A gas-to-particle conversion mechanism helps to explain atmospheric particle formation through clustering of iodine oxides

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Emitted from the oceans, iodine-bearing molecules are ubiquitous in the atmosphere and a source of new atmospheric aerosol particles of potentially global significance. However, its inclusion in atmospheric models is hindered by a lack of understanding of the first steps of the photochemical gas-to-particle conversion mechanism. Our laboratory results show that under a high humidity and low HOx regime, the recently proposed nucleating molecule (iodic acid, HOIO2) does not form rapidly enough, and gas-to-particle conversion proceeds by clustering of iodine oxides (IₓOᵧ), albeit at slower rates than under dryer conditions. Moreover, we show experimentally that gas-phase HOIO2 is not necessary for the formation of HOIO2-containing particles. These insights help to explain new particle formation in the relatively dry polar regions and, more generally, provide for the first time a thermochemically feasible molecular mechanism from ocean iodine emissions to atmospheric particles that is currently missing in model calculations of aerosol radiative forcing.
The impacts of iodine on tropospheric and stratospheric chemistry were anticipated by seminal work published in the 80s and 90s. The characterization of global iodine sources and the demonstration of its ubiquitous presence in the marine boundary layer (MBL) and the free troposphere, and the stratosphere have enabled an assessment of the important role of iodine in O3 depletion in past, present, and future climate scenarios. Iodine oxide-driven new particle formation was first observed in mid-latitude coastal locations and its high nucleation and growth rates may enable new iodine particles to survive fast scavenging by background aerosol and to develop into sea mist and fog. Iodine oxide particles (IOPs) have also been observed in the polar MBL. Field observations in diverse locations with completely different meteorological and chemical conditions suggest a wider relevance of this phenomenon in the global atmosphere. Laboratory studies have investigated the effect of different environmental variables on nm-sized IOPs. Recent ab initio studies have found a substantial reduction of reaction rate constants for HOI formation and evaporation (see Figs. 1 and 2) starting from standard chemistry (Supplementary Table 1). Figure 1a shows an average of mass spectra recorded for time delays of up to 20 ms between 248 nm pulsed laser photolysis (PLP) of a mixture of O3 and I2 at 10 Torr of N2 and 10.5 eV photoionization (PI). This “dry” spectrum shows positive ion peaks generated by near-threshold PI (Supplementary Table 2) of known neutral iodine species: I+ (m/z = 127), I2O+ (143), OI+ (159), I3+ (254), I4O+ (270), I5O+ (286), I6O+ (302), and I7O+ (318). A peak corresponding to I8O+ (m/z = 334) is absent. The predicted vertical ionization potential of I8O+ is 11.4 eV, but this molecule is not observed with the 11.6 eV PI beam either, as shown in Fig. 2. The major peaks of the higher m/z progressions observed in Fig. 1a are I3O+ (493), I3O+ (827), I4O+ (1161), I5O2+ (1495), and I5O2+ (1829), and I5O3+ (2163). Minor peaks which indicate up to four missing oxygen atoms are also observed. Starting from I3O+ and moving to higher m/z, the peaks are separated by I2O units (Fig. 1b), even though gas-phase I2O does not appear to form. The chemical composition of the main and last peak of each progression can be described as (I2O3)nOIO2. Molecular clusters with even numbers of iodine atoms (I2O+I2O)n are also detected but are very minor.

A succession of peaks in a mass spectrum does not necessarily reveal how a nucleation mechanism works. Laboratory time-resolved multiplexed experiments (Fig. 3) provide the sequence of reactions and are therefore essential to interpret mass spectra obtained in the field or in the chamber or flow tube steady-state experiments. The initial growth of the concentration versus time curves is generally faster for smaller iodine-bearing molecules, and the peak concentrations are reached in the following order: I2O → I2O2 → I4O2 → I5O2 → I6O2 → I7O2 → β-CD. Minor peaks which indicate formation and removal time scales of I2O+ and I3O+ would occur well above 10.5 eV, Supplementary Table 2). At longer time delays between PLP and PI, all peaks with the number of iodine atoms x ≤ 2 show kinetic growth at a similar rate compared with the larger clusters, indicating that the latter fragment into smaller constituent subunits following PI. This growth occurs at earlier delay times when the initial concentration of IO is higher (higher excimer laser energy or higher O3 concentration, Supplementary Fig. 3) and/or the PI energy is higher. Because of the second-order reactions involved, starting with the IO self-reaction, the formation and removal time scales of I2O depend on the initial concentration of IO, which itself depends on the fraction of O3 photolyzed. Thus, for high IO, I2O clustering is fast and a dominant sink compared to other slow reactions.

Addition of water (mixing ratio x(H2O) = 2%) at 10 Torr results in a limited reduction of the OIO+ and I3O+ signals (Fig. 1c). No reaction products are detected, except for the peak at m/z = 144, i.e., HOI+. This results from OH scavenging by I2, which also prevents any further HOI chemistry. The mass peak progressions in the presence of water remain the same: neither HOI2O nor HOI2-containing peaks (e.g., (I2O3)2HOI), are observed, and no clusters with an even number of iodine atoms emerge. The calculated ionization potential of HOI2O is 11.3 eV, yet again no signal is observed on a time scale of 4 ms when the PI beam is tuned to 11.6 eV (Fig. 2). Regarding larger oxyacid-containing clusters, the PI threshold is expected to decrease as the size of a cluster increases, and therefore they should photoionize or even photofragment at 10.5 eV. Thus, any hypothetical I3O+ + H2O reaction forming HOI2O occurs at a slower rate than the I2O+ clustering reactions under these conditions. Given the lack of reaction products upon addition of water, the limited decrease of the I2O+ signals indicates that
water partially inhibits the formation of large clusters, which results in a reduction of the photofragmentation signal.

Observing slow reactions requires increasing the concentration of the excess reactant (H₂O) and minimizing the effect of competitive reactions. At 350 Torr and x(H₂O) = 2%, for PLP-PI delays of up to 5 ms, the peaks observed at low pressure in the mass spectrum remain, and oxyacid clusters do not appear (Fig. 2). The minor peaks at m/z = 177 (H₂IO₃⁺) and m/z = 335 (H₂IO₄⁺) do not exhibit kinetic change and are decoupled from photolysis-induced chemistry. Thus, they probably result from photofragmentation of large H₂O...I₂O₃ clusters or are produced from deposits around the ToF-MS skimmer.

Continuous broadband photolysis (BBP) experiments. We have also performed high-pressure steady-state experiments using continuous BBP. In these experiments, a residence time of a few seconds combined with continuous generation of I atom and high pressure should help in enhancing the concentration of slow-reaction products. Yet again, oxyacid products are not observed under these conditions (Fig. 2). Upper limits for the rate constants of possible HOIO₂-forming reactions can be obtained from kinetic modeling of our BBP experiments, and are discussed below. Separate flow tube measurements of atomic iodine by resonance fluorescence (ROFLEX) were performed to study the removal of I atoms in the presence of MBL-representative concentrations of O₃ and H₂O at 760 Torr. A slight enhancement of the I atom removal by O₃ in the presence of water was observed (Supplementary Fig. 4), which yields an effective rate constant of k(I + H₂O + O₃) = (2.0 ± 0.5) × 10⁻¹⁸ cm³ s⁻¹ molecule⁻¹ for x(O₃) = 92 ppbv and k(I + H₂O + O₃) = (2.0 ± 0.5) × 10⁻¹⁸ cm³ s⁻¹ molecule⁻¹ for x(O₃) = 184 ppbv.

