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Cox, RA; Bloss, William; Jones, RL; Rowley, DM

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OIO and the Atmospheric Cycle of Iodine

R.A. Cox, W.J. Bloss, R.L. Jones

Centre for Atmospheric Science, University Chemical Laboratory, University of Cambridge, UK

D.M. Rowley

Chemistry Department, University College London, UK

Abstract: IO and BrO radicals are intermediates in the atmospheric photo-oxidation of iodo- and bromocarbons and can act as catalysts for ozone loss. We have studied the kinetics and mechanisms of the reactions of IO with itself and with BrO to establish their role in the atmospheric chemistry of iodine. We have found that iodine dioxide, OIO, is produced in these reactions. The results of these and other experimental observations together with a recent computational study suggest an unexpectedly high photochemical stability for OIO. It is shown that OIO formation and its attachment to particles could account for the high enrichment of iodine in the small size fraction of marine aerosol, which is important for the transport of iodine from the sea to the continents. OIO may be a route to the formation of iodate, which is present in atmospheric precipitation. OIO formation also implies a reduced efficiency for iodine catalysed ozone loss.

Introduction

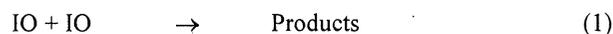
The atmospheric iodine cycle is composed of a major oceanic source in the form of volatile alkyl iodides, which undergo photochemical decomposition in the troposphere. The gaseous inorganic iodine species produced transfer to the atmospheric particulate or aerosol phase, and are subsequently removed by wet or dry deposition to the ocean or land [Moyers *et al.*, 1972; Cicerone, 1981].

Chameides and Davis [1980] first described the atmospheric photochemistry of iodine and drew attention to its potential role as a catalyst for tropospheric ozone loss. Photodissociation of alkyl iodides produces I atoms, which react rapidly with ambient ozone to form IO radicals. Reactions of I and IO with HO₂, IO and NO₂ lead to the formation of several photochemically unstable inorganic iodine species, the major component of which is predicted to be HOI [Jenkin, 1992; Davis *et al.*, 1996]. The recent direct spectroscopic observation of IO in the coastal atmosphere of western Ireland [Alicke *et al.*, 1998, 1999] provides strong support for the basic validity of this proposed mechanism. Solomon *et al.* [1994] have also proposed that iodine compounds may enter the lower stratosphere and lead to stratospheric ozone loss due to rapid catalytic cycles involving I and IO. In both regimes, the catalytic efficiency of iodine for ozone loss would be reduced by the transfer of iodine species to the particulate phase [Jenkin, 1993].

Measurements of inorganic iodine in the atmosphere show that both iodide, I⁻ and iodate, IO₃⁻ are present in atmospheric aerosols and in precipitation [Cicerone, 1981; Rancher and Kritz, 1980; Truesdale and Jones, 1996; Wimschneider and Heumann, 1995]. I/Na ratios in the small size fraction of the marine aerosol can be some 1000 times in excess of those found in sea water [Martins, 1973; Duce and Hoffman, 1976; Sturges and Barrie, 1988] indicating a significant net flux of inorganic iodine from the gaseous to the condensed phase. This is in direct contrast to aerosol Cl⁻ and Br⁻ which are often depleted relative to the X⁻/Na ratio in sea water.

There is little information available regarding the rates of the physical processes leading to the incorporation of specific I-containing molecules in the particulate phase. HOI may attach to aerosols, but because of its high reactivity with Cl⁻, iodine is expected to be released again to the gas phase as ICl [Vogt *et al.*, 1998; Crowley and Adams, 1998]. In the absence of any well defined loss process, it is currently assumed that the hitherto unidentified dimer of IO, I₂O₂, is predominantly responsible for transfer of IO_x to the condensed phase [Davis *et al.*, 1996; Jenkin, 1993, Vogt *et al.*, 1998].

In the course of our laboratory studies of the kinetics and mechanisms of the reactions



we have established that iodine dioxide, OIO, which has not previously been postulated as an atmospheric reservoir for iodine, is produced. We also found some indication for the formation of the I₂O₂ dimer of IO. Our experimental observations, together with recent computational studies of iodine oxides [Misra and Marshall, 1998] suggest an unexpectedly high photochemical stability for OIO.

