Gas phase reactions of iodide and bromide anions with ozone: evidence for stepwise and reversible reactions

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Despite the impacts – both positive and negative – of atmospheric ozone for life on Earth, there remain significant gaps in our knowledge of the products, mechanisms and rates of some of its most fundamental gas phase reactions. This incomplete understanding is largely due to the experimental challenges involved in the study of gas-phase reactions of ozone and, in particular, the identification of short-lived reaction intermediates. Here we report direct observation of the stepwise reaction of the halide anions iodide (I¯) and bromide (Br¯) with ozone to produce XO2¯ (where X = I and Br, respectively). These results substantially revise the rate constant for the I¯ + O3 reaction to 1.1(±0.5) × 10−17 cm3 molecule−1 s−1 (0.13% efficiency) and the Br¯ + O3 reaction to 6.2(±0.4) × 10−15 cm3 molecule−1 s−1 (0.001% efficiency). Exploiting five-orders of temporal dynamic range on a linear ion trap mass spectrometer enabled explicit measurement of the rate constants for the highly efficient intermediate, XO− + O2 and XO− + O3, reactions thus confirming a stepwise addition of three oxygen atoms (i.e., X + 3O3 → XO2− + 3O2) with the first addition representing the rate determining step. Evidence is also presented for (i) slow reverse reactions of XO− and X2O−, but not the XO2−, with molecular oxygen and (ii) the photodissociation of IO−, IO2− and IO3− to release I¯. Collectively, these results suggest relatively short lifetimes for Br− and I− in the troposphere with direct gas-phase oxidation by ozone playing a role in both the formation of atmospheric halogen oxidies and, conversely, in the ozone depletion associated with springtime polar bromine explosion events.

Introduction

Ozone can be considered a Janus molecule in the atmosphere; simultaneously serving contradictory roles in both protecting and threatening life on Earth. While in the upper atmosphere (stratosphere) ozone serves to protect life from damaging short wavelength radiation, in the lower atmosphere (troposphere) it is an aggressive oxidant causing significant damage to plant and animal life.1 One possible sink for atmospheric ozone is reactions with halogen anions, such as iodide (I¯) and bromide (Br¯), either in the gas phase or on aerosol surfaces.2-4 In the polar boundary layer, bromine explosion events are marked with accelerated depletion of tropospheric ozone.5-7 This observation is typically attributed to the heterogeneous reaction between Br2−, pre-concentrated in a thin layer on the surface of ice, and gaseous ozone forming molecular bromine in the presence of protons.8-10 A similar surface mediated effect from iodide in the Arctic icepack is also proposed to account for molecular iodine formation (often accompanying ozone depletion events).11

In solution and at surface-solution interfaces, studies of the oxidation of halide ions by ozone are extensive. Despite compelling evidence that ozone reacts with halide ions (particularly I¯ and Br¯) at the air-surface interface, the exact mechanism remains a topic of active debate.12-16 A common conclusion of such studies is a stepwise oxidation mechanism for halide ions, terminating at XO3−.17,18 Directly probing the interfacial chemistry is often complicated however, with the potential for multiple simultaneous and competing processes to occur. Whilst the importance of such heterogeneous processes cannot be dismissed, less attention has been paid to the fundamental chemistry of halide ions with ozone in the gas phase. Interestingly, gas phase bromide and iodide anions, along with some halogen oxide ions (e.g., IO−), have been detected in tropospheric measurements at the Jungfraujoch Research Station (Switzerland; altitude ~3400 m)19 as well as in the upper troposphere and lower stratosphere.4 Such observations stress the need to better understand the potential role of gas phase chemistries in dictating the formation and fate of these species.