Visual inspection of the BBP experiment through a viewport revealed a plume of smoke formed at the I₂ inlet under dry conditions (Supplementary Movie 1), which was quenched upon addition of H₂O. That is, water appears to hinder nucleation, rather than promoting it by forming HOIO₂. The observation of HOIO₂ evaporated from particles by resistive heating demonstrates the capability of detecting this molecule by PI-ToF-MS at

Fig. 1 Mass spectra and mass defect of iodine oxides. a Time-of-flight mass spectrum (ToF-MS) at photoionization energy (PIE) of 10.5 eV (10 Torr, [O₃] = 2 × 10¹⁵ molecule cm⁻³, no added H₂O) averaged over 20 ms after the photolysis laser pulse. Two sections of the spectrum are displayed with an offset and multiplied by 40 and 100 to show more clearly the peaks corresponding to higher m/z clusters. For the third section (red), the corresponding prephotolysis background is also shown. The asterisks indicate groups of peaks with even number of iodine atoms. ToF-MS signal in arbitrary units. b Mass-defect plot (the difference between molecular mass and the integer mass given by the sum of protons and neutrons in the nuclei) for the main clusters observed. c In blue, the difference between spectra with and without water (10.5 eV, 4 Torr, [O₃] = 4 × 10¹⁴ molecule cm⁻³). Negative peaks indicate losses and positive peaks formation of the corresponding species. Sections of the spectra with and without water are shown (black and red lines, respectively), multiplied by 10 for clarity.
measured at 10.5 eV, i.e., they can neither be assigned to HOIO$_2$ illustrated by the 450 Torr BBP dry spectrum (black line superposed to the green line). These peaks correspond to emerge (red and green lines) are for high pressure (350 and 450 Torr). However, these peaks do not depend on the gas-phase water concentration, as the time evolution of high signals at certain average signal level before PLP has been subtracted. Clear lines indicate the presence of HOI and a slight decrease of all I$_x$O$_y$ with pressure (PIE) of 10.5 eV below the ionization threshold. 

The experiment was started by 248-nm pulsed laser photolysis (PLP) of O$_3$ in the presence of I$_2$ at 10 Torr with 2% water mixing ratio ($6.5 \times 10^{15}$ molecule cm$^{-3}$). The average signal level before PLP has been subtracted. Clear lines indicate time evolution of high signals at certain m/z values (color-coded time-of-flight mass spectrometry (ToF-MS) signal in arbitrary units). Formation of IO ($m/z = 143$), HOI (144) and OIO (159) is followed by the appearance of I$_2$O$_y$, I$_2$O$_3$, and larger clusters with the odd number of iodine atoms. At late times all traces grow similarly as a result of photofragmentation of large I$_x$O$_y$. The time-resolved mass spectra obtained for humid conditions are almost identical to those obtained under dry conditions, except for the changes in the relative differences between the I$_2$O$_y$ peaks with pressure and the poorer signal-to-noise ratio at 11.6 eV, the spectra look very similar under all conditions studied. The only instances where some new peaks emerge (red and green lines) are for high pressure (350 and 450 Torr). However, these peaks do not depend on the gas-phase water concentration, as illustrated by the 450 Torr BBP dry spectrum (black line superposed to the green line). These peaks correspond to $m/z = 177$ and $m/z = 355$ and were measured at 10.5 eV, i.e., they can neither be assigned to HOIO$_2^+$ nor I$_2$O$_5^+$. They were also observed in our previous study under dry conditions$^{27}$. 

11.6 eV and provides insights into the formation of particulate HOIO$_2$ (Fig. 5). BBP of I$_2$O$_y$ mixtures at room temperature generates I$_2$O$_3$ and IOPs that travel for a few seconds down the flow tube toward the detection region. A few millimeters upstream of the sampling volume, the carrier gas and the particles are resistively heated (Supplementary Fig. 2) in order to observe evaporation products. The current through the filament was set to a value such that the I$_2$O$_3$ molecules carried by the gas thermally dissociated in the absence of water (disappearance of the higher mass peaks). Thus, the observed HOIO$_2$ and HOI cannot be products of gas-phase high-temperature I$_x$O$_y$ reactions, but evaporation products of IOPs formed upstream in the presence of water. Under dry conditions, the oxyacid evaporation signals reduce drastically. The other effect of heating IOPs is the expected thermal decomposition of solid/liquid-phase iodine oxides into molecular oxygen and iodine$^{36,37}$ (enhancement of the I$_2$ signal).

**Fig. 2** Mass Spectra of iodine oxides in the presence of water vapor. Time-of-flight mass spectra (ToF-MS) acquired under high water mixing ratios (2%) but otherwise different flow tube conditions, photolysis source (PLP pulsed laser photolysis, BBP broadband photolysis), and photoionization energy (PIE). The spectra are displayed in two separated m/z ranges for clarity. Except for the changes in the relative differences between the I$_2$O$_y$ peaks with pressure and the poorer signal-to-noise ratio at 11.6 eV, the spectra look very similar under all conditions studied. The only instances where some new peaks emerge (red and green lines) are for high pressure (350 and 450 Torr). However, these peaks do not depend on the gas-phase water concentration, as illustrated by the 450 Torr BBP dry spectrum (black line superposed to the green line). These peaks correspond to $m/z = 177$ and $m/z = 355$ and were measured at 10.5 eV, i.e., they can neither be assigned to HOIO$_2^+$ nor I$_2$O$_5^+$. They were also observed in our previous study under dry conditions$^{27}$. 

**Fig. 3** Example of time-resolved mass spectrum. The experiment was started by 248-nm pulsed laser photolysis (PLP) of O$_3$ in the presence of I$_2$ at 10 Torr with 2% water mixing ratio ($6.5 \times 10^{15}$ molecule cm$^{-3}$). The average signal level before PLP has been subtracted. Clear lines indicate time evolution of high signals at certain m/z values (color-coded time-of-flight mass spectrometry (ToF-MS) signal in arbitrary units). Formation of IO ($m/z = 143$), HOI (144) and OIO (159) is followed by the appearance of I$_2$O$_y$, I$_2$O$_3$, and larger clusters with the odd number of iodine atoms. At late times all traces grow similarly as a result of photofragmentation of large I$_x$O$_y$. The time-resolved mass spectra obtained for humid conditions are almost identical to those obtained under dry conditions, except for the presence of HOI and a slight decrease of all I$_x$O$_y$ signals. In this experiment, HOIO$_2$ would not be expected to be observed due to the photoionization energy (PIE) of 10.5 eV below the ionization threshold.

