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**Article:**

Gomez Martin, JC, Gálvez, O, Baeza-Romero, MT et al. (3 more authors) (2013) On the mechanism of iodine oxide particle formation. *Physical Chemistry Chemical Physics*, 15 (37). 15612 - 15622. ISSN 1463-9076

<https://doi.org/10.1039/c3cp51217g>

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**Abstract**View Article Online  
DOI: 10.1039/C3CP51217G

The formation of atmospherically relevant iodine oxides  $I_xO_y$  ( $x = 1, \dots, 3$ ,  $y = 1, \dots, 7$ ) has been studied experimentally using time-of-flight mass spectrometry combined with a soft ionisation source, complemented with ab initio electronic structure calculations of ionisation potentials and bond energies at a high level of theory presented in detail in the accompanying paper (Galvez, *et al.*, 2013). For the first time, direct experimental evidence of the  $I_2O_y$  ( $y = 1, \dots, 5$ ) molecules in the gas phase has been obtained. These chemical species are observed alongside their precursors (IO and OIO) in experiments where large amounts of aerosol are also generated. The measured relative concentrations of the  $I_xO_y$  molecules and their dependence on ozone concentration have been investigated by using chemical modelling and rate theory calculations. It is concluded that  $I_2O_4$  is the most plausible candidate to initiate nucleation, while the contribution of  $I_2O_5$  in the initial steps is likely to be marginal. The absence of large  $I_3O_y$  ( $y = 3, \dots, 6$ ) peaks in the mass spectra and the high stability of the  $I_2O_4$ - $I_2O_4$  dimer indicate that dimerisation of  $I_2O_4$  is the key step in iodine oxide particle nucleation.

## 1. Introduction

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Iodine oxides are ubiquitous in the marine and polar boundary layer,<sup>1-5</sup> where they form by ozone-driven photo-oxidation of iodocarbons and molecular iodine emitted from the sea or ice as a result of biotic and abiotic processes (see Saiz-Lopez et al.<sup>6</sup> and references therein):



From early laboratory studies on gas-phase iodine chemistry it is well known that the recombination of iodine monoxide (IO) precedes the formation of condensable chemical species, which can undergo nucleation and lead to the formation of optically detectable aerosol and solid deposition.<sup>7-10</sup> In fact, it has been shown that emission fluxes of molecular iodine from coastal macroalgae under oxidative stress at low tide are strong enough to sustain substantial secondary aerosol formation in the atmosphere.<sup>11-13</sup> This potential link between marine biota and a climatically sensitive variable such as the aerosol loading, besides photosensitized iodine-driven ozone depletion, has motivated numerous laboratory field studies in recent years.<sup>6</sup>

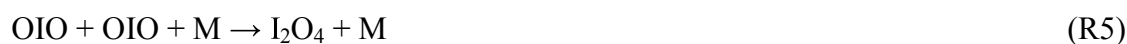
A number of theoretical and experimental studies have tried to rationalise the formation mechanism of iodine oxide particles (IOPs). The key gas phase precursor of IOPs is iodine dioxide, formed from the IO self reaction with a 40% branching ratio at 1 atm in N<sub>2</sub>.<sup>14, 15</sup>



Based on the heat of formation of OIO and RRKM calculations, the lifetime of IOIO against thermal decomposition at 1 Atm and 293 K has been estimated to be  $\sim 1$  s.<sup>16</sup> Also, tentative

assignments of the UV-vis spectrum of IOIO and estimates of its absorption cross sections, yield atmospheric lifetimes of tens of seconds.<sup>14, 15</sup> Therefore, it has been commonly assumed<sup>17</sup> that R3 proceeds effectively through R3a under boundary layer conditions, and that the following step of the particle formation mechanism involves only OIO. The photostability of this species<sup>18</sup> will on the other hand slow down the nucleation process.

Indirect evidence of IO and OIO recombination has been reported and rate coefficients of the order of  $1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 400 Torr have been estimated:<sup>15</sup>



However, unambiguous spectroscopic evidence of  $\text{I}_2\text{O}_3$ ,  $\text{I}_2\text{O}_4$  or other  $\text{I}_x\text{O}_y$  species has not been published. In fact, it has been the lack of experimental techniques able to discriminate between different iodine oxides in the gas phase<sup>14, 15, 18</sup> that has hindered clear progress in understanding this gas-to-particle conversion mechanism. Instead, a number of studies have focused on inferring mechanistic information from the physical and chemical properties of IOPs using ultrafine condensation particle counters, nano-differential mobility analysers, transmission electron microscopy, and quantitative x-ray analysis,<sup>19-23</sup> and from the bulk properties<sup>24, 25</sup> of the known stable solid phase iodine oxides ( $\text{I}_2\text{O}_4$ ,  $\text{I}_2\text{O}_5$ ,  $\text{I}_4\text{O}_9$ ).<sup>26</sup>

Initially, the chemical composition of the particles was suggested to be  $\text{I}_2\text{O}_4$ , based on the observed lack of hygroscopic growth of IOPs.<sup>20</sup> This led to the proposal of a mechanism where OIO was the nucleating monomer:



A semi-quantitative description of laboratory observed particle number densities and size distributions, based on the homogeneous nucleation of gas phase OIO (R6), was proposed.<sup>19</sup> However, subsequent studies reported a stoichiometric ratio I:O of  $\sim 2.5$ , indicating that the composition of the particles was more likely  $I_2O_5$ .<sup>21</sup> It was then proposed that  $I_2O_5$  could be the nucleating monomer, especially in view of its large calculated dipole moment.<sup>27</sup> A gas phase scheme based on oxidation steps for generation of  $I_2O_5$  was proposed:



where  $I_2O_2$ ,  $I_2O_3$  and  $I_2O_4$  would also form from reactions 3-5. Saunders and Plane<sup>21</sup> found that the rate coefficient of the oxidation steps R7-9 would need to be faster than  $6 \times 10^{-13}$  molecule<sup>-1</sup> cm<sup>-3</sup> s<sup>-1</sup> to enable gas phase  $I_2O_5$  to form faster than iodine oxides of lower O/I ratio under their experimental conditions.

However, it has been recently shown that the presence of  $O_3$  is not necessary to form particles, even though the final composition of IOPs is still  $I_2O_5$ .<sup>23</sup> It has been suggested<sup>23</sup> that such composition would then appear to result from re-structuring in the solid phase:



However, the thermally induced decomposition of  $I_2O_5$  occurs at 460 K.<sup>28, 29</sup> Electronic structure calculations have been published indicating stable  $I_4O_7$  and  $I_4O_8$  molecules.<sup>23</sup> This suggests that  $I_2O_3$  and  $I_2O_4$  formed in R4 and R5 would be the nucleating species rather than  $I_2O_5$ . Interestingly, increasing temperatures have an inhibiting effect on IOP formation, with the high negative activation energy observed ( $-78$  kJ mol<sup>-1</sup>) possibly reflecting the thermal decomposition of various iodine oxide aggregates.<sup>23</sup> According to the latest findings,<sup>23</sup> the

lack of hygroscopic growth of  $I_2O_5$  particles<sup>20</sup> (bulk  $I_2O_5$  is hygroscopic) would not be related to the chemical composition of the particles, but indicate that the adsorption of water onto the surface of the fractal-like IOP agglomerates leads to their collapse to form higher density particles, though of similar aerodynamic mobility.

In summary, even though valuable mechanistic information has been obtained by the analysis of IOP distribution properties under different chemical and physical conditions, the lack of direct qualitative and quantitative evidence about the precise mechanism persists. In fact, the IOP formation process in laboratory experiments has never been completely understood, with IOPs nucleating more slowly than expected - even under dry, room temperature conditions - but then growing faster than can be modelled using the current understanding of IOP formation described above (A. Mahajan and R. Saunders, personal communication).

In this paper we present a first experimental attempt to solve this problem by observing directly the formation of iodine oxides using photo-ionisation time of flight mass spectrometry (PI-TOF-MS)<sup>30</sup> coupled to a high pressure flow tube. Additionally, high level *ab initio* quantum calculations described in detail the accompanying paper<sup>31</sup> and master equation modelling are used synergistically to interpret the experimental results and gain new insights into the nucleation of IOPs.

## 2. Experimental

Preliminary experiments were performed at low-pressure ( $\sim 1$  Torr) where ground state atomic oxygen  $O(^3P)$ , generated via either 248 nm excimer laser photolysis of  $O_3$  or microwave discharge of  $O_2$ , was reacted with  $I_2$  to generate iodine oxides, which were sampled via a pinhole located in the wall of the flow tube.<sup>30</sup> These experiments failed to detect any oxides except IO, presumably due to wall losses, which is potentially a severe

problem with this off-axis sampling configuration. Consequently, the experiment was reconfigured so that the gas was sampled on-axis and at higher pressures ( $\sim 100$  Torr) in order to reduce the influence of wall losses, where the reagents flow down the entire length of the flow tube before being sampled into the mass spectrometer via a pinhole.