Monitoring reactions in the gas phase, such as under the vacuum conditions of a mass spectrometer, allows access to the short-lived or highly reactive intermediates in a controlled manner.20,21 Using a selected-ion flow tube, Williams et al. observed IO2− as the sole ionic product from the gas-phase reaction of iodide with ozone, and determined the second order rate constant to be 1.0 ± 0.25 × 10−11 cm3 molecule−1 s−1 (“1.1% efficiency).22 Identification of the ionic intermediates, mechanism and rates of formation for this oxidation process could not be ascertained from these data. While attempts were made to measure the analogous reaction with bromide, this reaction was noted to be comparatively very slow and falling outside the quantitative capabilities of the instrument, leading to an upper limit for the reaction of just 0.5 × 10−13 cm3 molecule−1 s−1 (< 0.05% efficiency). More recently, the reaction of I with ozone at ~300 K was experimentally measured in an ion trapping device.23 Detection of IO−, IO2− and IO3− product ions provided further evidence for the stepwise oxidation of I by ozone. The rate constants for the sequential oxidation reactions were estimated as 7(±2) × 10−12, 10(±2) × 10−9, and 16(±2) × 10−9 cm3 molecule−1 s−1 for I−, IO2− and IO3− respectively. This demonstrated that the first oxidation step (i.e., I− + O3 → IO− + O2) is the rate limiting step in the oxidation process, and that further oxidation of the intermediate IO− and IO2− ions by ozone to form IO3− is overwhelmingly faster. No reaction was observed for IO4− with ozone to form higher oxides (i.e., IO5−). Solvation had a significant effect on the measured reaction rates, with hydration of the iodide

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Practice problems would be here
precursor increasing the observed reaction rate with ozone by an order of magnitude.\textsuperscript{24}

Here we report a systematic experimental study of the reactions of bromide and iodide anions, and their associated oxides, with ozone across almost 5 orders of magnitude in temporal dynamic range. Exploiting consecutive reaction and re-isolation capabilities (i.e., MS\textsuperscript{3}) afforded by a modified commercial linear ion trap mass spectrometer, direct measurement of the reaction rates of the isolated intermediate iodide and bromide oxides with ozone for the first time. Moreover, the first measurements of the reaction of halo-oxide anions with oxygen under ambient conditions are reported, demonstrating the reversibility of halide reactions with ozone. Photodissociation of some halo-oxide anions to liberate halides is also demonstrated to be feasible at actinic wavelengths. Together these experiments significantly revise previously reported reaction rates as well as adding new reaction steps (and associated efficiencies) to the possible manifold of gas phase chemistry of halides in the atmosphere. This report thus provides a robust set of rate constants critical for anchoring theoretical models of these reactions in such environments.

**Experimental**

Ion-molecule reactions were conducted in the low-pressure ion trap region of a hybrid dual linear ion-trap mass spectrometer (LTQ Orbitrap Elite, Thermo Scientific, San Jose, CA, USA). Halide ions were generated from either potassium iodide (BDH Chemicals, Sydney, Australia) or potassium bromide (Sigma Aldrich, Castle Hill, Sydney, Australia) dissolved in methanol at a concentration of 10 μM and infused into the electrospray ionization (ESI) source at a flow rate of 10 μL min\textsuperscript{−1}. Precursor XO\textsuperscript{−} and XO\textsubscript{2}\textsuperscript{−} were produced by ESI of a 10 μM solution of NaIO\textsubscript{4} or KBrO\textsubscript{4} in methanol, with the in-source collision energy set to 75 V. All mass spectra were acquired using the native instrument control software (Xcalibur 3.0, Thermo Scientific).