**Iodine oxide particle-formation mechanism.** The chemistry initiating the formation of iodine oxide clusters and particles is reasonably well known (Supplementary Table 1). Therefore, deviations from the phenomenological growth and decay of IO and OIO documented in previous work$^{34,38}$ are considered as a sign of fragmentation, especially if the IO and OIO traces track the growth of larger molecules and clusters. Data at high IO$_x$ concentration clearly suffer from this problem (e.g., experiments #2 and #3 in Supplementary Fig. 3) and cannot be used for kinetic analysis, but it must be pointed out that all datasets are affected to some extent at long delay times. Some of the fragmentation energies of large molecules listed in Supplementary Table 2 are just slightly higher than 10.5 eV or even lower. Two-photon processes may also occur like in the case of water...
digital mode, and the PLP-PI delays were set manually in the delay generator. All traces (in concentration in cm
interpolated to a constant step time axis. Note that each row shows I
employed, orders of magnitude higher than the concentrations
unfocused laser beam is likely related to the high concentrations
resonance-enhanced multiphoton ionization (REMPI) with an
members of each row, except for the
assumed in the chemical mechanism (Table 1).

Fig. 4 I2Ox kinetics. Kinetic traces (blue circles, blue lines estimated statistical uncertainty from signal scatter) of the main peaks (blue line in the right upper panel) observed in a pulsed laser photolysis (PLP) experiment initiated by 193-nm photolysis of I2 in the presence of O3 at 9 Torr, with 10.5 eV photoionization (PI). The corresponding mass spectrum averaged for all delays is shown in the upper right corner panel. The data were recorded in the
digital mode, and the PLP-PI delays were set manually in the delay generator. All traces (in concentration in cm–3 versus time in ms) have been interpolated to a constant step time axis. Note that each row shows I
with the same number of iodine atoms. The vertical scale is the same for all members of each row, except for the first members of the second and third rows. The red lines show the kinetic traces obtained from a numerical model (Supplementary Tables 1 and 3), and the black squares show the difference between the measurements and the model. The arrows show the main paths assumed in the chemical mechanism (Table 1).

(see “Methods”), although the reason why water is observed by resonance-enhanced multiphoton ionization (REMPI) with an unfocused laser beam is likely related to the high concentrations employed, orders of magnitude higher than the concentrations of IxOy.

The I2O+ signal that is consistently detected in all experiments may originate from an I2O parent neutral rather than from fragmentation, possibly from a bimolecular reaction between IO and the products of its self-reaction. The observation of I2O2+ is consistent with IOIO being one of the major products of the IO self-reaction34,38, although the signal is very low even in the high-pressure experiments, which may indicate some fragmentation to IO+, or a small PI cross section. I2O3+ and I2O4+ can be linked to the corresponding neutrals, which are known products of the IO + OIO and OIO + OIO reactions. The main cluster progressions observed are separated by Δ(m/z) = 334 (I2O3), while I2O5 itself does not appear to form. Thus, I2O2, I2O3, and I2O4 are considered to be the precursors to iodine oxide molecular clusters. However, they do not appear to aggregate stepwise to form clusters. The ion clusters detected have the speci
cal elements I2n+1O2n+1m+(n ≥ 1, m = 0, 1, 2), i.e., odd numbers of iodine atoms. By looking at Supplementary Table 2, it can be seen that while I2Oy species may fragment to smaller ions, they cannot fragment to I2Oy+, and therefore we assume that the latter corresponds to I2Oy molecules formed in the flow tube.

There are many possible reactions that may generate the observed peaks in the PI mass spectra. Thermochemical data are required to eliminate irrelevant reactions from the chemical mechanism (Table 1). Reactions deemed to be endothermic or forming weakly bound adducts based on our calculations are excluded. For example, I2O3 does not form generally weak adducts with themselves, and this may explain why the I2O3 signals are negligible and, as a consequence, clusters with even numbers of iodine atoms do not form32. The most stable predicted adduct is I2O4y formed from the I2O3 self-reaction. However, our ab initio calculations suggest that this reaction also has an exothermic bimolecular channel making I2Oy. Alternative routes to I2Oy are I2Oy+ + Oy (y ≠ 3) followed by ozone-oxidation steps. Ozone has been found not to be required to form IOPs as long as an alternative source of oxygen atoms is available, but its presence leads to enhanced particle formation36. Thus, it could help in increasing the O/I ratio within each peak progression if the peaks with lower O/I form first from I2Oy+ + Oy.

I2O3, in particular, does not form stable adducts with other Oy and I2O (including itself)32, and we have not found any exothermic bimolecular reaction between I2O3 and IOy or I2O (Table 1). However, I2O3 does not accumulate in the flow tube, as shown in Fig. 4 and Supplementary Fig. 3. Therefore, we assume that it undergoes clustering with larger I2Oy. Further ab initio calculations are required to investigate if this is the actual fate of I2O3.
The list of reactions added to the initial chemistry in Supplementary Table 1 are listed in Table 2. The rate constants of the selected reactions are then adjusted to model the fast formation and decay of the I₅O₇ species, as shown in Fig. 4 (see the section “Kinetic Analysis” in “Methods”). Some reactions are grouped and assumed to have the same rate coefficient. Some rate coefficients are floated by the least-squares algorithm, while some others are changed manually. Not all coefficients can be allowed to float at the same time. Finding a reasonable result implies a few iterations. The criterion is always to minimize the difference between the measured traces and the simulations.

The rapid kinetics and smoke formation are astonishing, considering that the pressure is relatively low and that all reactions are second order. Removal rates of ~50 s⁻¹ with concentrations of 10¹¹ molecule cm⁻³ (Fig. 4 and Supplementary Fig. 3) involve rate constants of the order of 5 × 10⁻¹⁰ cm³ s⁻¹ molecule⁻¹. These are likely to be enabled by the large dipole moments characteristic of iodine oxides, inducing long-range capture forces. Kinetic modeling efforts are rendered semi-quantitative at this point by the unknown contribution of fragmentation of large clusters to the smaller molecules. However, a reasonable global fit to all available traces (Fig. 4) may be obtained using standard chemistry (Supplementary Table 1) and the combination of clustering and bimolecular reactions listed in Table 2. In this I₅O₇ nucleation mechanism, rapid pressure-independent bimolecular reactions between I₅O₇ molecular clusters form larger clusters with the observed odd numbers of iodine atoms ((I₅O₇)ₙOIO), e.g.:

\[
I₂O₇ + I₂O₇ \rightarrow I₅O₇ + IO⁻ \quad (r, s = 2 - 4; \ t = 4 - 7) \quad (1)
\]

\[
I₃O₅ + I₅O₇ \rightarrow I₅O₉ + IO⁻, IO⁺ \quad (u, v = 4 - 7; \ w = 10 - 12). \quad (2)
\]

In addition, third-body reactions at their high-pressure limit form aggregates, e.g.:

\[
IO₅ + I₂O₇ \rightarrow I₅O₉₊ₓ (x = 1, 2; \ y = 3, 4) \quad (3)
\]

\[
I₂O₇ + I₂O₇ \rightarrow I₅O₉₊₂ (y = 2 - 4; \ z = 4 - 7), \quad (4)
\]

where the O/I ratio of the aggregates may be subsequently increased through oxidation by O₃. HOIO₂-containing clusters have not been observed, and therefore no attempt has been made to model them.

