Computational studies of the isomers of ClO and ClIO₂
Implications for the stratospheric chemistry of iodine

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The geometries of three ClO 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 $\Delta H_{298}$ for ClO, ClO₂, ICIO, ClOO₂-, ClOIO₂, ClOIO, JOCIO and ICIO₂ of 74.7, 82.5, 172.4, 170.0, 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 ClOIO₂, ClOIO and OCIOI.

Introduction

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

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

\[
\begin{align*}
Cl + O₃ &\rightarrow ClO + O₂ \quad (1) \\
I + O₃ &\rightarrow IO + O₂ \quad (2) \\
ClO + IO &\rightarrow \text{products} \quad (3)
\end{align*}
\]

The products of reaction (3) were not then known experimentally. Solomon et al. noted that the cycle would be closed if the products were Cl + I + O₂, or if ClOIO or ClO could be 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.

The goal of the present work is to characterize three- and four-atom IClOₓ (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, as extended to iodoine-containing species by Glikhovets et al., and applied to IClO₂. 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. The first steps in standard geometry are to compute the geometry at 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 experimental and computational studies. 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 factor of 0.9646 yielded reasonable agreement.

<table>
<thead>
<tr>
<th>bond length /Å</th>
<th>wavenumber /cm⁻¹</th>
<th>method</th>
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<tbody>
<tr>
<td>1.868</td>
<td>673</td>
<td>experiment²</td>
</tr>
<tr>
<td>1.992</td>
<td>432</td>
<td>HF/6-31G(d), frequency scaled by 0.8929</td>
</tr>
<tr>
<td>1.939</td>
<td>718</td>
<td>MP2 = full/6-31G(d), frequency scaled by 0.9646</td>
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<tr>
<td>1.964</td>
<td>617</td>
<td>QCISD/6-31G(d)</td>
</tr>
<tr>
<td>2.005</td>
<td>376</td>
<td>HF/6-31G(d,p)</td>
</tr>
<tr>
<td>1.939</td>
<td>745</td>
<td>MP2 = full/6-31G(d,p)</td>
</tr>
<tr>
<td>1.952</td>
<td>641</td>
<td>B3LYP/6-31G(d,p)</td>
</tr>
<tr>
<td>1.964</td>
<td>594</td>
<td>QCISD/6-31G(d,p)</td>
</tr>
<tr>
<td>1.902</td>
<td>663</td>
<td>B3LYP/6-311 + G(3df)</td>
</tr>
<tr>
<td>1.899</td>
<td>671</td>
<td>QCISD/6-311 + G(3df)²</td>
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<tr>
<td>1.900</td>
<td>644</td>
<td>MP2 = fc/6-311 + G(3df)</td>
</tr>
<tr>
<td>1.888</td>
<td></td>
<td></td>
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² Ref. 11. Ref. 12.

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. 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 G2ZPE = MP2) methodology of Curtiss et al. 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 CIO isomers are shown in Fig. 1, and five CIO₂ 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 IOCI, OIOI(CI), IOOIO, and IOO(O). The CH₃I molecule posed a minimum at MP2 = full/6-31G(d) theory but not at MP2 = full/6-311+G(3df). The corresponding vibrational frequencies are summarized in Table 2. The absolute G2ZPE = 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

**CIO isomers**

The ab initio $\Delta H_0$ for the isodesmic reaction

$$\text{ClO} + \text{H}_2\text{O} \rightarrow \text{HOI} + \text{HOCI}$$  \hspace{1cm} (4)

was combined with literature $\Delta H_0$ values for $\text{H}_2\text{O}$, HOCI and HOI to obtain the value of $\Delta H_0^{\text{ClO}}$ given in Table 3. Relative G2 energies yield values of $\Delta H_0$ for IClO and ClO₂, 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, then yield $\Delta H_{298}$ for the CIO isomers given in Table 3. The least stable isomer is IClO₂, as might be expected by analogy with the CIBRO isomers, where Lee found BrCIO₂ to be the least stable form. A difference is that CIO is predicted to be more stable than CIO₂, a reversal of the earlier order for the bromine analogues. This may reflect a role for multiple I−O bonding: the
I–O distance in CIIO of about 1.81 \times 10^{-10} \text{ m} is significantly less than the distance of 2.02 \times 10^{-10} \text{ m} in CIIO.