Experimental Measurements

The laboratory measurements were performed using the technique of laser flash photolysis with kinetic UV-visible absorption spectroscopy employing a charged coupled device detection system [Rowley *et al.*, 1996; Harwood *et al.*, 1998]. Reaction initiation was achieved by 193 nm excimer laser photolysis of N₂O, giving N₂ and an excited oxygen atom, O(¹D), which was rapidly quenched to the ground state, O(³P) in the presence of 0.1-1.0 bar of N₂. For the IO self-reaction experiments, IO radicals were produced by reaction of O(³P) with I₂ or CF₃I, whilst for the BrO + IO reaction, IO and BrO radicals were formed by reaction of O(³P) with CF₃I, IBr and Br₂. Whilst CF₃I was employed as an IO precursor in recording the absorption cross sections of IO and OIO, this

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species was not used in experiments to determine the IO rate coefficients, due to additional radical loss processes involving CF_3 radicals.

Figure 1a shows characteristic spectra for the (A←X) transitions of BrO and IO, which were simultaneously recorded with a time resolution of $\sim 10 \mu\text{s}$. Figure 1b shows spectra in the visible region. In addition to the IO bands at wavelengths below 470 nm, a progression of bands commencing near 495 nm are clearly visible. These bands were also observed in the I_2 and the Br_2/IBr (or CF_3I) photolysis systems and correspond exactly to the spectrum observed by *Himmelmann et al.* [1996] in an I_2/O_3 photolysis system, which were assigned unequivocally to OIO.

Figure 2 shows the temporal behaviour of BrO, IO and OIO following the photolysis of a $\text{N}_2\text{O}/\text{CF}_3\text{I}/\text{Br}_2/\text{N}_2$ mixture. BrO and IO are produced rapidly following the photolysis pulse. Subsequently, IO decays rapidly in the presence of excess BrO, which decays more slowly. The OIO absorption appears immediately following IO production, maximising when approximately 50% of the IO has decayed, and subsequently decays back towards zero. OIO is clearly produced from IO and is probably removed by reaction with other radicals present in the photolysed mixture. Similar OIO time dependence was observed in the IO + IO reaction, with the amount of OIO formed for a given initial concentration of IO approximately the same in the presence and absence of BrO. In the BrO+IO experiments, reaction of IO with BrO

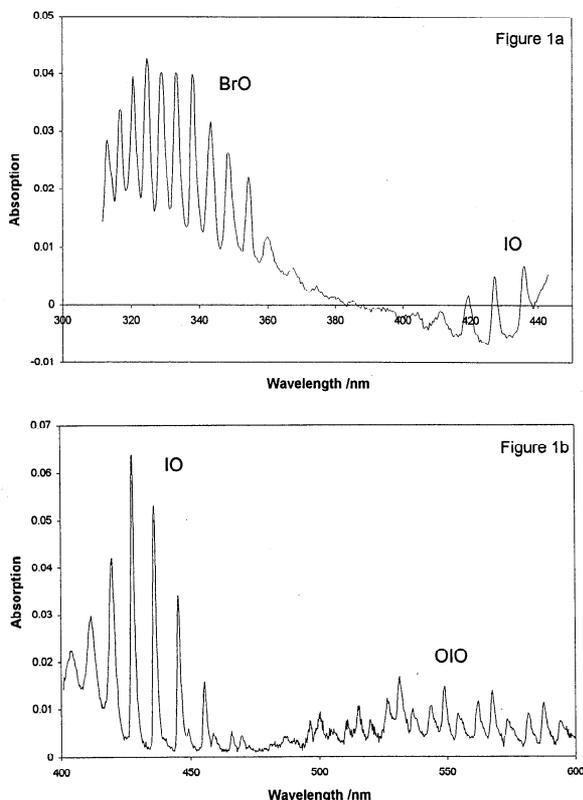


Figure 1. a) Post- relative to pre-photolysis absorption spectrum of a $\text{N}_2\text{O}/\text{Br}_2/\text{CF}_3\text{I}$ mixture, showing BrO and IO. The negative baseline above 380 nm arises due to the consumption of Br_2 during the formation of BrO; spectral resolution 1.7 nm FWHM. b) Post- relative to pre-photolysis absorption spectrum of a $\text{N}_2\text{O}/\text{CF}_3\text{I}$ mixture, showing IO and OIO; spectral resolution 1.13 nm FWHM.