Constraints to iodic acid-formation rates. Possible sources of gas-phase HOIO and HOIO₂ are reactions of IO₄ and I₃O₅ with water listed in Table 1. We have carried out high-level ab initio calculations to explore the transition states toward oxyacid formation from I₂O₇ + H₂O (y = 2, 3). The gas-phase I₂O₇ reaction (Supplementary Fig. 5) is more favorable than the I₃O₅ reaction (Supplementary Fig. 6), while the I₂O₄ reaction presents a small barrier (Supplementary Fig. 7). We have also hypothesized that wall reactions of iodine oxides with adsorbed H₂O may be an additional source of oxyacids in long-residence time experiments and field instruments with long inlets. However, Born--Oppenheimer molecular simulations (BOMD) rule out I₂O₇ reactions in the air-water interface (see “Methods”).

We have selected five exothermic reactions producing oxyacids listed in Table 1 in order to determine their rate constants from the experimental data and from our ab initio calculations. Active addition of high water concentrations in our BBP experiments at a PI energy of 11.6 eV does not result in a detectable signal of HOIO₂. Moreover, the co-products of these reactions HOI and HOIO are very weak or absent from the BBP mass spectra obtained at 10.5 eV. This suggests that these reactions are slow...
and cannot compete under our experimental conditions with the reactions removing I₂O₅ in the “dry” experiments. This, however, does not rule out the possibility that under atmospheric conditions, the situation reverses as a result of the low ambient I₂O₄ (\([I₂O₄] < 10^8 \text{ cm}^{-3}\)) have been measured in the field, i.e., three to four orders of magnitude lower than in our BBP experiments) and higher water concentrations. Thus, upper limits to the rate constants of these reactions need to be determined as a first step to establish the relative importance of the oxide and oxyacid clusters. This has been done by kinetic modelling of our long-residence time BBP steady-state experiments at 10.5 eV and 11.6 eV PI energy, where each process in Table 3 is included separately in the numerical model with different values of the rate constant. The calculated concentrations of the oxyacid co-products after a time equal to the residence time in the flow tube are used to scale their simulated peaks, which have the typical mass resolution of the measured spectra in the \(m/z = 140–200\) Da range. It is assumed that the PI cross section of each iodine oxyacid is equal to that of the nearest oxide. The upper limit of each rate constant \(k(I₂O₃ + H₂O)\) is taken to be that for which the simulated mass spectrometric signal at \(m/z = 144, m/z = 160\), and/or \(m/z = 176\) becomes indistinguishable from the background noise of the BBP experimental data. These upper limits can then be compared with rate constants calculated with the master equation solver MESMER\(^{39}\), using the molecular parameters (energies, vibrational frequencies, and rotational constants) derived from our ab initio calculations (Table 3).

A comparison between the simulated ion peaks and the observed mass spectra is shown in Fig. 6. Even though HOIO₂ is not expected to be observable at 10.5 eV, the data obtained at this photon energy help in reducing the upper limit of the rate constant of the I₂O₃ and I₂O₄ reactions. First, the concentrations of these two oxides, in particular, are enhanced at high pressure (the S/N ratio at 10.6 eV is 5 × 10\(^{-1}\)) of reactions forming iodine oxides and oxyacids.

### Table 1 Reaction enthalpies and barriers (in brackets) in kJ mol\(^{-1}\) of reactions forming iodine oxides and oxyacids.

| Reaction | \(\Delta H_e\) (298 K), this work\(^a\) | \(\Delta H_e\) (298 K), literature\(^b\) |
|----------|-------------------------------------|-------------------------------------|

\(^a\)Normal typescript: B3LYP/6-311+G(2d,p)(AE). Underlined: CCSD(T)/M06-2X/aug-cc-pVTZ+i-LANL2DZ. \(^b\)Calculated from published values of ab initio formation or reaction enthalpies. Normal typescript: CCSD(T)/MP2/aug-cc-pVTZ (AREP) from Galvez et al.\(^{32}\); italics: CCSD(T)//B3LYP/aug-cc-pVTZ (AREP) from Galvez et al.\(^{32}\); underlined: CCSD(T)/M06-2X/aug-cc-pVTZ+i-LANL2DZ from Kumar et al.\(^{30}\) (concerted pathways); bold: CCSD(T)/CBS//MP2/aug-cc-pVTZ (ECP28) from Khanniche et al.\(^{31}\).
The hypothetical composite reaction where atomic iodine complexes the experimental data.

The upper limit determined for the rate constant of a hypothetical composite reaction where atomic iodine complexes with water, and the resulting H₂O...I⁻ adduct reacts with O₃ to form oxyacids (Fig. 6a, e) can be compared with the rate constants obtained from the resonance fluorescence experiments on the removal of atomic iodine by O₃ in the presence of water vapor. The enhanced removal of I by O₃ in the presence of H₂O observed with the ROFLEX for x(O₃) = 92 ppbv (k(I + H₂O + O₃) = (2.9 ± 1.0) × 10⁻¹⁹ cm³ s⁻¹ molecule⁻¹) appears to agree with the upper limit determined from the ToF-MS experiments: k(I + H₂O + O₃) < 2.8 × 10⁻¹⁴ cm³ s⁻¹ molecule⁻¹. However, this is coincidental. The O₃ concentration in the ToF-MS experiments was three orders of magnitude larger than in the ROFLEX experiments, indicating that the rate constant in the former should be, if linearly extrapolated from the ROFLEX result, of the order of 2.9 × 10⁻¹⁶ cm³ s⁻¹ molecule⁻¹, i.e., well above the detection limit of ~10⁻¹⁸ cm³ s⁻¹ molecule⁻¹. Thus, the yield of HOIO and HOIO₂ from this process is <0.001, implying an oxyacid-formation rate constant of the order of 10⁻²² cm³ s⁻¹ molecule⁻¹ for atmospherically relevant O₃ concentrations. Therefore, the composite I + H₂O + O₃ reaction is not a sufficiently fast source of HOIO₂. This is very important because, as discussed in Supplementary Note 1, oxyacids can only be effective IOP nucleating species if their formation is decoupled from I₂O₃; otherwise, oxyacid nucleation needs to proceed through two slow second-order processes to form the first cluster. To explore the relative contribution of iodine oxides and oxyacids to the nucleation of IOPs, we have modeled a BBP flow tube experiment with longer residence time (200 s). Calculated rate constants of oxyacid–oxyacid and oxide–oxyacid aggregation and dissociation rates are listed in Supplementary Table 4. Modeled

### Table 2 Tentative mechanism of iodine oxide cluster formation (initiated by the reactions included in Supplementary Table 1).a.