For the on axis configuration, iodine oxides were generated by the slow dark reaction between  $I_2$  and  $O_3$ ,<sup>26</sup> where  $O_3$  ( $\sim 1\%$  in  $O_2$ ) was directly introduced into the flow tube (internal diameter = 1.0 cm, length = 70 cm), and mixed with He, which first passed through a trap containing  $I_2$  crystals and then a mixing manifold before entering the flow tube. The  $O_3$  concentration was determined in separate experiments where the flow was directed into an  $O_3$  optical absorption detector and the concentration of gas-phase  $I_2$  was estimated by assuming its equilibrium vapour pressure. Typical concentrations in these experiments were  $[I_2] \sim 4 \times 10^{15}$  molecule  $cm^{-3}$  and  $[O_3]$  was varied over the range from  $5 \times 10^{14}$  to  $2 \times 10^{16}$  molecule  $cm^{-3}$ . A 100  $\mu m$  pinhole coupling the flow tube to the mass spectrometer was employed, enabling a range of pressures between 40 and 200 Torr, where moderate wall losses and significant iodine oxide formation allowed detection of these species, while at the same time limiting aerosol generation. This was found to be important for enabling reproducible experiments to be carried out without immediately blocking the pinhole. The contact time is determined by assuming diffusion-enabled plug flow regime ( $Re \sim 0.5$ ,  $Pe \sim 7$ ,  $Da \sim 0.001$ ).<sup>32</sup>

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The PI-TOF-MS system used in this study has been described in detail elsewhere.<sup>30</sup> Species entering the mass spectrometer are ionized  $\sim 5$  cm from the pinhole by 118 nm VUV light, produced by frequency-tripling in Xe the 355 nm output from a YAG laser. Following photoionization the ions are extracted and accelerated into the field-free flight region, before being reflected onto an electron multiplier to produce a mass spectrum in analogue or in ion



counting mode (Fig. 1a). While the counting mode is sensitive to small signals (iodine oxides), the analogue mode allows observation of large signals (e.g.  $I_2$ ).<sup>34</sup> The mass resolution of the TOF-MS is better than 1 in 100 Da. It is therefore possible to resolve small clusters up to ~1200 Da with sufficient resolution to determine, e.g., whether  $I_2O_4$  or  $I_2O_5$  is the condensable unit of IOPs. Mass to charge calibration (Fig. 1b) is accurate to within 1 mass at  $m/z$  127 and 2 mass units at  $m/z$  493 ( $1\sigma$ ).

Quantum chemistry calculations were carried out to estimate the ionisation potentials (IPs) of the  $I_xO_y$  species (Table 1). Geometries of neutral species were first optimised at MP2 level using for the iodine atom a 46 electron shape-consistent averaged relativistic effective potential (AREP)<sup>35, 36</sup> combined with a valence-only aug-cc-pVTZ (aVTZ) basis set,<sup>37</sup> for oxygen, a conventional, all-electron aVTZ basis sets was used. Subsequent CCSD(T) single point calculations were performed on the neutral optimised geometries, both for the neutrals and the cations, in order to calculate the vertical ionisation energies. A full description of these theoretical studies is provided in an accompanying paper.<sup>31</sup> The calculated IPs shown in Table 1 are in the range from 8.6 to 11.4 eV, corresponding to photons of 144.3 – 108.8 nm, i.e. close to but generally below the photo-ionisation energy employed in the experiments (10.5 eV, corresponding to a photon of 118 nm).

### 3. Results

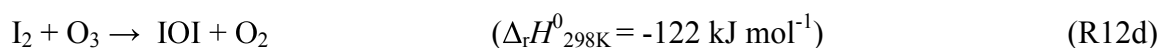
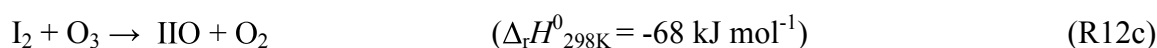
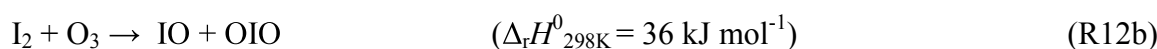
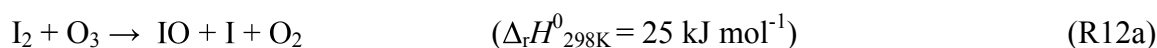
Examples of TOF spectra acquired in ion-counting mode at two different contact times (calculated from pressure and flow rates) are shown in Fig 2. Taking the ratio between the IO peak ( $m/z$  143) and the  $I_2O_4$  peak ( $m/z$  318) as a reference, the experiments at short contact time show a higher concentration of  $I_xO_y$  species relative to the IO precursor. Fig. 3 shows integrated peak signals for the major peaks present in the spectra of Fig. 1 from a typical sequence of experiments. Initially  $[O_3]$  was varied in a controlled manner but the progressive

blocking of the pinhole by aerosol caused the pressure to increase (Fig. 3a), eventually stopping the experiment until the pinhole was cleaned and the system re-evacuated. The most prominent signals all change in a similar manner with pressure and  $[O_3]$  (Fig. 3c and Fig. 4), and are positively and significantly correlated to IO. Another group of weak peaks (Fig. 3d, mostly  $I_3O_y$ ) are apparently reacting to the pressure cycle in the flow tube (anticorrelated to pressure) or are almost flat, as shown by their absence from the difference between high and low ozone spectra (Fig. 1b and 1d). Mass signals not showing a dependence on  $O_3$  (Fig. 3d) are interpreted as fragments of solid iodine oxide formed on the walls or the pinhole itself. In fact these signatures remain in spectra taken after the  $I_2$  and  $O_3$  flows into the flow tube were shut off.

The  $I_2$  concentration is high when  $[O_3]$  is not at its maximum; this generally causes signal saturation in ion counting mode (gap in the data around  $m/z$  254 in Fig. 2a). When such saturation is severe, no useful data can be gathered (the analogue mode can be used instead, see below). However, the atomic iodine signal (Fig. 3b) is generally representative of the  $I_2$  signal due to  $I_2$  fragmentation. This iodine signal ( $m/z$  143) also shows signs of counting saturation due to the large amounts of  $I_2$  in the system at low  $O_3$ . Note that atomic iodine generated in the flow tube is quickly scavenged by the large amounts of  $O_3$  present, so its concentration is low. The centre of the IO peak ( $m/z$  143) appeared to be distorted in some experiments; in these cases the peak was fitted with a Gaussian function in order to obtain the integrated area under the peak and preserve the relative scaling with the rest of the  $I_xO_y$  integrated peak signals. The maximum IO concentrations in the flow tube are of the order of  $10^{12} - 10^{13}$  molecule  $cm^{-3}$ , which should not cause counting saturation. In the analysis (see below) the large  $IO^+$  signal is interpreted as a result of fragmentation of larger molecules. The IO data in Fig. 3 and Fig. 4 are corrected for overload effects and shown at the same relative

scaling observed in the original spectra. The OIO peak (m/z 159) and the other smaller peaks are not distorted and no correction was needed.

The observed decay of the I<sub>2</sub> signal recorded in analogue mode (m/z 254 or m/z 127 for the I<sup>+</sup> fragment) in the presence of different concentrations of O<sub>3</sub> (Fig. 5) yields a rate coefficient  $k(298\text{ K}) = (3.2 \pm 0.5) \times 10^{-18} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ , in reasonable agreement with the only previous determination  $k(298\text{ K}) = (4.0 \pm 2.0) \times 10^{-18} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$  of the rate coefficient of the slow, spin forbidden gas phase reaction between I<sub>2</sub> and O<sub>3</sub>.<sup>26</sup>



where the enthalpies of reaction have been calculated using experimental values of the enthalpies of formation of I(<sup>2</sup>P<sub>3/2</sub>), I<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) and O<sub>3</sub>(<sup>1</sup>A<sub>1</sub>)<sup>38</sup>, IO(<sup>2</sup>Π<sub>3/2</sub>)<sup>39</sup> and OIO(<sup>2</sup>B<sub>1</sub>)<sup>16</sup> and the present calculations at the CCSD(T)//MP2 level of theory for the stable molecules IIO(<sup>1</sup>A') and IOI(<sup>1</sup>A<sub>1</sub>).<sup>31</sup>

Potential products of R12 in the mass spectra include IO (m/z 143), IO<sub>2</sub> (m/z 159) and I<sub>2</sub>O (m/z 270) (Fig. 2). The IO dimer, I<sub>2</sub>O<sub>2</sub> (IOIO) m/z 286 is generated by R3b with a ~0.3 branching ratio in 100 Torr of N<sub>2</sub>,<sup>15</sup> and it is relatively stable at this pressure according to calculations reported in the literature (lifetime >3 seconds).<sup>16</sup> Collisions with He are less effective in stabilising molecular aggregates than with N<sub>2</sub>, which reduces the amount of I<sub>2</sub>O<sub>2</sub> formation by about a factor of 2, but does not explain why the I<sub>2</sub>O<sub>2</sub> peak is minor compared to that of OIO. I<sub>2</sub>O<sub>3</sub> (m/z 302) and I<sub>2</sub>O<sub>4</sub> (m/z 318) are likely to be formed by R4 and R5 respectively. Reactions R3-R5 are relatively fast at 298 K and 100 Torr ( $k > 1 \times 10^{-11}$

molecule<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>).<sup>15</sup> However, all the key species have a very similar dependence on  $[O_3]$  with effective growth rate constants of the order of  $\sim 5 \times 10^{-18}$  molecule<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>, as a result of IO, precursor to all of them, being formed in the rate limiting reaction R12.