The instrument has been physically modified to allow reactant gas to enter the ion-trapping region.\textsuperscript{25} Ozone was generated external to the mass spectrometer by passing ultra-high purity (UHP) oxygen (Coregas, Sydney, Australia) through an ozone generator (Titan 30 UHC, Absolute Ozone, Edmonton, AB, Canada) at a flow rate of 100 mL min\textsuperscript{−1}. The power on the generator was set to typically produce 300 g Nm\textsuperscript{−1} (ca. 19.5 wt.% in O\textsubscript{2}) as measured by a high concentration ozone analyser (UV-106H, 2B Technologies, Boulder, CO, USA). The delivery of helium buffer gas (UHP, Coregas) into the ion trap was controlled by a fixed PEEKsil restriction (50 μm i.d. × 100 mm; Trajan Scientific P/N 0624252) as a part of a custom built gas-mixing manifold similar to that previously described.\textsuperscript{26} This by-passes the flow control mechanism supplied with the instrument and the flow of helium is controlled manually to give an ion gauge pressure of ca. 1.80 × 10\textsuperscript{−5} Torr in the ion trap vacuum chamber. Externally generated ozone was seeded into the flow of helium buffer gas through a chemically inert PEEKsil tube (25 μm i.d. × 100 mm; Trajan Scientific P/N 0624226). The concentration of ozone in the ion-trapping region of the instrument was calculated by monitoring the reaction of Ba\textsuperscript{2+} (from barium nitrate) and phenide (C\textsubscript{5}H\textsubscript{5}N\textsuperscript{−}; from collisional activation of benzoic acid) with ozone under pseudo-first order conditions and using the reported second order rate constant to titrate the concentration of ozone (see Supporting Information, Table S1).\textsuperscript{28} The concentration of oxygen in the ion-trap was determined by reaction with 3-carboxylatoadamantyl radical, using the previously determined second-order rate constant.\textsuperscript{27}

For ion-molecule reaction experiments, precursor ions were mass-selected using an isolation width of 1 Da, and a Normalised Collision Energy (NCE) of 0 – 1 (arb. units). For each halide precursor ion, a sequence was created that acquired mass spectra at a series of reaction times spanning 0.01 - 30 s for [X]\textsuperscript{−}, [XO]\textsuperscript{−}, and [XO\textsubscript{2}]\textsuperscript{−} within the same sequence. The temporal acquisition order was randomised to minimise any effects of drift in ozone concentration. Reactions with oxygen were performed using identical reaction conditions, but with the ozone generator switched off, ensuring only oxygen was introduced into the ion trap through the gas handling manifold. Further details are provided in the Supporting Information.

Photodissociation experiments were performed on a similar linear quadrupole ion trap mass spectrometer (Thermo Scientific LTQ-XL) that had been previously modified to allow optical access to the ion trapping region.\textsuperscript{28} Precursor ions were mass selected and irradiated with either a single pulse of 266 nm light from a Nd:YAG laser (Continuum Minilite II; 4.5 mJ/pulse @ 266nm) or 500 nm from a UV-VIS mid-band OPO nanosecond-pulse laser system (GWU-Lasertechnik flexiScan; 1.4 mJ/pulse @ 500nm).\textsuperscript{29}

**Kinetic analysis**

Integrated peak areas were extracted from the raw data files using a Python script which used the MSFileReader DLL (Thermo Scientific). An integration window of 1 Da was used for both precursor and product ions. The extracted mean precursor peak areas were then fit to a single exponential function of the form

\[
[X^-]_t = [X^-]_0 e^{-kt} + c
\]

(1)

to model pseudo-first order kinetics, where [X\textsuperscript{−}]\textsubscript{t} is the peak area of the precursor halide at a given reaction time, [X\textsuperscript{−}]\textsubscript{0} is the initial peak area, \(k\textsubscript{1}\) is the pseudo first order rate constant and \(c\) is a constant. Standard deviations (±1\sigma) of the measured peak areas for each time point were treated as a weighting function during the fitting procedure.

Second order rate constants (\(k\textsubscript{2}\)) were calculated from \(k\textsubscript{1}\) and the ozone concentration ([O\textsubscript{3}]; as measured above) through the following relation:

\[
k\textsubscript{2} = \frac{-k\textsubscript{1}}{[O\textsubscript{3}]} \]

(2)

Reaction efficiencies (\(\phi\)) were determined from the ratio of \(k\textsubscript{2}\) to the trajectory collision rate \(k\textsubscript{coll}\) at 320 K.\textsuperscript{27, 30, 31}

\[
\phi = \frac{k\textsubscript{2}}{k\textsubscript{coll}} \times 100
\]

(3)
\[ k_{\text{coll}} = 2\pi q \sqrt{\frac{\alpha}{\mu}} \]  

[4]

Where \( q \) is the unit charge, \( \alpha \) is the polarizability and \( \mu \) is the reduced mass of the system.