| #  | Reactionb | k/cm³ s⁻¹ molecule⁻¹c | Grouped reactions | Fit   |
|----|-----------|-----------------------|-------------------|-------|
| 1  | IO + IOIO → I₂O + OIO     | 5 × 10⁻¹²          |                   |       |
| 2  | OIO + IOIO → I₂O₂ + IO     | 1 × 10⁻¹¹          |                   |       |
| 3  | IOIO + IOIO → I₂O₄ + I₂O   | 1 × 10⁻¹¹          |                   |       |
| 4  | I₂O + O₃ → IOIO + O₂      | 8 × 10⁻¹⁴          |                   |       |
| 5  | I₂O₂ + O₃ → I₂O₃ + O₂     | 4 × 10⁻¹⁴          |                   |       |
| 6  | I₂O₃ + O₃ → I₂O₃ + O₂     | 8 × 10⁻¹⁴          |                   |       |
| 7  | OIO + IOIO → I₂O₄         | 3 × 10⁻¹²          |                   |       |
| 8  | IO + I₂O₄ → I₂O₅          | 3 × 10⁻¹¹          |                   |       |
| 9  | OIO + I₂O₄ → I₂O₅         | 5 × 10⁻¹¹          |                   |       |
| 10 | I₂O₂ + I₂O₄ → I₂O₅ + OIO  | 5 × 10⁻¹²          |                   |       |
| 11 | I₂O₃ + I₂O₄ → I₂O₄ + IO   | 1 × 10⁻¹⁰          |                   |       |
| 12 | I₂O₄ + O₃ → I₂O₅ + O₂     | 8 × 10⁻¹⁴          |                   |       |
| 13 | I₂O₅ + O₃ → I₂O₅ + O₂     | 1 × 10⁻¹³          |                   |       |
| 14 | I₂O₆ + O₃ → I₂O₆ + O₂     | 1 × 10⁻¹³          |                   |       |
| 15 | I₂O₇ + O₃ → I₂O₇ + O₂     | 1.7 × 10⁻¹⁰        |                   |       |
| 16 | I₂O₈ + I₂O₇ → I₂O₉ + O₃   | 1.7 × 10⁻¹⁰        |                   |       |
| 17 | I₂O₉ + I₂O₇ → I₂O₉ + O₃   | 1.7 × 10⁻¹⁰        |                   |       |
| 18 | I₂O₁₀ + I₂O₈ → I₂O₁₀ + O₃ | 1.7 × 10⁻¹⁰       |                   |       |
| 19 | I₂O₁₁ + I₂O₉ → I₂O₁₁ + O₃ | 1.7 × 10⁻¹⁰       |                   |       |
| 20 | I₂O₁₂ + I₂O₁₀ → I₂O₁₂ + O₃| 1.7 × 10⁻¹⁰       |                   |       |
| 21 | I₂O₁₀ + I₂O₈ → I₂O₁₀ + O₇ | 4 × 10⁻¹⁰          |                   |       |
| 22 | I₂O₁₂ + I₂O₁₀ → I₂O₁₂ + O₇| 4 × 10⁻¹⁰          |                   |       |
| 23 | I₂O₁₂ + I₂O₁₀ → I₂O₁₂ + O₇| 2 × 10⁻¹⁰          |                   |       |
| 24 | I₂O₁₂ + O₉ → I₂O₁₂ + O₇   | 2 × 10⁻¹⁰          |                   |       |
| 25 | I₂O₁₁ + O₈ → I₂O₁₁ + O₅   | 3 × 10⁻¹³          |                   |       |
| 26 | I₂O₁₀ + O₇ → I₂O₁₀ + O₃   | 3 × 10⁻¹³          |                   |       |
| 27 | I₂O₁₀ + I₂O₉ → I₂O₁₀ + O₂  | 2 × 10⁻¹³          |                   |       |
| 28 | I₂O₁₀ + I₂O₈ → I₂O₁₀ + O₂  | 2 × 10⁻¹³          |                   |       |
| 29 | I₂O₁₀ + I₂O₇ → I₂O₁₀ + O₂  | 2 × 10⁻¹³          |                   |       |
| 30 | I₂O₁₀ + I₂O₆ → I₂O₁₀ + O₂  | 2 × 10⁻¹³          |                   |       |
| 31 | I₂O₁₀ + I₂O₅ → I₂O₁₀ + O₂  | 2 × 10⁻¹³          |                   |       |
| 32 | I₂O₁₀ + I₂O₄ → I₂O₁₀ + O₂  | 2 × 10⁻¹³          |                   |       |
| 33 | I₂O₁₀ + I₂O₃ → I₂O₁₀ + O₂  | 2 × 10⁻¹³          |                   |       |
| 34 | I₂O₁₀ + I₂O₂ → I₂O₁₀ + O₂  | 2 × 10⁻¹³          |                   |       |
| 35 | I₂O₉ + I₂O₇ → I₂O₉ + O₇    | 1 × 10⁻¹⁰          |                   |       |
| 36 | I₂O₉ + I₂O₇ → I₂O₉ + O₇    | 1 × 10⁻¹⁰          |                   |       |
| 37 | I₂O₉ + I₂O₇ → I₂O₉ + O₇    | 1 × 10⁻¹⁰          |                   |       |
| 38 | I₂O₉ + I₂O₇ → I₂O₉ + O₇    | 1 × 10⁻¹⁰          |                   |       |
| 39 | I₂O₉ + I₂O₇ → I₂O₉ + O₇    | 1 × 10⁻¹⁰          |                   |       |

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aAb initio thermochemistry is available up to I₄O₁₂. Endothermic reactions and reactions forming weakly bound complexes are not included (see Table 1). For larger clusters, reactions are included in order to explain observed peaks and relative peak intensities.

bFor simplicity, only the forward association reactions are considered, i.e., unimolecular decomposition of the adduct is ignored, and therefore these are effective rate constants.

cRate constants from the global fit in Fig. 2.
Table 3 Calculated rate constants of possible oxyacid sources (\(T = 295\,\text{K}\)).

| Reaction                                      | \(k\) MESMER | \(k_{\text{upper-limit experimental}}\) |
|-----------------------------------------------|--------------|------------------------------------------|
| \(I + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2\cdot\text{I}\) | 2.4 \times 10^{-13} cm\(^3\) s\(^{-1}\) | 4.7 \times 10^{-12} cm\(^3\) s\(^{-1}\) |
| \(\text{H}_2\text{O}_2\cdot\text{I} \rightarrow \text{I} + \text{H}_2\text{O}\) | 1.7 \times 10^{6} s\(^{-1}\) | 3.4 \times 10^{7} s\(^{-1}\) |
| \(\text{H}_2\text{O}_2\cdot\text{I} + \text{O}_3 \rightarrow \text{HOI}/\text{HOIO}_2 + \text{HO}_2/\text{OH}\) | 100 s\(^{-1}\) | 100 s\(^{-1}\) |
| \(I + \text{H}_2\text{O} (\rightarrow \text{O}_3) \rightarrow \text{HOI}/\text{HOIO}_2 + \text{HO}_2/\text{OH}\) | 2.8 \times 10^{-19} cm\(^3\) s\(^{-1}\) | 2.1 \times 10^{-19} cm\(^3\) s\(^{-1}\) |
| \(I + \text{H}_2\text{O} \rightarrow \text{HOI}/\text{HOIO}_2\) | 1.9 \times 10^{-15} cm\(^3\) s\(^{-1}\) | 4.6 \times 10^{-14} cm\(^3\) s\(^{-1}\) |
| \(I + \text{H}_2\text{O} \rightarrow \text{HOI}/\text{HOIO}_2\) | 1.6 \times 10^{-7} s\(^{-1}\) | 4.0 \times 10^{-8} s\(^{-1}\) |