Very little I<sub>2</sub>O<sub>5</sub> (m/z 334) is seen compared to I<sub>2</sub>O<sub>4</sub>, which seems to indicate that the oxidation path (R9) is minor. However, this observation must be treated with caution, since the calculated ionisation potential of I<sub>2</sub>O<sub>5</sub> (Table 1) is above the photon energy of the 118 nm laser radiation, which could imply that the photo-ionisation cross section of I<sub>2</sub>O<sub>5</sub> is significantly smaller than that of I<sub>2</sub>O<sub>4</sub> at this wavelength. The fact that I<sub>2</sub>O<sub>5</sub> still ionises to some extent at this wavelength could be due to the internal energy of the molecule.

The I<sub>3</sub>O<sub>y</sub> mass peaks ( $y \leq 7$ ) are minor as shown in Fig. 2. Among these, I<sub>3</sub>O<sub>6</sub> (m/z 477) and I<sub>3</sub>O<sub>7</sub> (m/z 493) are the highest mass signals observed and the most prominent, but while the former does not change with O<sub>3</sub>, the latter does in a similar manner to the IO<sub>y</sub> and I<sub>2</sub>O<sub>y</sub> mass signals (Fig 2c). Also the very weak mass I<sub>3</sub>O<sub>5</sub> changes in a similar manner to the I<sub>3</sub>O<sub>7</sub> species. No mass signals larger than I<sub>3</sub>O<sub>7</sub> are observed.

Other mass signals appearing in the mass spectrum in Fig. 1 between m/z 28 and m/z 58 are related to acetone and its fragments. Acetone was used prior to experiments to clean the system and for signal optimisation purposes (it has a large photo-ionisation cross section). A persistent peak appears at m/z 204. This mass does not fit to the I<sub>x</sub>O<sub>y</sub> pattern and does not have a systematic dependence on [O<sub>3</sub>]. It is possibly related to the halocarbon wax coating the flow tube, employed to reduce wall losses.

#### 4. *Ab initio* and rate theory calculations

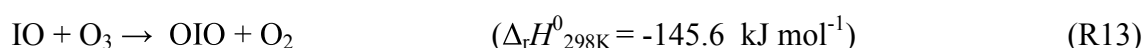
In order to estimate aggregation rate coefficients between iodine oxides (Table 2), we first explored potentially stable iodine oxide aggregates by calculating bond energies at the CCSD(T)//MP2 level of theory. The general weakness of the  $I_3O_y$  peaks in the mass spectra indicates that IO and OIO do not attach very efficiently to  $I_2O_y$ , and suggests that OIO is not the nucleating monomer as proposed in R6. We have performed quantum chemical calculations on a number of  $I_3O_y$  conformers with  $y = 4, \dots, 7$ , and have found that most of these species are very weakly bound (Table 2 shows bond dissociation energies of the most stable  $I_3O_y$ ,  $y = 4, \dots, 7$  conformers). In particular, the  $I_3O_7$  species investigated are bound by only  $\sim 50 \text{ kJ mol}^{-1}$ , which suggest that this mass, clearly varying with  $[O_3]$ , is most likely a fragment of a larger aggregate. Also, it must be noted that the  $I_3O_y$  species have an unpaired electron and are expected to be very reactive. An extensive study has been carried out on aggregates containing 4 iodine atoms, which is detailed in the accompanying paper.<sup>31</sup>

Rate coefficients for the association and dissociation reactions of various  $I_xO_y$  species (Table 2) have been calculated using the Master Equation Solver for Multi-Energy well Reactions (MESMER),<sup>40, 41</sup> taking MP2/ECP/aVZT rotational constants and vibrational frequencies, and the CCSD(T)//MP2/ECP/aVZT zero point corrected energies (B3LYP was used instead of MP2 for some calculations involving 4 iodine atoms, due to computational costs).<sup>31</sup> The ro-vibrational energy levels in the *ab initio* potential energy surface are grouped into energy grains, and the population in each grain is described by a set of coupled differential equations that account for collisional energy transfer within each grain as well as dissociation. Microcanonical rate coefficients for the unimolecular reactions that occur in each energy grain are calculated from the *ab initio* data. For barrierless association reactions such as the recombination of iodine oxides, the Inverse Laplace Transform method<sup>42, 43</sup> can be applied to calculate the microcanonical association rates from an estimate of the high pressure limiting rate coefficient for association, assumed to be equal to the collision number and temperature

independent. The microcanonical dissociation rate coefficients are then determined by detailed balance. The exponential down model is used for describing collisional energy transfer probabilities ( $\Delta E_{\text{down}} = 250 \text{ cm}^{-1}$ ). Lennard-Jones parameters for the interaction of the aggregates with the bath gas (He) are estimated following the procedure recommended by Gilbert and Smith<sup>44</sup> ( $\sigma$  ranging from 5 to 7 Å,  $\varepsilon = 300 \text{ K}$ ). Parameter selection is guided by a fit to the available experimental data for the IO self-reaction rate coefficient and branching ratios.

## 5. Discussion

R12 is the initial precursor to the iodine oxides observed in this study. R12a could proceed via formation of a very short lived IOO(<sup>2</sup>A'') intermediate,<sup>45, 46</sup> and its endothermicity is consistent with the activation energy of  $25.0 \pm 1.2 \text{ kJ mol}^{-1}$  observed for R12.<sup>26</sup> R12b and R12d require insertion of an oxygen atom and therefore are expected to present barriers. Channel R12c should in principle be the dominant exit channel in view of its exothermicity, but the weakness of the m/z 270 peak (I<sub>2</sub>O) and the dominance of the m/z 143 peak (IO) in our spectra (Fig. 3) suggests that there is also a barrier in this channel. In fact, it is likely that the m/z 270 signal results at least in part from photo-fragmentation of I<sub>2</sub>O<sub>y</sub>. Given the instability of IOO (bond energy 10-20 kJ mol<sup>-1</sup>)<sup>45, 46</sup> and the endothermicity of R12b, the peak at m/z 159 is most likely due to the stable IO<sub>2</sub> isomer, OIO. OIO is generated from the IO self reaction (R3),<sup>15</sup> and could also be produced by the slow reaction ( $k \leq 5.0 \times 10^{-16} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ ):<sup>47</sup>



Note however that for the estimated IO peak concentration of  $\sim 10^{13}$  molecule  $\text{cm}^{-3}$  the order rate of IO removal (to form OIO) by R3 is  $\sim 800 \text{ s}^{-1}$ , while IO removal (to form OIO) via R13 with  $[\text{O}_3] \sim 10^{16}$  molecule  $\text{cm}^{-3}$  would only proceed at  $\sim 5 \text{ s}^{-1}$ .

### *Kinetic Modelling*

Based on the observations above, kinetic modelling of the chemistry initiated by R12 has been carried out in order to achieve a coherent picture of the mass spectra. Since simple kinetic modelling shows that the dependence on  $\text{O}_3$  of all species is to a large extent determined by R12, the objective of this modelling is explaining the relative intensities of the different peaks. Using experimental and calculated rate coefficients with He as the bath gas (Table 2) and the initial concentrations of  $\text{I}_2$  and  $\text{O}_3$ , the model is integrated using a solver of stiff differential equations.<sup>48</sup> The simulated data is globally fitted to the key species observed (IO, OIO,  $\text{I}_2\text{O}_2$ ,  $\text{I}_2\text{O}_3$ ,  $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_5$ ) using a non-linear least squares algorithm, by floating selected concentration scaling factors and/or rate coefficients, as well as a first order loss rate to account for wall losses and aerosol uptake of all these species. No explicit weighting is applied to the data, although in such a global fit the original relative scaling of the different observed signals ( $S_{\text{IO}} > S_{\text{OIO}} > S_{\text{I}_2\text{O}_4} > S_{\text{I}_2\text{O}_2} \approx S_{\text{I}_2\text{O}_3}$ ) implies that the most prominent peaks carry more weight in the fit.

In the simplest modelling case (Fig. 4a-4f), the following assumptions are made:

- 1) The photo-ionisation cross sections at 118 nm of the observed  $\text{I}_x\text{O}_y$  species are the same and no fragmentation takes place. This implies that the relative signals are assumed to be representative of the relative concentrations.
- 2) The chemical mechanism is well defined (bold case reactions in Table 2)
- 3) All  $\text{I}_x\text{O}_y$  are lost to the walls (or aerosols) with the same efficiency.

Thus, a common concentration scaling factor to convert signal into concentration is fitted alongside the wall loss rate, and all the literature and calculated rate constants are fixed. This exploratory modelling exercise allows us to assess which processes are defined and which assumptions in the model may be deficient. The  $I_2O_2$  and  $I_2O_3$  signals are an order of magnitude too small compared with the simulated concentrations (Fig. 4c and 4d). Another important observation is that the model does not produce enough OIO and  $I_2O_4$  to match the observed signal (Fig. 4b and 4e). This could result from an insufficient mechanistic description in the model (i.e. reactions missing in Table 2) and/or poor estimates of the kinetic parameters for R3-R5 and R7-R9. However, this situation could be also resolved if assumption 1 is removed, i.e. if photo-ionization cross-sections are larger for OIO and  $I_2O_4$  compared to  $I_2O_2$  and  $I_2O_3$ . It is also likely that fragmentation of  $I_2O_2$  and  $I_2O_3$  contributes to enhance the IO and OIO signals.