While the accuracy of the rate measurements is estimated as \( \pm 50\% \), the precision of the measurements is better than \( \pm 10\% \).

**Results**

**IO\textsuperscript{-} reactions with ozone**

Mass-selection of iodide anions (m/z 127) within the ion trap mass spectrometer in the presence of ozone gave rise to the mass spectrum shown in Figure 1A. The predominant product ion is observed at m/z 175, consistent with formation of iodate (IO\textsuperscript{3-}). The structure can be assigned as iodate by comparison of the reactivity and photodissociation of IO\textsuperscript{3-} formed from IO\textsuperscript{4-} (Figures S1 and S4). Increasing the trapping time resulted in an apparent pseudo-first order decay of the iodide signal, with a half-life of ca. 25.25 s at the reaction conditions employed (Figure 1B). Neither the decay of I\textsuperscript{-} nor the formation of reaction products were observed in the absence of ozone (i.e., identical experimental conditions but with the ozone generator inactive). Closer examination of the mass spectrum in Figure 1A revealed two lower abundance reaction products at m/z 143 and m/z 159, assigned as hypoiodite (IO\textsuperscript{-}) and iodite (IO\textsubscript{2}\textsuperscript{-}), respectively. Subsequent mass-selection allowed the interception of these reaction intermediates and enabled the reaction kinetics of each of these ions with ozone to be explicitly monitored. Re-isolation of IO\textsuperscript{-} (Figure 1C, 1D) and IO\textsubscript{2}\textsuperscript{-} (Figure 1E, 1F) in the presence of ozone revealed that both ions exhibit a significantly faster pseudo-first order decay, compared to I\textsuperscript{-}, under...
the same reaction conditions. Reactions of IO\(^{-}\) and IO\(^{2-}\) with ozone were found to generate IO\(^2\)\(^{-}\) as the ultimate reaction product at m/z 175 (Figure 1C and 1E, respectively). Consistent with previous reports,\(^{23}\) no higher oxidation products were observed beyond IO\(^2\)\(^{-}\) for the reaction of any IO\(^{-}\) precursor ion with ozone. The fitted rate constants for these reactions are reported in Table 1. Importantly, the mass spectrum obtained from isolation and reaction of IO\(^{-}\) (Figure 1C) also contained a product ion at m/z 127, corresponding to regeneration of I\(^{-}\). Similarly, product ions consistent with I\(^{-}\) and IO\(^{-}\) were observed upon isolation and reaction of IO\(^{2-}\) (Figure 1E).

In order to determine the origin of these reduced iodinate species, the reactivity of the intermediate IO\(^{-}\) and IO\(^{2-}\) anions was examined solely with oxygen under the same conditions. Because these species react rapidly with ozone, an alternative synthetic strategy was required. Electrospray ionization of NaIO\(_3\) in methanol produced abundant IO\(^{-}\) ions at m/z 191, and subsequent activation of these ions by energetic collisions (collision-induced dissociation, CID) or ultraviolet photons (photodissociation) yielded product ions corresponding to the lower oxides (Figure S1; Supporting Information). Applying source-based CID when infusing NaIO\(_4\) generated the intermediate iodine oxides directly in high abundance, without the need for mass-selection of the periodate precursor ion (Figure S1A). The iodine oxides produced in this manner react at the same rate and efficiency with ozone as those produced by the oxidation of iodide (Figure 1), confirming that they are indeed the same species. Isolation of IO\(^{-}\) (m/z 143; Figure 2A) in the presence of oxygen yields I\(^{-}\) (m/z 127) in low abundance, even after 10 s of reaction time. Similarly, isolation of IO\(^{2-}\) (m/z 159; Figure 2B) under identical conditions forms IO\(^{-}\) and I\(^{-}\) in minor abundance (m/z 143 and 127, respectively). Under the same conditions, isolation of IO\(^3\)\(^{-}\) (m/z 175) yielded no discernible reaction products (Figure S2; Supporting Information).