*Adjusted to obtain a net rate constant equal to the effective rate constant determined by resonance fluorescence with the ROXEL machine. For \(\text{O}_3\) = 2.5 \times 10^{12} molecule cm\(^{-3}\) (100 ppbv at 760 Torr), the corresponding rate constant would need to be: \(k = 4 \times 10^{-11} \text{cm}^3\text{s}^{-1}\text{ molecule}^{-1}\).

The same loss rate of the I-water adduct is assumed for the IO-water adduct. Adjusted to obtain a net rate constant equal to the effective rate constant determined by resonance fluorescence with the ROXEL machine. For \(\text{O}_3\) = 2.5 \times 10^{12} molecule cm\(^{-3}\) (100 ppbv at 760 Torr), the corresponding rate constant would need to be: \(k = 4 \times 10^{-11} \text{cm}^3\text{s}^{-1}\text{ molecule}^{-1}\).

The HOIO-HOIO\(_2\) potential well is deep enough to enable collisional stabilization of the adduct at high pressure. We have no evidence of a peak at \(m/z = 336\) in our high-pressure mass spectra.

Fig. 6 Determination of upper limits to oxyacid-formation rate constants. Time-of-flight mass spectra (ToF-MS) obtained with photoionization energies (PIE) of 10.5 eV (panels a–d) and 11.6 eV (panels e–h) in broadband photolysis (BBP) experiments at 450 Torr and 30 Torr, respectively, without added water (blue line) and with 2% water mixing ratio (black line). Note that the labels of y and x axes are the same for all panels in the same column. The vertical black lines indicate the position of the oxide and oxyacids in the m/z axis: from left to right: IO, HOI, OIO, HOIO, HOIO\(_2\). Simulated oxyacid ion peaks (thick lines) resulting from four different kinetic modeling scenarios with different rate constants are overlaid to the measured spectra: \(I + \text{H}_2\text{O} + \text{O}_3 \rightarrow \text{HOI}/\text{HOIO}_2 + \text{HO}_2/\text{OH}\) (a, b), \(\text{IOIO} + \text{H}_2\text{O} \rightarrow \text{HOI} + \text{HOIO}_2\) (b, f), \(\text{I}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HOI} + \text{HOIO}_2\) (c, g), \(\text{I}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{HOIO} + \text{HOIO}_2\) (d, h), and \(I + \text{H}_2\text{O} + \text{O}_3 \rightarrow \text{OH} + \text{HOIO}_2\). Note that reactions producing HO\(_x\) also would result in the generation of HOI (panels a, e).
concentrations are presented in Supplementary Fig. 8 as a function of water vapor concentration ([H2O]) concentrations between laboratory experiments23 and ambient. Despite the many assumptions involved in this exercise, a conclusion that can be drawn is that molecular clusters descending directly from HOIO and HOIO2 can only become dominant at high water concentration (>5 × 10^{16} molecule cm^{-3}), and if the direct precursor of these oxyacids is atomic iodine. If the precursors of these oxyacids are oxides—which is more likely—nucleation is started by iodine oxides.

Discussion

Our laboratory results strongly support an atmospheric gas-to-particle conversion mechanism where the initial clustering steps are driven by I2O3 bimolecular and third-body reactions, both under dry and wet conditions. The mechanism of atmospheric IOP formation proposed in Fig. 7 is based on the set of reactions (Table 2) that best reproduces the time-resolved mass spectrometric data (Fig. 4) in the presence and absence of water, as described in the “Results” section. The IOP pyrolysis experiments show that HOI and HOIO2 are constituents of these particles, even though we did not observe them in the gas phase at room temperature, which implies that they are not indispensable IOP gas-phase precursors. This evidences the transformation of the I2O3 clusters into oxyacid-containing clusters within the flow tube residence time, which confirms earlier predictions about the composition of I2O3 IOPs in the MBL.28 This scenario is represented in Fig. 7 by the hydration of the I2O3 units present in the iodine oxide clusters with the composition (I2O3)nOIO. We reported previously that the number and the size of IOPs reduces when they are formed in the presence of water26. Particle capillary collapse following water uptake could not alone explain those observations. The attachment of water molecules to molecular clusters may have the effect of reducing cluster formation and particle coagulation rates. At the molecular cluster level of the mass spectrometric observations discussed here, the addition of water results in a consistent reduction of the intensity of all masses without concomitant formation of products, which we have interpreted as inhibition of photofragmentation of larger clusters. We found previously16,32 that the key iodine oxide I2O4 forms a relatively stable complex with water, such that under the conditions prevailing in the MBL, a large fraction of I2O3 molecules would be hydrated as I2O3...H2O (> 40%). This could block the I2O3 halogen-bonding sites, and the subsequent necessary geometrical rearrangement for the reaction of I2O3 with itself or with I2O5 to proceed may result in barriers in the corresponding PES. The same may occur for larger molecular clusters. It should be noted that I2O3...H2O clusters are not observed in our experiments, which may be because they promptly dissociate following absorption of vacuum ultraviolet (VUV) photons.

A possible role of iodine in the formation and growth of new particles near the tropical tropopause has been proposed9. This would be favored by low water concentrations, but it must be noted that if the mixing ratios of I2O3 are low, the clustering process slows down compared to photolysis (photolysis lifetimes of tens of seconds10,40 versus reaction lifetimes of hours, Supplementary Table 5). In mid-latitude coastal regions, particle production probability shows a strong negative correlation with water vapor fluxes and relative humidity31. This is consistent with our laboratory observations of water slowing down IOP formation26, and not consistent with a mechanism which results in a positive dependence on water vapor. In the polar MBL, active iodine (IO3) mixing ratios are in general lower than in macroalgae-rich mid-latitude locations5, and consequently lower I2O3 mixing ratios should result in slower IOP formation rates (Supplementary Table 5). However, nucleation is likely to be favored not only by enhanced stability of molecular clusters at low temperature26 but also because the water content of the atmosphere is lower. In fact, nucleation events observed in the Arctic21 are coincident with periods of low RH.