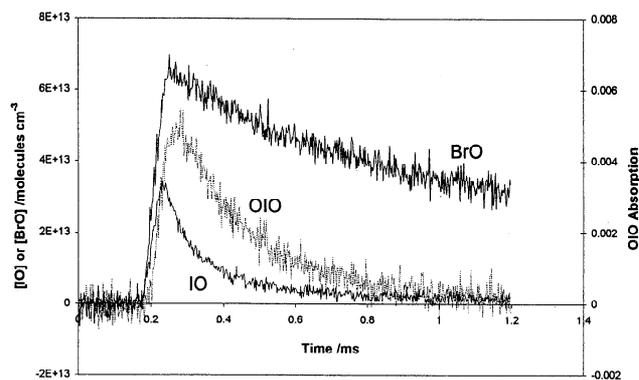


Figure 2. Temporal profiles for IO, BrO and OIO following photolysis of a $\text{N}_2\text{O}/\text{Br}_2/\text{CF}_3\text{I}$ mixture. The OIO concentration could not be derived directly without prior knowledge of $\sigma(\text{OIO})$. The absorption due to OIO at 548.6 nm is given on the right hand axis.

accounted for over 75% of the IO loss, therefore OIO must be produced in similar yields in both the BrO + IO and the IO + IO reactions.

The overall rate coefficients for the BrO + IO and IO + IO reactions were obtained by numerical fitting of the radical decay profiles using a kinetic model of the post photolysis chemistry. Details of this analysis will be presented in separate papers where the extensive amount of kinetic and mechanistic data obtained, including temperature and pressure dependencies, will be presented. The following values for the rate constants were obtained at room temperature:

$$k_1 = (8.2 \pm 1.0) \times 10^{-11} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$k_2 = (8.5 \pm 1.5) \times 10^{-11} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

These values agree extremely well with recent literature values for the rate constants for the IO + IO and IO + BrO reactions, which have been determined in several other laboratories using different techniques [*Laszlo et al.*, 1995; *Harwood et al.*, 1997; *Gilles et al.*, 1997; *Laszlo et al.*, 1997; *Bedjanian et al.*, 1998].

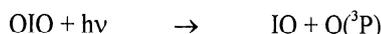
Since the absolute absorption cross sections of OIO are unknown the yield of OIO and its branching ratio from the IO + XO reactions cannot be determined directly from these experiments. *Bedjanian et al.* [1998] have recently studied the IO + BrO reaction, and determined the branching ratio for the production of Br + OIO to be in the range 0.65 - 1.0. We have used this result to quantify the yield of OIO produced in the IO self-reaction system, where the sole source of OIO is reaction 1, and to determine a value for the OIO cross section. The branching ratio for OIO formation in reaction 1 was found to be in the range 0.38 ± 0.08 , the spread reflecting the range of values for k_{2b}/k_2 , resulting in a cross section for OIO of $(1.09 \pm 0.21) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 548.6 nm (spectral resolution = 1.13 nm FWHM). Thus OIO formation is a very significant channel of both reactions 1 and 2.

Atmospheric Photostability of OIO

Misra and Marshall [1998] have recently conducted a computational study of the iodine oxides. They used *ab initio* methods to calculate standard thermodynamic constants for a number of iodine species including I_2O , OIO, IOOI, IOIO and

IO_2 which are all potential products of the $\text{IO} + \text{IO}$ reaction. The calculations predict OIO to be the major product of the IO self-reaction, with $\Delta_r H^\circ(\text{OIO}) = 76.7 \text{ kJ mol}^{-1}$, making its formation from $\text{IO} + \text{IO}$ and $\text{IO} + \text{BrO}$ exothermic by 48.3 and 46.8 kJ mol^{-1} respectively. The uncertainty in these calculated values is estimated to be $\pm 15 \text{ kJ mol}^{-1}$.