Together, these results show that the oxidation of I\(^{-}\) by ozone occurs stepwise, with sequential production of IO\(^{-}\) and IO\(^{2-}\), ultimately forming IO\(^3\)\(^{-}\). Critically, isolation and interrogation of the reactive IO\(^{-}\) and IO\(^{2-}\) intermediates has enabled the first explicit measurement of the back reaction of these species with oxygen, which reforms the lower oxides. The reaction manifold is shown in Scheme 1.

\[
\begin{align*}
X^- + O_3 &\xrightleftharpoons[k_1]{k_{-1}} XO^- + O_2 \\
XO^- + O_3 &\xrightarrow[k_{33}]{k_{-33}} XO_2^- + O_2 \\
XO_2^- + O_3 &\xrightarrow[k_{34}]{k_{-34}} XO_3^- + O_2 \\
XO_3^- + O_3 &\xrightarrow[k_{35}]{k_{-35}} XO_4^- + O_2 
\end{align*}
\]

Scheme 1: Reaction manifold for the sequential, reversible oxidation of halide anions by ozone (X = Br and I).

**BrO\(_x\) reactions with ozone**

As shown in Figure 3A, isolation of \(^{79}\)Br\(^{\text{iso}}\) (m/z 79) in the presence of ozone yields a product ion at m/z 127, consistent with bromate (\(^{79}\)BrO\(_5\)). The reactivity of the \(^{81}\)Br isotope was also probed and found to be identical (Figure S3; Supporting Information). Even after 20 s of reaction time however, the abundance of BrO\(_3\)\(^{-}\) is less than

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**Figure 3:** Mass spectra and kinetic traces for the \(^{79}\)Br bromide isotope reacting with ozone. [A] Mass spectrum of \(^{79}\)Br (m/z 79) reacting with ozone for 20 s, [B] kinetic plot showing decay of \(^{79}\)Br\(^{\text{iso}}\) and growth of BrO\(_3\)\(^{-}\) (m/z 127), [C] Mass spectrum of \(^{79}\)BrO\(_3\)\(^{-}\) (m/z 95) reacting with ozone for 40 ms, [D] associated kinetic plot showing decay of m/z 95, growth and subsequent decay of m/z 111 and ultimate growth of m/z 127, [E] Mass spectrum of \(^{79}\)BrO\(_3\)\(^{-}\) (m/z 111) reacting with ozone for 100 ms, [F] associated kinetic plot showing decay of m/z 111 and growth of m/z 127. Arrows in the lower panels indicate the time point for the associated mass spectra. The peaks in (A) denoted * and ‡ are Br\(^{\text{iso}}\)\(_2\)\(_3\)_\(_2\)\(_2\)\(_2\) and Br\(^{\text{iso}}\)\(_2\)\(_3\)_\(_2\)\(_2\)\(_2\)\(_2\) (H\(_2\)O\(_2\)) hydration products.
Table 1: Second order reaction rate constants (s cm⁻³ molecule⁻¹ s⁻¹) and reaction efficiencies (f, %) for the forward and reverse reactions of iodide and bromide, determined by fitting the kinetic traces shown in Figures 1, 3 and S3. The numbers reported for the reverse reactions represent upper limits for the reaction rates. Errors indicate ±1 standard deviation.

| Reaction                     | k_f(s⁻¹) | f (%)  | k_r(s⁻¹) | f (%)  |
|------------------------------|----------|--------|----------|--------|
| I⁻ + O₂ ≈ IO⁻ + O₂           | 1.1±0.5 × 10⁻¹² | 0.13   | 3.2±0.7 × 10⁻¹⁴ | 0.002  |
| 10⁻² + O₂ ≈ 10⁻² + O₂         | 7.1±0.5 × 10⁻¹⁰ | 90.8   | 1.3±0.4 × 10⁻¹⁴ | 0.004  |
| 10⁻² + O₂ ≈ 10⁻² + O₂         | 6.9±0.5 × 10⁻¹⁰ | 83.5   | -        | -      |
| Br⁻ + O₂ ≈ BrO⁻ + O₂          | 6.2±0.4 × 10⁻¹⁵ | 0.001  | 3.8±0.3 × 10⁻¹⁴ | 0.006  |
| BrO⁻ + O₂ ≈ BrO₂⁻ + O₂        | 3.9±0.6 × 10⁻¹⁰ | 43.7   | 1.6±0.2 × 10⁻¹⁵ | 0.003  |
| BrO₂⁻ + O₂ ≈ BrO₂⁻ + O₂       | 1.7±0.2 × 10⁻¹⁰ | 19.7   | -        | -      |