### ***Effect of photo-ionisation and photo-fragmentation***

In general, for any observed peak at  $m/z$   $i$  (note we consider here only singly ionised species and 1 photon processes) the TOF integrated peak signal  $S_i$  can be expressed as the sum of contributions from the photo-ionisation of the neutral parent mass associated to  $i$  ( $j=i$ ) and all other ( $j > i$ ) neutral species fragmenting to  $i$ :

$$S_i = K \times E \times \sum_j \sigma_j(\lambda) \times \phi_{ij}(\lambda) \times [j] \quad (E1)$$

where  $K$  is a constant characteristic of the instrument,  $E$  is the laser pulse energy,  $\sigma_j(\lambda)$  is the total photo-ionisation cross section of species  $j$  at the laser wavelength  $\lambda$ ,  $\phi_{ij}(\lambda)$  is the ionic photo-fragmentation branching ratio for production of  $m/z$   $i$  from neutral  $j$  (including  $j = i$ ) and  $[j]$  is the concentration of the neutral species with mass  $j$ .<sup>49</sup> When the concentration time-



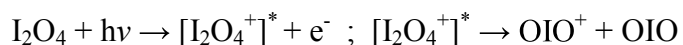
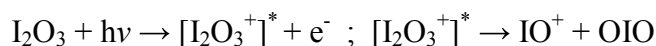
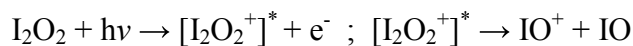
profiles are very similar as in the present case (R12 rate limiting) then we have  $[i]_0 \approx [i]_{50} \approx [i]_{100}$  and (E1) reduces to:

$$S_i \approx K \times E \times [i] \times \sum_j \sigma_j(\lambda) \times \phi_{ij}(\lambda) \times R_{ij} = C_i \times [i] \quad (\text{E2})$$

where  $R_{ij} = [j] / [i]$ . In summary, a PI-TOF-MS signal at  $m/z$   $i$  can appear to be larger than others not only due to a larger  $[i]$ , but also as a result of a larger photo-ionisation cross section and/or branching ratio of the parent mass ( $j = i$ ), or to the addition of further contributions from fragmentation of neutral species with larger  $m/z$  ( $j > i$ ), resulting in an enhanced  $C_i$ . It must be remembered that in general the approximation made in E2 is not applicable in all cases: when the different signals present different kinetic behaviour, the overlap of parent and fragment signal causes  $C_i$  being dependent on reaction contact time or reactant concentration ( $\text{O}_3$  in our case). In that case, a  $C_i(t, [\text{O}_3])$  needs to be fitted for every time or concentration, or alternatively the effective cross sections  $\sigma_j \times \phi_{ij}$  in E1 would need to be independently fitted. This problem resembles the overlap of optical absorption signals, and has been addressed in previous studies by using a tuneable photo-ionisation source.<sup>50</sup>

Panels (g)-(l) in Fig. 4 show the results of a second modelling case where, following E2, the scaling factors for IO, OIO,  $\text{I}_2\text{O}_2$ ,  $\text{I}_2\text{O}_3$  and  $\text{I}_2\text{O}_4$  are allowed to float independently in order to fit the observations (i.e. assumption 1 is removed).  $C_{\text{I}_2\text{O}_5}$  is initially fixed to be equal to  $C_{\text{I}_0}$  due to the low weight of  $S_{\text{I}_2\text{O}_5}$  in the fit. The fitted concentration scaling factors are shown in the lower right corner of each panel of Fig. 4. In principle, it would be possible to feed back the  $C_i$  obtained from the fit into E2, to derive cross sections  $\sigma_j$  and branching ratios  $\phi_{ij}$  from a system of equations. This requires however a calibration of the instrumental factor to determine  $K$  and  $E$  and, in addition, a number of assumptions would need to be made in order to reduce the number of unknowns to the number of equations. The first fragmentation ion is

usually coming from dissociation of the weakest bond in the parent molecule, where the ion signal is from the most ionisable dissociation fragment. Therefore it is reasonable to expect the following fragmentation:



where  $[\text{I}_2\text{O}_y^+]^*$  ( $y = 2-4$ ) are molecular ions in an electronic excited state.<sup>49</sup> But the extent of fragmentation is difficult to theoretically predict. Even though this could not be accomplished in the present study, the ratios between the  $C_i$  values provide some information about photo-ionisation. The particular exercise in Fig. 4 yields  $C_{\text{I}_2\text{O}_2} \sim C_{\text{IO}}/18$  and  $C_{\text{I}_2\text{O}_3} \sim C_{\text{IO}}/61$ , which suggests that the parent molecules  $\text{I}_2\text{O}_2$  and  $\text{I}_2\text{O}_3$  are fragmenting extensively rather than due to small total ionization cross-sections, i.e.  $\phi_{ii}$  (branching ratios for the parent neutral species) are small compared with  $\phi_{ij}$  (photo-fragmentation branching ratios). The ratio  $C_{\text{I}_2\text{O}_4} \sim C_{\text{OIO}}/1.6$  is much smaller than the above ratios and therefore suggests that  $\text{I}_2\text{O}_4$  ionizes with much less fragmentation compared to  $\text{I}_2\text{O}_2$  and  $\text{I}_2\text{O}_3$ . If the above fragmentation schemes are operating, i.e. fragmentation via the weakest bond, then the suggestion that  $\text{I}_2\text{O}_2$  and  $\text{I}_2\text{O}_3$  are fragmenting to a greater extent than  $\text{I}_2\text{O}_4$  is borne out by the fact that the scaling factor for IO is 1.4 times larger than for OIO. It is possible as well that the  $\text{I}_2\text{O}$  signal ( $m/z$  270) corresponds to photo-fragmentation of  $\text{I}_2\text{O}_y$  rather than originating from R12c. Although  $\text{I}_2\text{O}$  has not been included in the model, this signal could be also accounted for including a small branching ( $\sim 2\%$ ) for channel R12c and assuming  $C_{\text{I}_2\text{O}} \approx C_{\text{IO}}$ , without affecting significantly the results for the major species. Fragmentation of higher oxides could also contribute to enhance  $S_{\text{I}_2\text{O}_4}$  relative to  $S_{\text{I}_2\text{O}_2}$  and  $S_{\text{I}_2\text{O}_3}$ .

### *Sensitivity to kinetic parameters*

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DOI: 10.1039/C3CP51217G

An explanation for the small  $I_2O_y$  signals alternative to photo-fragmentation could be chemical or aggregation reactions of these species (i.e. keep assumption 1 and remove assumption 2). Our quantum calculations and previous theoretical studies<sup>16, 51</sup> show that the thermal decomposition of  $I_2O_2$ ,  $I_2O_3$  and  $I_2O_4$  is too slow to cause significant loss on the time scale of tens of seconds. The absence of large, ozone-dependent  $I_3O_y$  ( $y = 3, \dots, 5$ ) signals suggest that aggregation of  $I_2O_2$  and  $I_2O_3$  with IO and OIO is not favoured, and in fact our calculations indicate that the  $I_3O_y$  aggregates are not strongly bound (see bond dissociation energies in Table 2). Slow rate coefficients for R7-R9 have been considered so far (assumed to be the same as for R13) (Table 2). Our modelling shows that R7 would need to be as fast as  $1 \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$  to at least match the order of magnitude of the observed  $I_2O_2$  signal when assumption 1 is considered, and in addition the  $O_3$  dependence would go in the wrong direction (Fig. 4d shows an  $I_2O_2$  simulated trace for this fast oxidation case). Moreover, it is not possible to fit successfully the data considering the same rate constant for R7-R9, and therefore we infer that these reactions are not responsible for the relative signals observed. Finally, a modelling case where the rate coefficients of R4 and R5 and the branching ratios of R3 are floated along with a single common scaling factor produces a satisfactory fit. However, the optimal values of  $k_{3b}/k_3$  and  $k_4$  resulting from this exercise are one order of magnitude lower than our estimated values included in Table 2, which are based on a combination of experiments in  $N_2$ <sup>15</sup> and rate theory calculations (see below). It can be concluded that, although there is some degree of uncertainty in the kinetic parameters of this fairly simple chemical system (factor of 2, based on the variation of different parameters in the rate theory calculations with MESMER), the observed PI-TOF-MS signals are to a large extent determined by photo-ionisation and photo-fragmentation.

The sensitivity to the variation of key kinetic parameters within the range of estimated uncertainty is summarised in Table 3, where the effect on the fitted photo-ionisation scaling factors, the loss rate and goodness-of-fit parameter  $\chi^2$  are shown ( $\chi^2 = 4.5$  for the base case in Table 2 and Fig. 4g-4l). The model is run using always the same chemical scheme shown in Table 2, but for different values of the kinetic parameters relevant to the  $I_2O_y$  species spanning their range of estimated uncertainty, and the percentage of variation of each  $C_i$  with respect to the base case run is calculated. For reactions R7-9 a common rate coefficient is assumed and varied over 2 orders of magnitude with the objective of obtaining an upper limit of this parameter. Doubling (runs 1, 3 and 5) or halving (runs 2, 4 and 6) the values of  $k_{3b}/k_3$ ,  $k_4$  and  $k_5$  does not have a big impact in the quality of the fit. The  $C_i$  coefficients change to accommodate such variations, and in most cases these variations overlap with the parameter error estimates of the base case fit, which highlights the need of different kinetic traces to obtain more information from this kind of system (i.e. find a source reaction which is not rate limiting).