**ClO₂** isomers

The \( \Delta_H_{d} (\text{ClOOI}) \) was assessed via the isosmotic reaction

\[
\text{ClOOI} + 2\text{H}_2\text{O} \rightarrow \text{HOI} + \text{HOCI} + \text{HOOH} \quad (5)
\]

and relative G2 energies were then employed to obtain \( \Delta H_{d} \) for the other four isomers considered here. As for the triatomic species, \( \text{ab initio} \) \( \Delta H_{298} \) data were used to derive \( \Delta H_{d} \) (Table 3). The most stable isomer is predicted to be hypervalent CIOO₂, and it is noteworthy that this isomer has a pair of especially short I–O bonds, only 1.77 \times 10^{-10} \text{ m} long. The next most stable isomer, ClOIO, has one such short bond and another 2.02 \times 10^{-10} \text{ m} long. IOOCI is the halogenated analogue of hydrogen peroxide. Lack of hypervalency here suggests that a ‘regular’ I–O single bond length is about 2.04 \times 10^{-10} \text{ m}, and provides a baseline for comparison with IO distances in other molecules. The cyclic IOClO species exhibits very long I–O and Cl–O bonds, and might be viewed as an adduct between IO and ClO. The least stable isomer is ClOClO₂, which contains no IO bonds and an I–Cl separation of about 2.71 \times 10^{-10} \text{ m}, long compared to the separation of 2.33 \times 10^{-10} \text{ m} in diatomic ICl.\(^{16}\) This last species could be viewed as an adduct between atomic iodine and OCIO.

**Implications for the IO + ClO reaction**

Fig. 3 shows the thermochemistry of ClO₂ computed here together with information for other Cl–I–O species (Table 4).\(^{16,17,19,22}\) The solid lines connect species that can be interconverted by breaking or making one bond, i.e., without complex rearrangements. Transition states have not been characterized and therefore some of the exothermic pathways could be blocked by significant barriers. However, consideration of the thermochemistry alone allows the variety of possible products to be narrowed. Endothermic processes must have significant activation energies and therefore will be less significant under stratospheric conditions.

Reaction (3) could be viewed as a direct abstraction. For this case, the possible products are shown on the left hand side of Fig. 3, and this figure reveals that the only exothermic products are I + ClO₂ (OCIO and ClOIO have similar thermochemistry).\(^{29}\)

![Fig. 3 Enthalpies of formation of Cl–I–O–O species at 298 K (see Tables 3 and 4)](image)

**Table 4 Literature thermochemistry of Cl–I–O species**

<table>
<thead>
<tr>
<th>species</th>
<th>( \Delta H_{298} )(^{\text{a}} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>106.8(^{\text{a}})</td>
</tr>
<tr>
<td>ClO</td>
<td>96.2(^{\text{b}})</td>
</tr>
<tr>
<td>O</td>
<td>249.2(^{\text{a}})</td>
</tr>
<tr>
<td>ClO₂</td>
<td>96.2(^{\text{b}})</td>
</tr>
<tr>
<td>Cl</td>
<td>120.9(^{\text{b}})</td>
</tr>
<tr>
<td>Cl₂</td>
<td>102.1(^{\text{e}})</td>
</tr>
<tr>
<td>ClO₂</td>
<td>102.1(^{\text{e}})</td>
</tr>
<tr>
<td>ClOCl</td>
<td>17.5(^{\text{f}})</td>
</tr>
<tr>
<td>ClO₂</td>
<td>111.2(^{\text{f}})</td>
</tr>
<tr>
<td>ClOClO₂</td>
<td>-63.3(^{\text{g}})</td>
</tr>
</tbody>
</table>

\(^{a}\) Ref. 19, \(^{b}\) Ref. 17, \(^{c}\) Ref. 16, \(^{d}\) Ref. 20.