1% that of Br⁻. As shown in the kinetic trace (Figure 3B), the observed pseudo-first order reaction rate is slow compared to iodide under the same conditions. Low abundance intermediates are also observed at m/z 95 and m/z 111, corresponding to hypobromite (BrO⁻) and bromite (BrO₂⁻), respectively. Subsequent re-isolation of BrO⁻ in the presence of ozone resulted in rapid depletion of the precursor ion (Figure 3D), and formation of both BrO₂⁻ and BrO⁻ (Figure 3C). Similarly, BrO₂⁻ reacted rapidly with ozone to ultimately form BrO⁻ (Figure 3E, 3F). As for iodide, no further oxidation products were observed beyond BrO⁻.

The spectra acquired from isolation of BrO⁻ (Figure 3C) and BrO₂⁻ (Figure 3E) both exhibited evidence for regeneration of Br⁻ (m/z 79). In the absence of ozone, electrospray ionization of KBrO₃ with in-source activation yields an abundant source of BrO⁻ and BrO₂⁻ ions. Isolation of ⁷⁹BrO⁻ (m/z 95; Figure 4A) in the presence of oxygen for 10 s yields a minor signal corresponding to ⁷⁹Br⁻ (m/z 79). Under the same conditions, ⁷⁹BrO₂⁻ (m/z 111; Figure 4B) similarly forms small amounts of ⁷⁹Br⁻ and ⁸¹Br⁻ (m/z 95 and 79, respectively). BrO⁻ was unreactive towards oxygen under these conditions (data not shown).

Discussion

A major advantage of the present ion-trap mass spectrometry strategy for investigating the reactions of halide ions with ozone or oxygen is the ability to isolate and individually monitor the reactivity of the intermediate halogen oxide anions. To our knowledge, this is the first time that these reactive ionic species have been explicitly mass-selected and their reactivity with either ozone or oxygen probed. Moreover, generation of the halogen oxides XO⁻ and XO₂⁻ from NaO₂ or KBrO₂ in the absence of ozone enables unambiguous measurements of the reverse reaction rates implicated by the equilibria in Scheme 1. Table 1 summarises both the forward and reverse reactions for iodide and bromide, along with an estimate of the reaction efficiencies.

Forward reactions: The rate coefficients reported here are based upon the agreement of multiple independent titrations of the ozone concentration for the ion trap instrumentation deployed herein. The ozone number density of 3.8(±0.2) × 10¹⁰ molecule cm⁻³ was determined using two independent ion-molecule reactions (see Supporting Information Table S1 and Figures S5, S6). Using these benchmarks, the initial oxidation step is confirmed to be the rate limiting step for both the iodide and bromide reactions with ozone. This observation agrees with recent ab initio calculations, which indicate that this is the rate determining step with a moderate reaction barrier.⁵² The reaction rate for the I⁻ + O₃ reaction measured here (1.1±0.5 × 10⁻¹² cm³ molecule⁻¹ s⁻¹) is slower than the previously reported rates from selected ion flow tube (10 × 10⁻¹² cm³ molecule⁻¹ s⁻¹) or ion trapping experiments (7±2 × 10⁻¹² cm³ molecule⁻¹ s⁻¹). In the selected ion flow tube measurement, the authors acknowledge that the measured rate is only twice the limit of detection for their apparatus. In the case of both the SIFT and prior ion-trapping measurements, ozone
concentration in the reaction region is estimated based on external measurements. As noted above, the measurements undertaken here required multiple independent measurements of ozone number density in the reaction region and thus we recommend 1.1(±0.5) × 10^{-12} cm^{3} molecule^{-1} s^{-1} as the revised rate constant for this transformation. Pleasingly, our revised value is close to the rate predicted by transition state theory (0.87 × 10^{-12} cm^{3} molecule^{-1} s^{-1}).23 For the Br + O_{3} reaction, this first oxidation step is over two orders of magnitude slower than the analogous step for iodide, with a reaction rate of 6.4(±0.4) × 10^{-15} cm^{3} molecule^{-1} s^{-1}. Previous SIFT measurements have also shown that this is a slow reaction (<5.0 × 10^{-13} cm^{3} molecule^{-1} s^{-1}).23 This decrease in reactivity is consistent with the lower oxidation potential for bromide compared to iodide.