Including R7-9 in the model (model runs 7, 10 and 13) notably changes the quality and also leads to an over-parameterised fit, as revealed by large errors of the fitted parameters. It can be seen that  $k_{7-9} = 1 \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$  increases significantly the value of  $\chi^2$ . The fit quality is also poorer even with  $k_{7-9} = 5 \times 10^{-15} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ , only a factor of 10 higher than the value assumed in Table 2. Such increases in  $\chi^2$  result from a poorer fitting of the  $I_2O_y$  species, and also partially from the larger amounts of  $I_2O_5$  generated in the model, which are not consistent with  $I_2O_5$  having the same  $C_i$  as IO. The loss rate increases as well to compensate for the fast growth of  $I_2O_5$ . This poorer fitting reflects the fact that at some point reactions R7-9 start having an influence on the dependence of  $I_2O_y$  on ozone. If the scaling factor  $C_{I_2O_5}$  is allowed to vary (runs 8, 11 and 14),  $\chi^2$  comes reasonably close to the base case value (5.08) when  $k_{7-9} = 5 \times 10^{-15} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ . In a separate set of runs (9, 12 and 15)

$S_{I2O5}$  is excluded from the observational vector. Although the  $\chi^2$  values of these three runs are not comparable to the rest, the trend of decreasing  $\chi^2$  with decreasing  $k_{7-9}$  is clear. From this sensitivity analysis a conservative upper limit of  $k_{7-9} < 1 \times 10^{-14}$  molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup> can be deduced based on the marginal difference in quality between runs 11 and 14.

### ***Link to IOP formation***

We have used the model run 11 (Table 3) ( $k_{7-9} = 1 \times 10^{-14}$  molecule<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>) to make an assessment of what is the most likely step after formation of the I<sub>2</sub>O<sub>y</sub> molecules. Fig. 6 shows the time dependence of the major species generated by the chemical mechanism for a model run with [O<sub>3</sub>] ~ 2 × 10<sup>16</sup> molecule cm<sup>-3</sup>. The dashed lines indicate the contact time corresponding to the spectra in Fig. 2b and 2d and show how the relative signals would change significantly in time. In particular, this implies distortion of the IO parent mass signal at shorter contact times by fragmentation of I<sub>2</sub>O<sub>2</sub> and I<sub>2</sub>O<sub>3</sub>. These two oxides are formed at high concentrations, but according to our quantum calculations, they do not form any stable aggregate, and therefore they will be simply lost to walls or taken up by aerosol. By contrast, I<sub>2</sub>O<sub>4</sub> forms a stable aggregate, I<sub>4</sub>O<sub>8</sub>. The insert panel in Fig. 6 shows that when the C<sub>I2O4</sub> scaling factor is applied to the I<sub>3</sub>O<sub>7</sub> signal observed, the agreement between scaled signal and modelled concentration is remarkably good. Although this is far from an unambiguous assignment, it suggests that the I<sub>3</sub>O<sub>7</sub> signal is likely to result from I<sub>4</sub>O<sub>8</sub> fragmentation, also considering that there are no other I<sub>x</sub>O<sub>y</sub> species at a sufficiently high concentration to generate such fragment. Alternatively, I<sub>3</sub>O<sub>7</sub> could result from fragmentation of IOPs formed by the attachment of any other I<sub>x</sub>O<sub>y</sub> to I<sub>4</sub>O<sub>8</sub>.

Finally, it is worth paying some attention to the fate of I<sub>2</sub>O<sub>5</sub>. When the upper limit for  $k_{7-9}$  is considered, significant concentrations of I<sub>2</sub>O<sub>5</sub> are generated by the model (~ 1 × 10<sup>10</sup> molecule cm<sup>-3</sup>), which may appear in the experiments as a small  $S_{I2O5}$ , possibly as a result of

a below-threshold photo-ionisation cross section. Species with high enough concentration to be potentially important sinks for  $I_2O_5$  are IO, OIO and  $I_2O_3$ . However, our calculations indicate that they do not form stable bonds with  $I_2O_5$ . In particular, the different conformers of the  $I_2O_5 \cdots OIO$  adduct are too weakly bound, so this has to be discounted as a potential sink (as well as an explanation of the  $I_3O_7$  signal). Thus,  $I_2O_5$  is a minor species compared to  $I_2O_2$  and  $I_2O_3$ , with a similar inability to form stable homo- or heterodimers, apart from  $I_4O_9$ . Its main fate could be hypothesised as well as wall loss and uptake by the growing IOP population descending from  $I_4O_8$ . It is difficult to envisage a path from gas phase  $I_2O_5$  to the solid particles of this composition reported in the literature.<sup>21, 23</sup> This would necessarily involve a preferential uptake of  $I_2O_5$  by  $I_4O_8$ ,  $I_4O_9$  and by the aggregates subsequently formed in order to gradually increase the O:I stoichiometric ratio of the IOPs to values closer to 2.5. However, the fact that particles form in the absence of ozone<sup>23</sup> suggest that gas phase  $I_2O_5$  does not play any special role.

## 6. Conclusions

The products of the slow  $I_2 + O_3$  reaction in the dark have been found to be mainly I and IO, generated by a slightly endothermic channel. The use of this reaction as precursor of iodine oxides in a high pressure-slow flow tube equipped with PI-TOF-MS has been shown to be a promising approach for studying the first steps of iodine oxides nucleation and their photochemistry. For the first time direct observation of key gas-phase  $I_xO_y$  species with  $x \geq 2$  has been reported. Ozone is unlikely to make a major contribution to the formation of  $I_2O_y$ , since the dependence on  $O_3$  of the  $I_2O_y$  species is inconsistent with fast oxidation reactions. A conservative upper limit to the rate constant of ozone oxidation steps has been derived ( $k_{7-9} < 1 \times 10^{-14} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ ), which rules out the evolution of  $I_2O_5$  stoichiometry IOPs directly from  $I_2O_5$  gas phase nucleation.<sup>21, 23</sup> The relative intensity of the PI-TOF-MS signals

observed has been mainly attributed to photo-fragmentation, which is severe in the case of  $\text{I}_2\text{O}_2$  and  $\text{I}_2\text{O}_3$  at 118 nm. View Article Online  
DOI: 10.1039/C3CP51217G

$\text{I}_3\text{O}_y$  ( $y < 6$ ) species do not form in significant amounts in the gas phase. In view of the instability of aggregates involving  $\text{I}_2\text{O}_2$  and  $\text{I}_2\text{O}_3$  indicated by our quantum calculations, the dimerisation of  $\text{I}_2\text{O}_4$  is likely to be the key reaction at this stage, considering the unusual stability of the  $\text{I}_4\text{O}_8$  aggregate.  $\text{I}_4\text{O}_8$  should probably be regarded as the smallest IOP.  $\text{I}_2\text{O}_2$  and  $\text{I}_2\text{O}_3$  are dead ends in the nucleation mechanism, but they possibly attach to  $\text{I}_4\text{O}_8$ . A fragment with  $\text{I}_3\text{O}_7$  stoichiometry is observed, which can be related either to  $\text{I}_4\text{O}_8$  or to clusters formed by the aggregation of  $\text{I}_4\text{O}_8$  and any other  $\text{I}_x\text{O}_y$ . Even though  $\text{I}_2\text{O}_5$  has an IP above the photo-ionisation energy employed in this study according to our quantum calculations, it seems to play a marginal role in view of the slow ozone oxidation rate coefficients. The  $\text{I}_2\text{O}_5$  composition of particles previously reported is therefore likely a result from  $\text{I}_2$  liberation in the solid-phase.