Although we cannot rule out the formation of gas-phase HOIO2 (and HOIO) from I2O3 in the atmosphere (see lifetimes in Supplementary Table 5), we have shown that oxyacids are unlikely to be major nucleating species of IOPs. Moreover, we have evidence indicating that CI-API-ToF-MS IO3− signals attributed to gas-phase HOIO2 prior to reaction using two reagent ions—nitrate and acetate—may require some re-interpretation (see Supplementary Note 2 and Supplementary Table 3). Besides collisional fragmentation issues of this technique41, IO3− ions are exothermic reaction products of the dissociative charge transfer between I2O3 (y = 2, 3, 4) and NO3− (and CH3COO−), and therefore it is likely that I2O3 contributes significantly to the IO3− signal. The apparent paradox is that the IO3− CI-API-ToF measurements23 remains a very useful proxy for tracking iodine nucleation in the field, because it may result from ionization of I2O3 and/or HOIO2 generated by I2O3 + H2O. Nevertheless, connecting the dots between these observations and those of precursors and smaller gas-phase species (I2, I, IO, HOI, OIO)29 is crucial to facilitating the development of a chemical mechanism that can be adapted for atmospheric modeling purposes. To our best knowledge, ours is the first complete iodine gas-to-particle conversion mechanism (Fig. 7) supported by direct experimental evidence.
Future modeling work should adapt this scheme to carry out a global assessment of the contribution of iodine new particle formation to the atmospheric aerosol burden and its associated radiative forcing.

**Methods**

**Pulsed laser and continuous broad band photolysis.** A PLP system (Supplementary Fig. 1) was employed to generate iodine oxides from the 193-nm or 248-nm photon dissociation of I₂O₅ mixtures in a 3.75-mm diameter tubular reactor chamber. Alternatively, a Xenon lamp was used for continuous BP of I₂ in the presence of O₃. A flow of 0.2–20 s/m of N₂ carrier gas (99.999%) was introduced in the reactor, depending on the target pressure. I₂ molecules were entrained in the carrier flow by passing a smaller flow of carrier gas (10–500 sccm) through a heated, temperature-controlled flow tube containing I₂ crystals. O₃ was added by flowing the precursor through an electrical discharge. The excimer laser and the lamp beams were passed unfocussed through a quartz viewport along the tube main axis. An atmospheric pressure bubbler was employed to entrain water vapor into the carrier flow at approximately the equilibrium vapor pressure, resulting in a water mixing ratio of ~2% in the flow tube ([(H₂O)] = 2.3 × 10¹⁷ molecule cm⁻³ at 350 torr and 295 K). The pressure in the reactor was set by a throttle valve placed between the reactor and an Edwards 80 roots blower—oil rotary pump combination. The flows were set using MKS calibrated mass flow controllers, and pressure was measured using a set of 10 Torr and 1000 Torr MKS Baratron pressure transducers. O₃ and I₂ concentrations were measured using a Herriott-type absorption cell situated upstream of the reactor.

**Photoionization time-of-flight mass spectrometry.** PI-ToF-Ms systems at Leeds University have been employed extensively to study reaction kinetics relevant to combustion-related and tropospheric organic and halogen chemistry and upper atmospheric chemistry of meteoric metals. The first direct observation of I₂O₃ (x ≥ 2) gas-phase species was achieved using the older of these two systems. The new mass system employed in this work has been described in detail in a previous publication.

The gas in the reactor tube (Supplementary Fig. 1) is sampled on the axis via a skimmer cone with a 200-μm pinhole using a scroll pump-backed turbo-molecular pump. PI of molecules and clusters takes place in the ionization chamber (P = 10⁻³–10⁻⁵ Torr) before mass spectrometric detection. Alternatively, a differentially pumped roughing chamber can be inserted between the reactor and the PI chamber for experiments requiring high pressure (P > 20 Torr). In this configuration, the gas is sampled via a 500-μm pinhole into the roughing chamber, forming a high-density jet that is directed toward the 200-μm pinhole skimmer cone. The skimmer chamber is fitted with viewports, allowing a pulsed laser beam to be directed through the high-density region of the sampled gas jet. VUV ionization is achieved by tightly focusing in a rare-gas cell (Xe) the third harmonic of a Nd:YAG pump. PI of molecules and clusters takes place in the ionization chamber (P = 10⁻³–10⁻⁵ Torr) before mass spectrometric detection. Alternatively, a differentially pumped roughing chamber can be inserted between the reactor and the PI chamber for experiments requiring high pressure (P > 20 Torr). In this configuration, the gas is sampled via a 500-μm pinhole into the roughing chamber, forming a high-density jet that is directed toward the 200-μm pinhole skimmer cone. The skimmer chamber is fitted with viewports, allowing a pulsed laser beam to be directed through the high-density region of the sampled gas jet. VUV ionization is achieved by tightly focusing in a rare-gas cell (Xe) the third harmonic of a Nd:YAG laser (Continuum Surelite 10-II), which produces VUV radiation by frequency tripling (118.2 nm, or equivalently 10.5 eV)⁴⁻⁶. The 118.2-nm radiation is delivered to the PI chamber by a waveguide, which is a ¼ glass tube with either constant inner diameter or tapered for enhanced PI efficiency. This technique shows an excellent detection limit for organic molecules such as acetone (10⁷ molecule cm⁻³ in a single accumulation in analog mode), which is used as a standard for optimizing the performance of the instrument. The conversion efficiency for a VUV photon is negligible in a rare gas low (< 10⁻³), and therefore VUV PI is a viable method for molecules with substantial PI cross-sections (> 10⁻¹⁸ cm² molecule⁻¹). Possible interference from the 355-nm fundamental, if not separated from the VUV third harmonic, needs to be considered. This is important for molecules with UV–vis absorption bands, low ionization energy and high photon conversion efficiency. For example, water is detected at m/z = 18 (Fig. 1) using the 118.2-nm (10.5 eV) PI beam, even though its ionization potential is 12.621 eV. This most likely results from REMPI, where the intermediate state at 118.2 nm is the C electronic state or a Rydberg state of water⁴⁰, and a 355-nm photon is enough for reaching the ground state of the ion. Although the PI beam is diverging in the ionization chamber, this appears to be compensated by the high water vapor concentrations employed. A 106.7 nm (11.6 eV) PI beam can also be generated by frequency tripling the second harmonic of a 532-nm pumped dye laser running on DCM dye. The power of this beam is approximately an order of magnitude lower than that of the 10.5 eV beam. The concentrations resulting from PI of molecules in the sampled gas jet are accelerated toward the ToF-MS (Kore Technology) by a set of ion optics. This machine has been described in detail elsewhere. A pre-amplifier coupled to the positive ion detector provides simultaneous analog and digital outputs. The analog output, which can be modulated linearly by varying the detector gain, is intended for registering large signals from species with high PI efficiency and/or high concentration. This output is recorded by using a digital oscilloscope (Picoscope 6000). The mass peaks appear in the time axis of the oscilloscope delayed with respect to the PI laser pulse by a characteristic time of flight. The peaks are then digitized and processed on a PC for further analysis. A limitation of this method is that signals can cause detector overload after the corresponding peak during a significant lapse, which appears as a negative signal with respect to the spectrum baseline. Thus, peaks of other species arriving at the detector closely after the species causing a large peak are affected by this interference. Overloads can be eliminated by tuning down the detector gain, but this also reduces the sensitivity to small signals. To prevent detector overload by I₂ and I₂⁺, their mass peaks were gated out by pulsed biasing of the ion optics using a house-built dual-gating box.