The subsequent reactions of IO_{2} and IO_{3}^{-} with ozone proceed at close to the collision rate with efficiencies of 90.8 and 83.5%, respectively. The second order rate constants extracted here are significantly slower than those reported by Teiwes et al.,23 however it was noted in that study that the rates exceeded the maximum collision rates predicted by Langevin theory; likely indicating a greater uncertainty in ozone number density. In our system, the BrO^{-} anion reacts with ozone at a reasonably high rate with a reaction efficiency of 43.7%, while the subsequent oxidation of BrO_{2} to BrO_{3}^{-} is slower, with a calculated reaction efficiency of 19.7%. For IO^{-} and BrO^{-}, the high reaction efficiencies are in accord with the computed potential energy diagrams that predicted transitions states falling below the entrance channel for the forward reaction with ozone.32 Moreover, the oxidation of iodide to iodate is also calculated to be barrierless. Interestingly therefore, the observation of the corresponding reaction of BrO_{2} with ozone falling below 20% efficiency might imply the existence of a moderate, as yet unidentified, barrier to this final oxidation step.

Reverse reactions: As shown in Scheme 1, the initial and second oxidation steps for both halogen anions by ozone are in equilibrium with a back reaction of the higher oxide reacting with molecular oxygen thus regenerating the initial halide ion. To our knowledge, no prior kinetic measurements exist for the reactions of the halogen oxide anions with molecular oxygen. In our ion-trap measurements, these reactions are slow, with minimal depletion of the precursor even after 10 s in the presence of oxygen (Figures 2 and 4). For IO^{-} and IO_{2}^{-}, an upper estimate for these rates is 3.2(±0.7) × 10^{-14} and 1.3(±0.4) × 10^{-14} cm^{3} molecule^{-1} s^{-1}, respectively, while for BrO^{-} and BrO_{2}^{-}, the upper limits are 3.8(±0.3) × 10^{-14} and 1.6 (±0.2) × 10^{-15} cm^{3} molecule^{-1} s^{-1}. No reaction products could be detected from the reaction of IO_{3}^{-} or BrO_{3}^{-} with O_{3}. These observations are supported by previously reported potential energy surfaces for the reactions of iodide and bromide with ozone,23 which show a large barrier to reverse reaction of oxygen with XO_{3}^{-}.

For iodide, the measured back reaction rates are two orders of magnitude slower than the slowest forward reaction with ozone, and thus are unlikely to significantly contribute to regeneration of the precursor ion population in the mass spectrometer. Even noting that the number density of molecular oxygen will be ca. 4 times greater than that of ozone under our experimental conditions (IO_{3})_2 ~ 20 wt.% O_{3}, the decay of iodide will be dominated by the forward reaction. Accordingly, the forward reactions with ozone can be treated as pseudo-first order. In contrast, the measured forward and reverse rates for the reaction of bromide with ozone are of approximately equal magnitude. This implies that the forward reaction is unlikely to be a significant contributor to the formation of bromine oxides in oxygen-rich atmospheres with only trace levels of ozone. However, the back reactions with O_{3} are expected to be sensitive to both temperature and pressure, given that they are thermodynamically up-hill, and rate constants may be lower in the atmosphere than in the present experiments. Efforts to theoretically model these reaction rates, benchmarked against the accurate measurements reported here, are currently underway. Photodissociation experiments conducted here show that the halide plus ozone reaction manifold can also be ‘reversed’ by photochemistry, with each of IO_{2}, IO_{3}^{-} and IO_{4}^{-} losing one or more oxygen atoms upon exposure to UV radiation at 266 nm (close to the shortest tropospheric irradiation wavelength), while at 500 nm (near the peak of the solar irradiation) all but IO_{3}^{-} exhibit photofragmentation to yield the naked halide (Figure S4; Supporting Information). While IO_{3}^{-} showed no reverse reaction with oxygen, it is possible that UV-photoactivation at higher elevations could liberate IO_{3}^{-}, which could subsequently react with O_{3} to form IO_{4}^{-} and I^{-}.