Further work is needed to improve the sensitivity and reproducibility in the experimental system – especially regarding blocking of the pinhole and reduction of wall losses, in order allow a wider range of concentrations, pressures and contact times. Also, tuneable ionisation radiation could be used to avoid fragmentation of  $\text{I}_2\text{O}_2$  and  $\text{I}_2\text{O}_3$ . Future studies using the  $\text{I}_2 + \text{O}_3$  synthesis method should focus on the determination of the photochemical properties of  $\text{I}_x\text{O}_y$ , which is one of the largest uncertainties in atmospheric iodine models.<sup>6</sup>

### Acknowledgements

This work was supported by the Natural Environment Research Council (grant NE/E005659/1). O. G. acknowledges financial support from Ministerio de Ciencia e Innovación, “Ramón y Cajal” program, and Project FIS2010-16455

## Tables

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DOI: 10.1039/C3CP51217G**Table 1.** Ionization potentials of atomic and molecular iodine and of iodine oxides

| Ion  | m/z | Ionization energy (eV) / Wavelength (nm) |                             |  |
|--|-----|--|-----------------------------|--|
|  |     | Literature<br>(Experimental)             | Literature<br>(Theoretical) | This work<br>(Theoretical <sup>d</sup> ) |
| I <sup>+</sup> ( <sup>3</sup> P)                             | 127 | 10.451 <sup>a</sup> / 118.7              |                             | 10.35 / 119.9                            |
| HI <sup>+</sup> ( <sup>2</sup> Σ)                            | 128 | 10.381 <sup>a</sup> / 119.5              |                             | 10.50 / 118.2                            |
| I <sub>2</sub> <sup>+</sup> ( <sup>2</sup> Σ)                | 254 | 9.3995 <sup>a</sup> / 132.0              |                             | 9.47 / 131.0                             |
| IO <sup>+</sup> ( <sup>3</sup> Σ)                            | 143 | 9.745±0.017 <sup>b</sup> / 127.3         |                             | 9.56 / 129.8                             |
| OIO <sup>+</sup> ( <sup>1</sup> B)                           | 159 |  | 9.793 <sup>c</sup> / 126.7  | 9.72 / 127.6                             |
| IIO <sup>+</sup> ( <sup>2</sup> A)                           | 270 |  |                             | 9.02 / 137.5                             |
| IOIO <sup>+</sup> ( <sup>2</sup> A)                          | 286 |  |                             | 9.13 / 135.9                             |
| OI(I)O <sup>+</sup> ( <sup>2</sup> A)                        | 286 |  |                             | 10.38 / 119.5                            |
| I <sub>2</sub> O <sub>3</sub> <sup>+</sup> ( <sup>2</sup> A) | 302 |  |                             | 9.97 / 124.4                             |
| I <sub>2</sub> O <sub>4</sub> <sup>+</sup> ( <sup>2</sup> A) | 318 |  |                             | 9.26 / 134.0                             |
| I <sub>2</sub> O <sub>5</sub> <sup>+</sup> ( <sup>2</sup> A) | 334 |  |                             | 11.38 / 108.9                            |
| I <sub>3</sub> O <sub>5</sub> <sup>+</sup> ( <sup>1</sup> A) | 461 |  |                             | 9.46 / 131.1                             |
| I <sub>3</sub> O <sub>6</sub> <sup>+</sup> ( <sup>1</sup> A) | 477 |  |                             | 9.06 / 136.9                             |
| I <sub>3</sub> O <sub>7</sub> <sup>+</sup> ( <sup>1</sup> A) | 493 |  |                             | 8.69 / 142.8                             |

<sup>a</sup> JANAF tables<sup>52</sup>. <sup>b</sup> Reference<sup>53</sup>. Given as adiabatic <sup>c</sup> Reference<sup>54</sup>. Given as adiabatic. Estimation based in the performance of different levels of theory on the reproduction of the experimental ionization potentials of OCIO and OBrO<sup>d</sup> CCSD(T)//MP2/AREP/aVTZ. Given as vertical.



Table 2. Chemical Mechanism (T = 298 K, P = 100 Torr)

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| R#         | Reaction <sup>a</sup>  | $k / \text{molecule}^{-1} \text{cm}^3 \text{s}^{-1}$ | Reference/Notes           |            |
|------------|--|--|---------------------------|------------|
| <b>2</b>   | <b>I + O<sub>3</sub> → IO + O<sub>2</sub></b>  | $1.3 \times 10^{-12}$                                | <sup>55</sup>             |            |
| <b>3a</b>  | <b>IO + IO → I + OIO</b>   | $7.0 \times 10^{-11}$                                | <sup>15 c</sup>           |            |
| <b>3b</b>  | <b>IO + IO → I<sub>2</sub>O<sub>2</sub></b>  | $1.0 \times 10^{-11}$                                | <sup>15 c</sup>           |            |
| <b>4</b>   | <b>IO + OIO → I<sub>2</sub>O<sub>3</sub></b>   | $4.2 \times 10^{-11}$                                | Calculated <sup>d,e</sup> |            |
| <b>5</b>   | <b>OIO + OIO → I<sub>2</sub>O<sub>4</sub></b>  | $1.7 \times 10^{-11}$                                | Calculated <sup>e</sup>   |            |
| 7          | I <sub>2</sub> O <sub>2</sub> + O <sub>3</sub> → I <sub>2</sub> O <sub>3</sub> + O <sub>2</sub>    | $5.0 \times 10^{-16}$                                | Assumed (R13)             |            |
| 8          | I <sub>2</sub> O <sub>3</sub> + O <sub>3</sub> → I <sub>2</sub> O <sub>4</sub> + O <sub>2</sub>    | $5.0 \times 10^{-16}$                                | Assumed (R13)             |            |
| 9          | I <sub>2</sub> O <sub>4</sub> + O <sub>3</sub> → I <sub>2</sub> O <sub>5</sub> + O <sub>2</sub>    | $5.0 \times 10^{-16}$                                | Assumed (R13)             |            |
| <b>12a</b> | <b>I<sub>2</sub> + O<sub>3</sub> → I + IO + O<sub>2</sub></b>                                      | $3.2 \times 10^{-18}$                                | Exp. decay, this work     |            |
| 13         | IO + O <sub>3</sub> → OIO + O <sub>2</sub>   | $5.0 \times 10^{-16}$                                | <sup>47</sup>             |            |
| 15         | I <sub>2</sub> O <sub>4</sub> + IO → I <sub>3</sub> O <sub>5</sub>                                 | $1.5 \times 10^{-11}$                                | Calculated                |            |
| 16         | I <sub>2</sub> O <sub>4</sub> + OIO → I <sub>3</sub> O <sub>6</sub>                                | $2.8 \times 10^{-12}$                                | Calculated                |            |
| 17         | I <sub>2</sub> O <sub>5</sub> + OIO → I <sub>3</sub> O <sub>7</sub>                                | $1.0 \times 10^{-13}$                                | Calculated                |            |
| 18         | I <sub>2</sub> O <sub>3</sub> + I <sub>2</sub> O <sub>3</sub> → I <sub>4</sub> O <sub>6</sub>      | $1.4 \times 10^{-12}$                                | Calculated                |            |
| 19         | I <sub>2</sub> O <sub>3</sub> + I <sub>2</sub> O <sub>4</sub> → I <sub>4</sub> O <sub>7</sub>      | $2.7 \times 10^{-11}$                                | Calculated                |            |
| 20         | I <sub>2</sub> O <sub>3</sub> + I <sub>2</sub> O <sub>5</sub> → I <sub>4</sub> O <sub>8</sub> (C1) | $1.9 \times 10^{-11}$                                | Calculated                |            |
| 21         | I <sub>2</sub> O <sub>4</sub> + I <sub>2</sub> O <sub>4</sub> → I <sub>4</sub> O <sub>8</sub> (C2) | $2.7 \times 10^{-10}$                                | Calculated                |            |
| 22         | I <sub>2</sub> O <sub>4</sub> + I <sub>2</sub> O <sub>5</sub> → I <sub>4</sub> O <sub>9</sub>      | $1.2 \times 10^{-11}$                                | Calculated                |            |
| 23         | I <sub>2</sub> O <sub>5</sub> + I <sub>2</sub> O <sub>5</sub> → I <sub>4</sub> O <sub>10</sub>     | $7.0 \times 10^{-11}$                                | Calculated                |            |
| R#         | Reaction   | $D_0 / \text{kJ mol}^{-1}$ <sup>b</sup>              | $k' / \text{s}^{-1}$      |            |
| 24         | I <sub>2</sub> O <sub>2</sub> → I + OIO  | 84   | $1.2 \times 10^{-3}$      | Calculated |
| 25         | I <sub>2</sub> O <sub>3</sub> → IO + OIO   | 161  | Stable                    | Calculated |
| 26         | I <sub>2</sub> O <sub>4</sub> → OIO + OIO  | 98   | $1.1 \times 10^{-2}$      | Calculated |
| 27         | I <sub>3</sub> O <sub>5</sub> → I <sub>2</sub> O <sub>4</sub> + IO                                 | 62   | $6.2 \times 10^4$         | Calculated |
| 28         | I <sub>3</sub> O <sub>6</sub> → I <sub>2</sub> O <sub>4</sub> + OIO                                | 74   | $3.5 \times 10^4$         | Calculated |
| 29         | I <sub>3</sub> O <sub>7</sub> → I <sub>2</sub> O <sub>5</sub> + OIO                                | 32   | $3.7 \times 10^7$         | Calculated |
| 30         | I <sub>4</sub> O <sub>6</sub> → I <sub>2</sub> O <sub>3</sub> + I <sub>2</sub> O <sub>3</sub>      | 58   | $7.5 \times 10^5$         | Calculated |
| 31         | I <sub>4</sub> O <sub>7</sub> → I <sub>2</sub> O <sub>3</sub> + I <sub>2</sub> O <sub>4</sub>      | 79   | $1.6 \times 10^4$         | Calculated |
| 32         | I <sub>4</sub> O <sub>8</sub> (C1) → I <sub>2</sub> O <sub>3</sub> + I <sub>2</sub> O <sub>5</sub> | 86   | $2.8 \times 10^3$         | Calculated |
| 33         | I <sub>4</sub> O <sub>8</sub> (C2) → I <sub>2</sub> O <sub>4</sub> + I <sub>2</sub> O <sub>4</sub> | 141  | Stable                    | Calculated |
| 34         | I <sub>4</sub> O <sub>9</sub> → I <sub>2</sub> O <sub>4</sub> + I <sub>2</sub> O <sub>5</sub>      | 107  | 8.7                       | Calculated |
| 35         | I <sub>4</sub> O <sub>10</sub> → I <sub>2</sub> O <sub>5</sub> + I <sub>2</sub> O <sub>5</sub>     | 88   | $1.9 \times 10^3$         | Calculated |
| 36         | <b>I<sub>x</sub>O<sub>y</sub> → loss</b>   | -  | 32                        | Fitted     |

