latter authors proposed that rapid convection within tropical storms might transport tropospheric CH₃I and similar compounds into the stratosphere before they are photolyzed. Even small quantities of iodine may have a significant effect on stratospheric ozone chemistry, through acceleration of the chlorine–ozone cycle *via* the mechanism:

The products of reaction (3) were not then known experimentally. Solomon *et al.*² noted that the cycle would be closed if the products were Cl + I + O₂, or if ClOO or ICl were formed and then decomposed rapidly to halogen atoms. Reaction (3) was responsible for most of the ozone destruction modeled in the lower stratosphere at mid-latitudes.²

The goal of the present work is to characterize three- and four-atom ICIO_x (*x* = 1 or 2) species that might be intermediates or final products of reaction (3). None of these molecules have been detected experimentally and it is hoped that the computed geometries and vibrational frequencies may assist in their identification by rovibrational spectroscopy. Their thermochemistry is derived by a combination of *ab initio* analysis and isodesmic reactions, and the results allow discussion of likely products for reaction (3).

Methodology

All computations were made with the Gaussian 94 program suite.⁸ Gaussian-2 (G2) theory,⁹ as extended to iodine-containing species by Glukhovtsev *et al.*,¹⁰ was applied to ICIO_x. All-electron basis sets were employed in non-relativistic calculations. Earlier good accord with experimental results suggests that relativistic effects are either small or cancel.¹⁰ 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, this is clearly not the case for a test molecule, IO (see Table 1), which has been the subject of experimental¹¹ and computational studies.^{12,13} With a larger 6-311G(d,p) basis set a variety of computational levels, including QCISD and density functional theory (DFT), also yield poor results for the bond length. Only the largest 6-311 + G(3df) basis set yields good accord, and here we have employed MP2 = fc/6-311 + G(3df) calculations for the geometries. Unfortunately, frequency calculations at this level were prohibitively expensive. Table 1 shows that the MP2 = full/6-31G(d) wavenumber scaled by a standard factor¹⁴ of 0.9646 yielded reasonable

Table 1 IO bond length and frequency at various levels of theory

bond length /10 ⁻¹⁰ m	wavenumber /cm ⁻¹	method
1.868	673	experiment ^a
1.992	432	HF/6-31G(d), frequency scaled by 0.8929
1.939	718	MP2 = full/6-31G(d), frequency scaled by 0.9646
1.964	617	QCISD/6-31G(d)
2.005	376	HF/6-311G(d,p)
1.939	745	MP2 = full/6-311G(d,p)
1.952	641	B3LYP/6-311G(d,p)
1.964	594	QCISD/6-311G(d,p)
1.902	663	B3LYP/6-311 + G(3df)
1.899	671	QCISD/6-311 + G(3df) ^b
1.900	644	QCISD(T)/6-311 + G(3df) ^b
1.888	—	MP2 = fc/6-311 + G(3df)

^a Ref. 11. ^b Ref. 12.

Fig. 1 Geometries of ClIO isomers computed at the MP2 = fc/6-311 + G(3df) level of theory. Distances in 10^{-10} m and angles in degrees. 1 ClOI, 2 ICIO, 3 ClIO.

Fig. 2 Geometries of ClIO₂ isomers computed at the MP2 = fc/6-311 + G(3df) level of theory. Distances in 10^{-10} m and angles in degrees. 1 ClOOI (dihedral angle 84.6°), 2 planar IOClO, 3 ICIO₂, 4 ClIOO, 5 ClOIO (dihedral angle 77.3°).

Table 2 Frequencies of ICIO_x isomers at the MP2 = full/6-31G(d) level (scaled by 0.9646)

species	wavenumber/cm ⁻¹
ClOOI	88, 240, 387, 523, 630, 738
IOClO	161, 210, 332, 631, 740, 885
ICIO ₂	97, 134, 287, 463, 1156, 1285
ClIO ₂	161, 204, 293, 299, 960, 979
ClOIO	79, 177, 218, 444, 669, 939
ICIO	102, 217, 1242
ClOI	204, 500, 688
ClIO	165, 293, 935