Implications in the atmosphere: As gas phase Br^{-}, I^{-} and IO_{3}^{-} anions have been detected in the atmosphere,4, 19 it is interesting to consider the potential significance of the gas phase I^{-} and Br^{-} oxidation reactions described herein. Given a typical tropospheric concentration of ozone at ~40 ppb (10^{12} molecule cm^{-3}), application of the rate constants ascertained from our measurements suggest atmospheric lifetimes of I^{-} and Br^{-} toward O_{3} are ca. 1 s and 100 s, respectively. In the absence of other atmospheric sinks for these halides, conversion to XO^{-} by ozone represents a plausible outcome. Once formed the fate of XO^{-} is less clear, given that it can be further oxidized by O_{3} reduced by reaction with O_{2} or subject to photolysis to reform X^{-}. The atmospheric lifetimes of the four studied XO^{-} and XO_{3}^{-} ions toward 40 ppb O_{3} are all on the order of about 1 ms indicating facile conversion through to XO_{2}^{-}, which has been detected for the case of IO_{3}^{-}.28 Notably each step in this manifold would consume an equivalent of ozone such that a single halide could remove three ozone molecules (i.e., X^{-} + 3O_{3} → XO_{2}^{-} + 3O_{2}). Although seemingly a rapid pathway for ozone depletion, our discovery of the reactions of halo-oxides with molecular oxygen suggests that the lifetimes of XO^{-} and XO_{3}^{-} ions would be as short as ca. 10 – 100 µs and would regenerate both the halide anion and ozone. As discussed, however, the low rate coefficients for these reactions makes them sensitive to temperature and pressure, suggesting that these lifetime predictions could vary significantly with altitude. Moreover, it has been predicted from computation that solvation by water molecules stabilises the Br^{-}···OOO anion-molecule complex,2 while also lowering the potential barrier for this reaction to proceed. These atmospheric clusters may therefore work to accelerate ozonolysis rates. Finally, the implications of the photolysis of XO^{-} and XO_{3}^{-} at visible wavelengths and XO_{3}^{-} in the UV also need to be considered. The photodissociation of halogen oxides to reform lower oxide and/or halide ions that then undergo reaction with O_{3} could potentially promote photo-catalytic the destruction of ozone. The potential significance of this process for the atmosphere may depend on whether photolysis yields singlet (^1D, more probable in the UV) or triplet (^3P, more probably for visible wavelengths) atomic oxygen with the latter able to recombine with molecular oxygen to
yield ozone thus mitigating the potential for photo-catalytic depletion. Future detailed investigations of the spectroscopy of halo-oxides will provide critical insights into the significance of such photochemistry in the atmosphere.

Conclusions

Using a linear quadrupole ion trap, we have systematically explored the reactivity of the I⁻ and Br²⁻ anions, and their associated oxides, with ozone. Knowledge of the reaction rate constants for both the forward and back reactions, and characterisation of the gas phase reaction mechanism will provide a key insights into the formation and fate of these species in the atmosphere and foundational knowledge for the characterisation of these chemicals in the solution phase as well as at the gas-liquid interface.

Conflicts of interest

The authors declare no conflicts of interest.

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Notes and references

An electronic data archive of the raw mass spectrometry data is available from the QUT Research Data Finder at https://researchdatafinder.qut.edu.au/display/n2748

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