The above value of $\Delta_r H^\circ(\text{OIO})$ gives a computed value for the O-IO bond strength of $288.2 \text{ kJ mol}^{-1}$ and a threshold for photodissociation *via* the reaction:



of 418 nm. The bond strength is consistent with that predicted relative to OCIO, on the basis of the reduced-mass corrected frequencies of their ν_1 (symmetric stretch) vibrations [Himmelmann *et al.*, 1996] (D_0 (O-IO) $\sim 290 \text{ kJ mol}^{-1}$). Recent matrix isolation studies [Maier and Bothur, 1997] have suggested that the stronger than expected bonding within OIO may arise from partial double-bonding character within the molecule. The visible absorption spectrum of OIO

covers the wavelength region 480 - 660 nm. A photodissociation threshold of 480 nm would require an unreasonably large error ($\sim 40 \text{ kJ mol}^{-1}$) for the computed $\Delta_r H^\circ(\text{OIO})$. Absorption at $\lambda < 480 \text{ nm}$ is weak if it occurs at all and therefore rapid atmospheric photolysis of OIO in the near UV to give $\text{O}({}^3\text{P}) + \text{IO}$ will not occur as it does for OCIO. The alternate photolysis channel giving $\text{O}_2 + \text{X}$ ($\text{X} = \text{Cl}$ or I) has only been observed in OCIO photolysis under collision-free conditions [Vaida and Simon, 1995]. This is unlikely to be an important route for OIO, in view of the low quantum yield for iodine photosensitised decomposition of ozone [Jenkin *et al.*, 1985], which is incompatible with efficient I atom regeneration from the $\text{IO} + \text{IO}$ reaction. Although OIO is a transient species in our experiments, the concentrations of radical species which could react with OIO in the atmosphere are orders of magnitude lower. Using the reactivity of OCIO as an analogy, we expect negligible reaction of OIO with closed shell molecules, and reaction of OIO with NO and polyatomic radicals such as HO_2 to be rather slow, $k < 1 \times 10^{-12} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$. Using typical concentrations of NO and HO_2 for the clean troposphere (of 10 pptv for each) an OIO lifetime of at least 1 hour with respect to chemical reaction is obtained. We conclude that OIO may be a relatively stable radical in the atmosphere.

Reactions 1 and 2 are likely to be minor pathways for IO reaction in the atmosphere, but since the major pathways, *e.g.* reaction with HO_2 or NO_2 , give rise to HOI and IONO_2 which are photolysed rapidly to reform I atoms, OIO could be a significant reservoir for inorganic iodine. The implications of this are twofold. Firstly, OIO could attach to atmospheric particles and provide a route to the formation of higher oxidation states of iodine such as IO_3^- in precipitation. The second implication concerns the catalytic cycles leading to ozone loss:



If OIO undergoes photolysis to produce $\text{O}({}^3\text{P}) + \text{IO}$, O_3 is regenerated from the $\text{O}({}^3\text{P}) + \text{O}_2$ reaction, leading to a null cycle with respect to ozone loss. However if OIO does not undergo photolysis and is converted to a higher iodine oxide, a catalytic species (I) is lost, inhibiting further ozone removal.

Atmospheric Implications

We have carried out calculations using a photochemical box model to simulate the chemistry of iodine in the marine boundary layer. The basic model [Cox, 1999] includes ozone, NO_x and HO_x radical chemistry appropriate to the mid-latitude MBL, with full diurnal photolysis and physical exchange at the box boundaries. A chemical scheme for gas-phase and particulate iodine similar to that used by Jenkin [1992] involving I, IO, I_2O_2 , OIO, HI, HOI and IONO_2 was added to the basic model. Rate parameters and branching ratios for the gas phase reactions were updated from recent laboratory studies. The IO self reaction was assumed to produce $\text{OIO} + \text{I}$ (38%), $2\text{I} + \text{O}_2$ (12%) and I_2O_2 (50%).

Heterogeneous reactive uptake of HI, HOI, I_2O_2 , OIO and IONO_2 on the marine aerosol was calculated using a fixed uptake coefficient of $\gamma = 0.05$ giving $k_{\text{loss}} = 1 \times 10^{-5} \text{ s}^{-1}$ [Jenkin, 1992]. Only I_2O_2 and OIO were permanently removed on the aerosol, as HI, HOI and IONO_2 were assumed to react with sea salt with release of iodine back to the gas phase.