<sup>a</sup> The key reactions for reproducing observed species in the base case run appear in bold case <sup>b</sup> Dissociation energies of the species at the left hand side of the dissociation reaction have been obtained from *ab initio* calculations at CCSD(T)/MP2/AREP/aVTZ. <sup>c</sup> Corrected for He as bath gas. <sup>d</sup> MESMER calculations use the CCSD(T) dissociation energies  $D_0$  included in the table, vibrational frequencies and rotational constants at MP2/AREP/aVTZ level of theory (except I<sub>4</sub>O<sub>7</sub>, I<sub>4</sub>O<sub>9</sub> and I<sub>4</sub>O<sub>10</sub>, for which the B3LYP/AREP/aVTZ level was used)<sup>31</sup>. Lennard-Jones parameters for interaction with He bath gas taken from ref. <sup>44</sup> and  $\Delta E_{\text{down}} = 250 \text{ cm}^{-1}$  (T-independent). <sup>e</sup> Rate coefficients in N<sub>2</sub> at 150 Torr are  $\sim 8 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ . The calculations are carried out to reproduce this number and then repeated for He as bath gas.<sup>15</sup>

**Table 3.** Sensitivity of photo-ionisation scaling factors to kinetic parametersView Article Online  
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| param        | #             | $\delta k$     | $\Delta C/C_{10}^a$ | $\Delta C/C_{O10}$ | $\Delta C/C_{1202}$ | $\Delta C/C_{1203}$ | $\Delta C/C_{1204}$ | $\Delta C/C_{1205}$ | $\Delta k'/k'_{\text{loss}}$ | $\chi^2{}^b$ |
|--------------|---------------|----------------|---------------------|--------------------|---------------------|---------------------|---------------------|---------------------|------------------------------|--------------|
| $k_{3b}/k_3$ | 1             | $\times 2$     | 3                   | 24                 | -34                 | 42                  | 30                  | -                   | 19                           | 4.83         |
|              | 2             | $\div 2$       | -1                  | -6                 | 70                  | -7                  | -5 <sup>e</sup>     | -                   | -1                           | 4.52         |
| $k_4$        | 3             | $\times 2$     | 8                   | 54                 | 41                  | 9                   | 48                  | -                   | 30                           | 4.77         |
|              | 4             | $\div 2$       | -6                  | -27                | -26                 | 7                   | -26                 | -                   | -20                          | 4.44         |
| $k_5$        | 5             | $\times 2$     | -1                  | 13                 | -1                  | 12                  | -14                 | -                   | 1                            | 4.57         |
|              | 6             | $\div 2$       | 1                   | -8                 | 0                   | -8                  | 15                  | -                   | -1                           | 4.47         |
| $k_{7-9}$    | 7             | $\times 200$   | 108                 | 897 <sup>f</sup>   | 1885                | 4831                | 1038                | -                   | 574                          | 5.87         |
|              | 8             | $\times 200^c$ | 106                 | 897                | 1868                | 4814                | 1036                | -61                 | 565                          | 5.69         |
|              | 9             | $\times 200^d$ | 108                 | 897                | 1871                | 4813                | 1030                | -                   | 572                          | 4.11         |
|              | 10            | $\times 20$    | 105                 | 897                | 1389                | 4088                | 1087                | -                   | 567                          | 5.56         |
|              | 11            | $\times 20^c$  | 6                   | 17                 | 154                 | 168                 | -1                  | -96                 | 19                           | 5.08         |
|              | 12            | $\times 20^d$  | 9                   | 32                 | 188                 | 235                 | 19                  | -                   | 46                           | 3.90         |
|              | 13            | $\times 10$    | 14                  | 59                 | 184                 | 280                 | 64                  | -                   | 89                           | 5.38         |
|              | 14            | $\times 10^c$  | 4                   | 9                  | 83                  | 80                  | -12                 | -94                 | 9                            | 4.81         |
| 15           | $\times 10^d$ | 5              | 16                  | 99                 | 106                 | -2                  | -                   | 22                  | 3.60                         |              |

<sup>a</sup> % change of the fitted coefficient relative to the corresponding result of the base case fit using the kinetic parameters in Table 2 (base case fit coefficients given in Fig. 4g-4l). <sup>b</sup> The base case fit chi-square value is  $\chi^2 = 4.5$  <sup>c</sup> An scaling factor  $C_{1205}$  is also allowed to float. Changes are relative to  $C_{10} = C_{1205}$  in the base case fit <sup>d</sup>  $S_{1205}$  excluded from the fit <sup>e</sup> Italics indicate coefficients with estimated errors larger than 30%. <sup>f</sup> Small typescript indicate coefficients with estimated errors larger than 50%

**Figure captions**

**Figure 1.** Panel (a): raw signal vs. time of flight (TOF) (note the logarithmic scale). Panel (b): mass to charge calibration linear fit.

**Figure 2.** TOF spectra after contact times of 10 s (panel (a)) and 25 s (panel (b)), in each case for  $O_3$  concentrations differing by one order of magnitude (red:  $[O_3] \sim 1 \times 10^{15}$  molecule  $cm^{-3}$ , black  $[O_3] \sim 1 \times 10^{16}$  molecule  $cm^{-3}$ ). The blue spectra were obtained by averaging respectively 13 and 7 spectra taken at the same contact time. Panels (b) and (d) show the spectra resulting from subtracting the red spectra from the black spectra in the upper panels. The high mass window appears multiplied by 20 on the right hand side panels for clarity. The saturated  $I_2$  peak has been removed from panels (a) and (b) for clarity.

**Figure 3.** Panel (a): evolution of pressure and ozone concentration during a typical experiment sequence. Panel (b): integrated peak signal for the I, IO and OIO peaks for every experiment. The iodine atom signal corresponds to  $I_2$  fragmentation ( $O_3$  scavenges quickly iodine atoms for the system and these are below detection limit). Note that I and IO are anticorrelated. Panel (c): the same for mass signals showing positive and significant correlation with IO and OIO. Panel (d): the same for mass signals showing negative correlation with IO and positive correlation with I, and negative correlation with pressure.

**Figure 4.** Results of fitting simulated data (lines) using the model in Table 2 to the observed  $O_3$  dependence of integrated peak signals (symbols). Left panel column (a)-(f): simulated concentrations are fitted to observations with all species having the same floating signal scaling factor. Right panel column (g)-(l): best fit and base case run for sensitivity studies, where circles denote species with a common floating signal scaling factor. Species with other symbols have their own floating scaling factor. Note that panels (c), (d), (i) and (j) are in a logarithmic scale to emphasise the failure of the common scaling factor approach due to the

weak  $I_2O_2$  and  $I_2O_3$  signals. The dashed line in panel (d) is a result of a different fit with a common scaling factor and including a fast  $I_2O_2 + O_3$  reaction (see text for details).

**Figure 5.** Pseudo first order decay of the  $I_2$  integrated peak signal recorded in analogue mode (parent ion empty squares and  $I^+$  fragment solid squares). The lines represent linear regressions of the logarithm of the signal vs. the product of ozone concentration and contact time.

**Figure 6.** Simulated curves (log scale) as a function of contact time for the highest  $O_3$  concentration in Fig 4 ( $2 \times 10^{16}$  molecule  $cm^{-3}$ ). The vertical dashed lines indicate the contact times corresponding to the spectra shown in Fig. 3. The insert panel shows the  $I_2O_4$  and  $I_3O_7$  signals scaled with the  $I_2O_4$  scaling coefficient  $C_{I_2O_4}$ , compared to the model output for  $I_2O_4$  and  $I_4O_8$  as a function of  $[O_3]$ .