The three ClO₂ isomers are all highly endothermic with respect to IO + ClO and therefore are unlikely products of reaction (3). All the ClO₂ isomers are exothermic and are potential adducts of IO + ClO. The most strongly bound is ClO₂ itself, but formation of this structure requires a complex atom rearrangement, as does formation of ClOCl₂. ClOIO is the most favorable adduct that can be formed without breaking any bonds. Initially energized ClOIO could be collisionally stabilized or may fragment, by rupture of the Cl–O bond. This fragmentation is endothermic, so that ClOIO represents a potential final sink for IO + ClO. As a sink, it will inhibit the cycle of reactions (1)–(3) until it is decomposed, either photolytically or by reaction with other species. Fig. 3 indicates that I + Cl + O₂ are endothermic products of IO + ClO, and therefore that reaction (3) may not directly lead to a closed cycle. Entropy favors dissociation of ClOIO which could provide a path to I + Cl + O₂.

Our data permit a quantitative assessment of the channel

\[
\text{IO} + \text{ClO(+M)} \rightarrow \text{ClOIO(+M)} \quad (6)
\]

At 298 K the computed entropy for ClOIO is 329 J K\(^{-1}\) mol\(^{-1}\). In conjunction with literature entropies for ClO and IO\(^{11}\) this implies \( \Delta S_{298} = -136 \text{ J K}^{-1} \text{ mol}^{-1} \) for reaction (6). From Tables 3 and 4 and a recent determination of the thermochemistry of IO\(^{20}\), \( \Delta H_{298} = -106 \text{ kJ mol}^{-1} \). Thus the equilibrium constant at 298 K (for a standard state of 10\(^7\) Pa) is 3.5 \times 10\(^{11}\). On the assumption of a high-pressure limiting rate constant \( k_{0} \approx 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) for the association of the two radicals IO and ClO, the implied lifetime for dissociation of ClOIO to IO + ClO (the reciprocal of the reverse rate constant \( k_{a} \)) is of the order of 10\(^3\) s at 298 K. Therefore ClOIO is stable under atmospheric conditions. A quantum RRK analysis\(^{21,22}\) of reaction (6) indicates that at 10\(^5\) Pa and below, \( k_{b} \) would be close to the low-pressure limit with a third-order value of about 10\(^{-31}\) cm\(^6\) molecule\(^{-2}\) s\(^{-1}\). Competition between adduct formation and other channels may lead to a pressure- and temperature-dependent effectiveness of iodine as a promoter of chlorine-catalyzed ozone destruction.

We note that the direct abstraction products of reaction (3), I + ClO₂, can also be formed by addition/fragmentation reactions involving IOOCI and IOClO intermediates. Because energetically allowed fragmentation of the initially excited adducts is probably fast compared to collisional stabilization, IOOCI and IOClO are more likely to decompose to I + ClO₂ than be final products. If ClO₂ is a major product of reaction (3) then the impact of iodine on ozone depletion will be reduced. This is because the sequence

\[
\text{OCIO} + h\nu \rightarrow \text{ClO} + \text{O} \quad (7)
\]

\[
\text{O} + \text{O}_2 \rightarrow \text{O}_3 \quad (8)
\]

together with reactions (2) and (3) would then form a null cycle with no net loss of \( \text{O}_3 \). Very recent experiments by Turner et al.\(^{23}\) and Bedjanian et al.\(^{24}\) confirm that OCIO

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

\textit{Ab initio} methods have been used to characterize the geometries, vibrational frequencies and enthalpies of formation of isomers of CIO and ClO$_2$. The results were used to investigate possible products of the IO + CIO reaction. There are both indirect pathways from IO + CIO to I + 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 CIOI, CIOOI and OCIOI. Because of the fairly low bond strengths within these adducts, we speculate that they may easily photolyze to release atomic halogens. CIOOI and OCIOI can decompose to I + 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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References

17. A. Misra, PhD Dissertation, University of North Texas, 1997, $A(DR)$ was computed as $-85.2$ kJ mol$^{-1}$. For comparison, in ref. 13 a value of $-70.2$ kJ mol$^{-1}$ was derived.
22. P. R. Westmoreland, BLQRRK program, 1993. Assumed Lennard-Jones collision parameters for CIOI were $\sigma = 5 \times 10^{-10}$ m and $\epsilon/k_B = 500$ K. For N$_2$ bath gas the predicted $k_e$ is $(-1.7$ and $0.8) \times 10^{-30}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ at 200 and 298 K, respectively.