The digital output is provided to a counting system (time-to-digital converter, TDC) by means of a fast comparator. The Kore Technology TDC counts ions within a sequence of flight-time bins (0.5 ns) referred to the PI laser pulse. In this way, a histogram of counts versus time of flight, i.e., a mass spectrum) is built. The counting method is suitable for capturing small signals (low concentration or low PI efficiency). The signal remains proportional to concentration for low counting rates. Although spectra measured with this technique are not affected by detector overload for high counting rates, departure from linearity occurs and the peaks appear saturated.

Lasers and detectors are synchronized using a delay generator (Quantum Composers, 9518). In every measuring cycle, the delay generator triggers the Nd:YAG laser and after a few microseconds triggers the TDC or the scope to establish the time zero event of each measuring cycle. In addition, the delay generator triggers the excimer laser that is actually used as a time zero trigger. The delay between the photolysis and the PI laser is scanned in order to sample reaction kinetics. In a typical digital experiment, 1000 digital spectra were accumulated for each reactant concentration and laser pulse delay, which at a 5-Hz laser-repetition rate takes 200 s. The built-in software of the MS-ToF does not handle synchronization of the delay generator and the TDC, and therefore the delays were set manually, at the cost of a poorer time resolution. Once the accumulation was complete, the delay between laser pulses and/or concentration of reagents was changed, and a new accumulation started. Kinetic experiments using the digital output are shown in Fig. 4 and Supplementary Fig. 3 (Exp. #1). Alternatively, the mass spectra of the analog mode were acquired using automatically the delay between the lasers using a LabView program, which was coded to operate synchronously the delay generators and the digital oscilloscope. Typically, around 30 delay scans were average in analog mode. Kinetic experiments using the analog output are illustrated in Supplementary Fig. 3 (Exp. #2 and #3).

**Resonance fluorescence.** Additional experiments to study the influence of water on the removal of atomic iodine were carried out with the Resonance and off-Resonance Fluorescence by Lamp Excitation (ROFLEX) machine in an atmospheric pressure BBF flow tube set up. A 3–15 slm flow of synthetic air carrying molecular iodine (10⁻¹³ mole) and ozone (10⁻¹⁲ molecule cm⁻³) was passed through a‐cm-diameter, 50-cm-long quartz tube where it was irradiated by an Xe arc lamp. The main flow and flow rates were varied to keep the concentration of I₂ and O₃ constant while changing the residence time of the gas mixture on the tube. The gas mixture was sampled at the end of the flow tube by using a small aperture into the ROFLEX chamber at 40 Torr. Iodine atomic resonance fluorescence is excited by a temperature-stabilized iodine radiofrequency lamp, and collected perpendicularly by using a VUV-sensitive channel photomultiplier in counting mode. The data collected in these experiments is plotted in Supplementary Fig. 4. The analysis of this dataset using numerical kinetic modeling is explained below.

**Kinetic analysis.** The processed PI-ToF-MS data consist of integrated peak signals (proportional to concentration) versus laser delay time in the case of PLP experiments or in the case of BBF experiments, which correspond to a single time point, time being the residence time in the flow tube. The data obtained with the ROFLEX machine comprises the iodine atomic resonance fluorescence signal versus residence time in the flow tube.

Simple chemical systems can be described by sets of ordinary differential equations (ODEs) that are analytically solvable. In these cases, a measured data can be fitted to analytical expressions using a least-squares method, from which reaction rates can be extracted. This can be done for example in the case of the resonance fluorescence experiments if we assume that the only relevant reactions describing the behavior of atomic iodine are:

\[ I + hv \rightarrow I + I \]  
(5)

\[ I + O₃ \rightarrow I + I + O₂ \]  
(6)

\[ I + O \rightarrow IO + O \]  
(7)

Because of the fast photolytic removal of I₂, an effective iodine loss rate in the presence of water can be extracted by simply fitting exponential decays to the time traces and calculating the differences between the removal rates with and without water. This, however, would not allow the concentration of O₃ to be estimated because IO reactions recycling atomic iodine are ignored:

\[ IO + IO \rightarrow I + O₂ \]  
(8)

\[ IO + hv \rightarrow I + O₂ \]  
(9)

\[ O₂ + O \rightarrow O₂ + O + M \]  
(10)

Multiplexed detection systems like the PI-ToF-MS provide simultaneous data from many molecules. To explain their kinetic traces, complex mechanisms with many reactions need to be constructed (e.g., Supplementary Tables 1 and 2). For
these, the corresponding ODEs are coupled and not amenable to analytical solution. By combining an ODE numerical integrator and a nonlinear least-squares algorithm to fit simulated curves to the observed ones, some of the unknown reaction rate constants of the system may be determined, provided that the problem has enough degrees of freedom and that the free parameters are uncorrelated. When the initial conditions are known (concentration of precursors and laser energies), it is possible to derive the scaling factors of the signals observed by setting them as floating parameters. We use a standard integrator for stiff ODE problems (i.e., containing reaction rates spanning orders of magnitude) and a constrained nonlinear multivariable least-squares method from the Mathematics Matlab toolboxes.

The data that support the findings of this study are available from the corresponding authors on reasonable request.

Iodine oxide particle pyrolysis

The set up was modified to conduct a set of BPB-pyrolysis experiments by placing near the sampling point an iron wire shaped into a 10-mm diameter coil connected to a power supply by electrical feedthrough.

Iodine oxide (IO) reactions (Table 1 and Supplementary Table 3) that are not available in the literature were obtained by using the B3LYP functional combined with the 6-31G(d,p) basis set. For all reactions, unscaled vibrational frequencies calculated from the ab initio PES. For barrierless association reactions, the inverse Laplace coefficients are then determined by detailed balance. Collisional energy transfer probabilities are calculated by using the aug-cc-pVDZ basis set for H and O, and the effective core potential LANL2DZ basis set for Iodine atoms (M06-2X level of theory, using the aug-cc-pVDZ+LANL2DZ. Normal-mode vibrational frequency analyses were carried out, and the stable minimum and all positive vibrational frequencies. Energies were refined at the CCSD(T) level of theory with the aug-cc-pVTZ+LANL2DZ basis set. For all reactions, unscaled vibrational frequencies calculated with the M06-2X/aug-cc-pVDZ+LANL2DZ method were used to estimate the zero-point energy (ZPE) corrections.

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Author contributions
A.S.L. devised the research, J.C.G.M., M.A.B., and J.M.C.P. designed the experimental set up, and J.C.G.M. and T.R.L. carried out the experiments and analyzed the data; J.M.C.P., J.C.G.M., M.K., and J.S.F. carried out electronic structure and master equation calculations; J.C.G.M. wrote the paper with contributions from all co-authors.

Competing interests
The authors declare no competing interests.

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