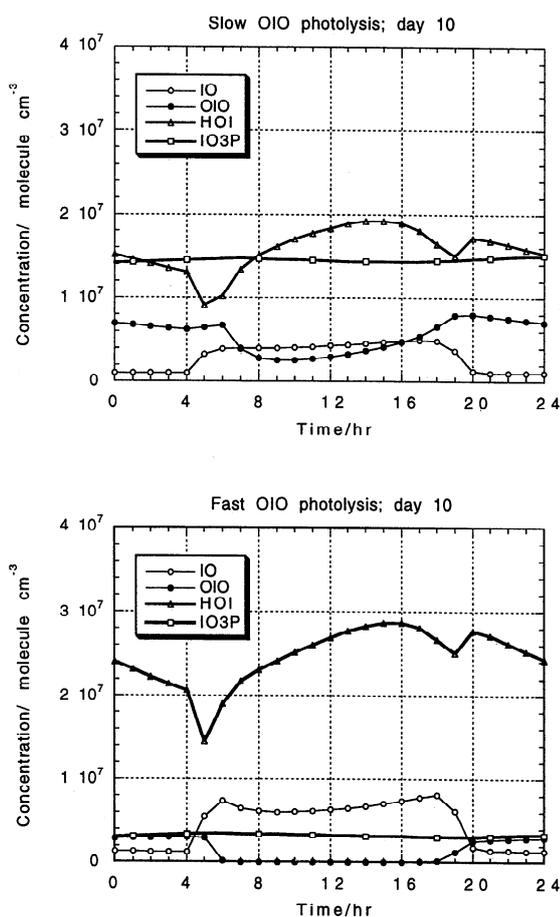


Figure 3. Diurnal concentration profiles for principal iodine species calculated for day 10 in a time dependent model of the photochemistry of the background marine boundary layer for conditions at 51°N on 21 July. The photolysis of 3 ppt CH_3I was the sole source of gas phase inorganic iodine species, which were removed by photolysis, deposition or attachment to sea salt aerosol. The upper panel shows results with fast photolysis of OIO to give $\text{O} + \text{IO}$ ($J = 0.28 \text{ s}^{-1}$); lower panel with slow photolysis of OIO ($J = 1.2 \times 10^{-5} \text{ s}^{-1}$). In both cases OIO was assumed to attach to the aerosol with an uptake coefficient of 0.05. IO3P is the OIO-derived iodine in the condensed phase.

Absorption cross sections for OIO, I₂O₂, IONO₂ and HOI were taken from recent measurements conducted in our laboratory. For OIO, it was assumed either that absorption in the visible vibronic spectrum led to dissociation to O(³P) + IO with unit quantum efficiency giving $J = 0.28 \text{ s}^{-1}$ (using the cross sections determined), or that photolysis only occurred at wavelengths below 418 nm, where absorption is weak, $J = 1.2 \times 10^{-5} \text{ s}^{-1}$, *i.e.* similar to CH₃I. All other quantum yields were assumed to be unity. OIO was assumed to react with NO ($k = 1.0 \times 10^{-12} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$) and OH (to give HOI, $k = 6.0 \times 10^{-12} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$) based upon the known reactivity of OCIO.

Figure 3 shows some results from these simulations using 3 ppt CH₃I as the only iodine source gas. If OIO is photolysed rapidly HOI is predicted to be the major gas phase iodine reservoir and particulate iodine derived from OIO (represented by IO3P) remains small (lower panel). If OIO photolysis is slow ($J = 1.2 \times 10^{-5} \text{ s}^{-1}$; upper panel) OIO becomes a significant gas-phase iodine reservoir. After 10 days reaction most of the iodine accumulates as OIO adsorbed in the particulate phase. This could account for the high enrichment of iodine in the small size fraction of the marine aerosol. The ozone loss due to iodine chemistry was reduced by a factor of two. These results broadly confirm the qualitative expectations noted above. The model predicts that OIO should be present at concentrations readily detectable by long-path visible absorption spectroscopy in situations where iodine sources are sufficient to produce detectable levels of IO, such as have already been reported from the Irish coast [Alicke *et al.*, 1998, 1999]. Observation of atmospheric OIO would provide a convincing test for the mechanisms proposed here. Furthermore, laboratory investigations are urgently required to confirm the photochemical stability of OIO.

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W.J. Bloss, R.A. Cox and R.L. Jones, Centre for Atmospheric Science, University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK.

D.M. Rowley, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK.

(e-mail: wjb1000, rac26 and rlj1001@cus.cam.ac.uk and d.m.rowley@ucl.ac.uk)

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