Table 3 Energies of ClIO_x isomers

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
ClIO	-7451.80534	77.4	74.7	12.8
ClOI	-7451.80218	85.7	82.5	12.3
ICIO	-7451.76832	174.6	172.4	13.3
ClIO ₂	-7526.90196	21.4	17.0	15.5
ClOIO	-7526.86547	117.2	113.4	16.1
ClOOI	-7526.85809	136.6	132.0	15.2
IOClO	-7526.84726	165.0	159.9	14.8
ICIO ₂	-7526.83617	194.1	189.8	15.5

^a 1 au $\approx$ 2625 kJ mol⁻¹.

accord with the measured IO wavenumber. We therefore picked MP2 = full/6-31G(d) as a level of theory for which frequency calculations were computationally affordable, yet reliable. As a further test, we note that at this level the computed I—O stretching wavenumbers for CH₃IO and CH₃OI are 782 and 526 cm⁻¹. These values are in reasonable agreement with the measured values of 724 and 528 cm⁻¹.¹⁵ At present there are few experimental data to check the reliability of low frequency bending involving I—O bonds.

Next, a series of calculations were carried out at each 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.*¹⁴ The only modification of their procedure here is the use of geometries obtained with a larger basis set. Inclusion of zero-point energy yields relative enthalpies at 0 K. The vibrational frequencies were also employed to calculate enthalpy corrections to 298 K, $H_{298} - H_0$.

Results

The geometries of three ClIO isomers are shown in Fig. 1, and five ClIO₂ isomers are shown in Fig. 2. Other initial geometries tested, which did not lead to new minima at HF/6-31G(d) or MP2 = full/6-31G(d) levels of theory, were IOClO, OOI(Cl), ICIOO and ClIOO. OCIO yielded a minimum at MP2 = full/6-31G(d) theory but not at MP2 = fc/6-311 + G(3df). The corresponding vibrational frequencies are summarized in Table 2. The absolute G2(ZPE = MP2) energies are listed in Table 3, together with the *ab initio* $H_{298} - H_0$ values and the enthalpies of formation (see below).

Discussion

ClIO isomers

The *ab initio* ΔH_0 for the isodesmic reaction

was combined with literature $\Delta_f H_0$ values¹⁶ for H₂O, HOCl and HOI¹⁷ to obtain the value of $\Delta_f H_0(\text{ClOI})$ given in Table 3. Relative G2 energies yield values of $\Delta_f H_0$ for ICIO and ClIO, which are expected to be accurate to within about 10 kJ mol⁻¹. This uncertainty includes an allowance for uncertainty in the thermochemical input parameters, especially HOI. The *ab initio* $H_{298} - H_0$ data, combined with values for the elements in their standard states,¹⁶ then yield $\Delta_f H_{298}$ for the ClIO isomers given in Table 3. The least stable isomer is ICIO, as might be expected by analogy with the ClBrO isomers, where Lee found BrClO to be the least stable form.¹⁸ A difference is that ClIO is predicted to be more stable than ClOI, a reversal of the earlier order for the bromine analogues. This may reflect a role for multiple I—O bonding: the

is indeed a dominant product of reaction (3). These experiments also suggest a significant role for another product channel, $\text{ICl} + \text{O}_2$, which as shown on Fig. 3 is highly exothermic, as well as the $\text{I} + \text{Cl} + \text{O}_2$ channel.

Conclusions

Ab initio methods have been used to characterize the geometries, vibrational frequencies and enthalpies of formation of isomers of ClIO and ClIO_2 . The results were used to investigate possible products of the $\text{IO} + \text{ClO}$ reaction. There are both indirect pathways from $\text{IO} + \text{ClO}$ to $\text{I} + \text{ClO}_2$ via bound intermediates, and a direct path via abstraction. The other products which are exothermic and capable of being formed without complex rearrangements are ClOIO , ClOOI and OCIOI . Because of the fairly low bond strengths within these adducts, we speculate that they may easily photolyze to release atomic halogens. ClOOI and OCIOI can decompose to $\text{I} + \text{ClO}_2$. To the extent that these compounds act as sinks for iodine or lead to OCIO , they will reduce the effectiveness of the ozone destruction cycle (1)–(3).

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