## Figures

Figure 1

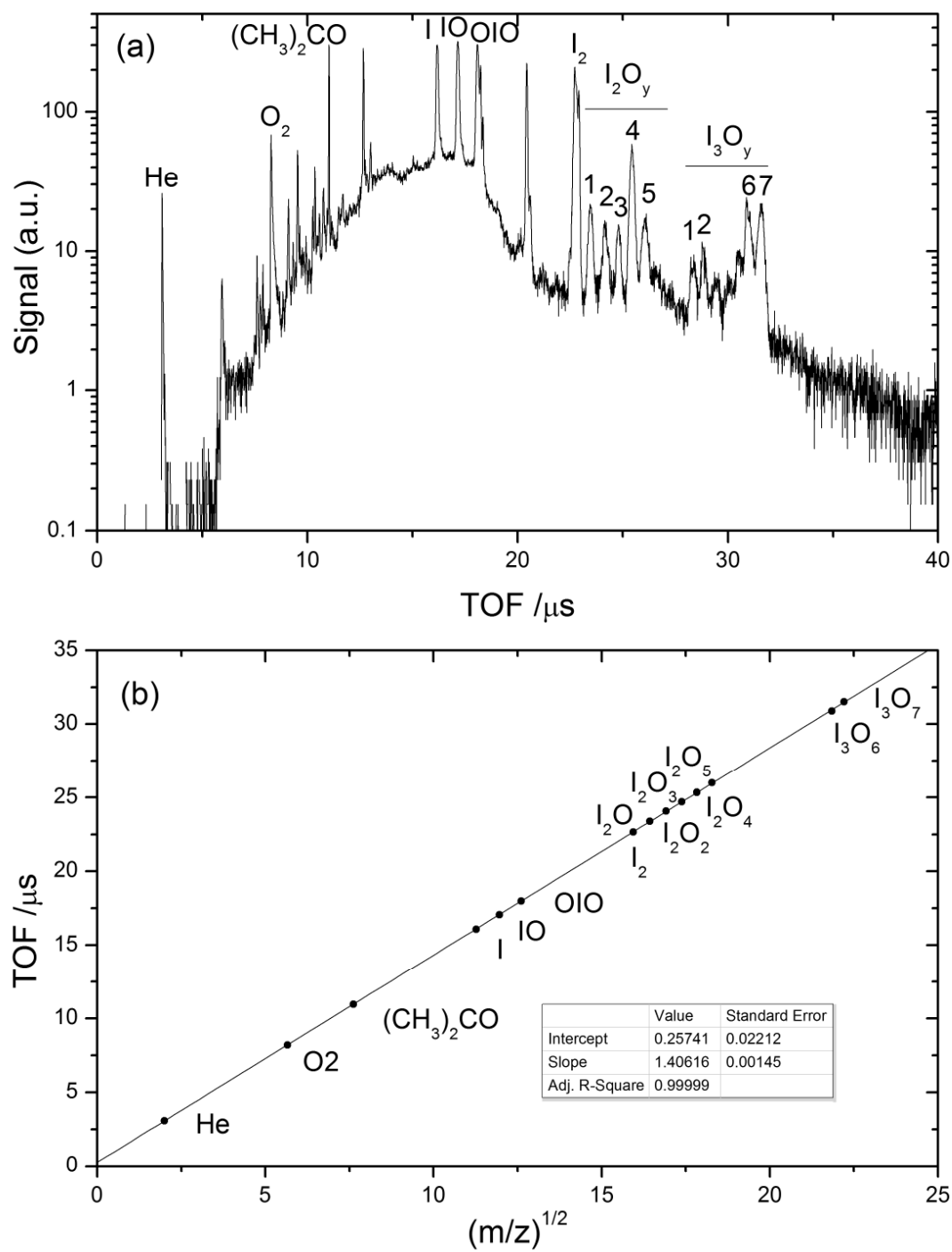


Figure 2

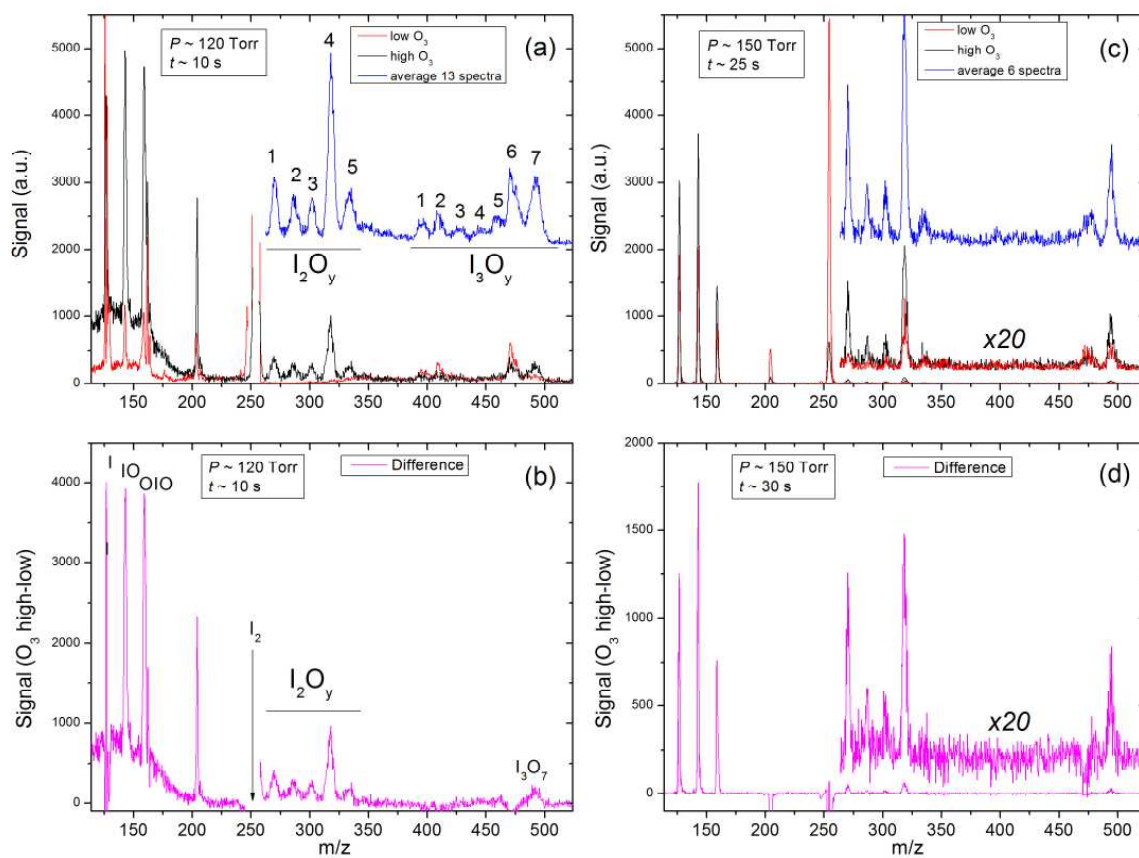
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Figure 3

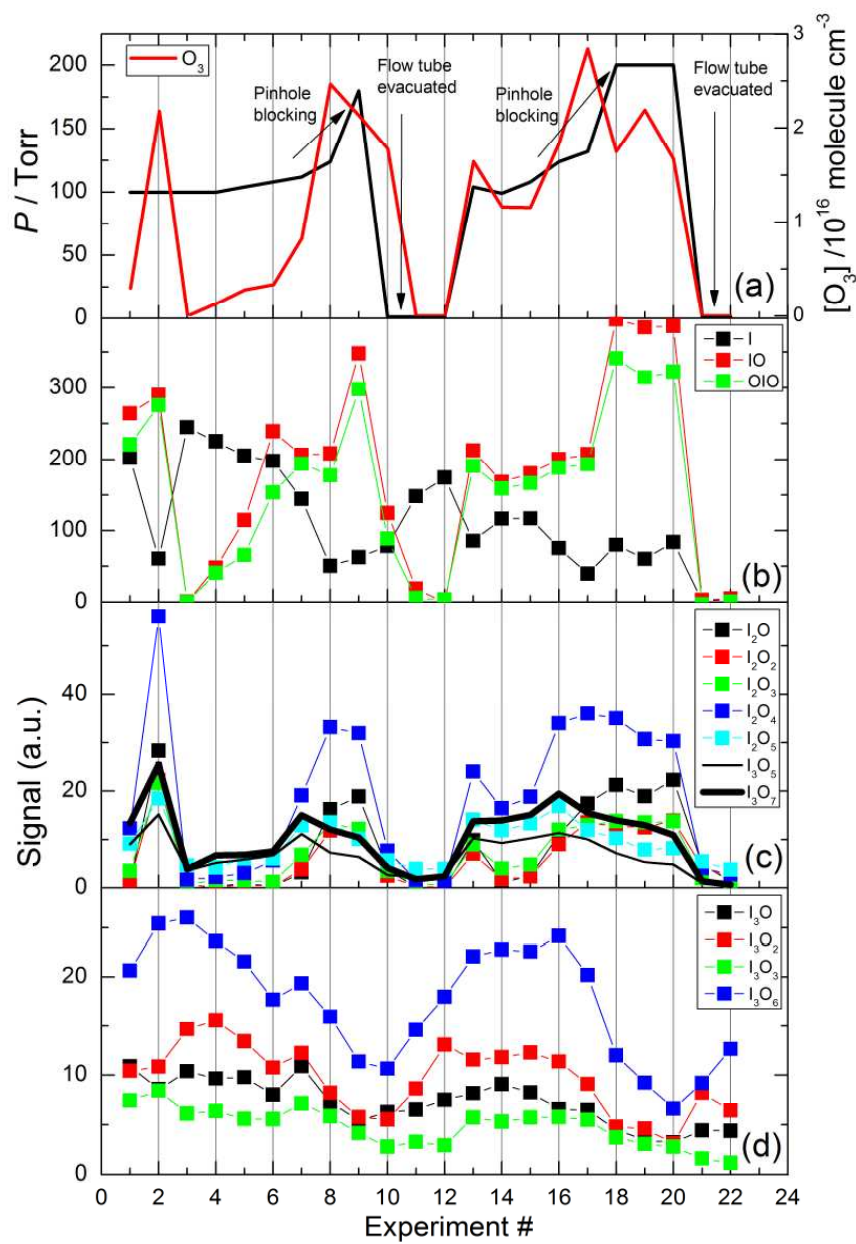
View Article Online  
DOI: 10.1039/C3CP51217G

Figure 4

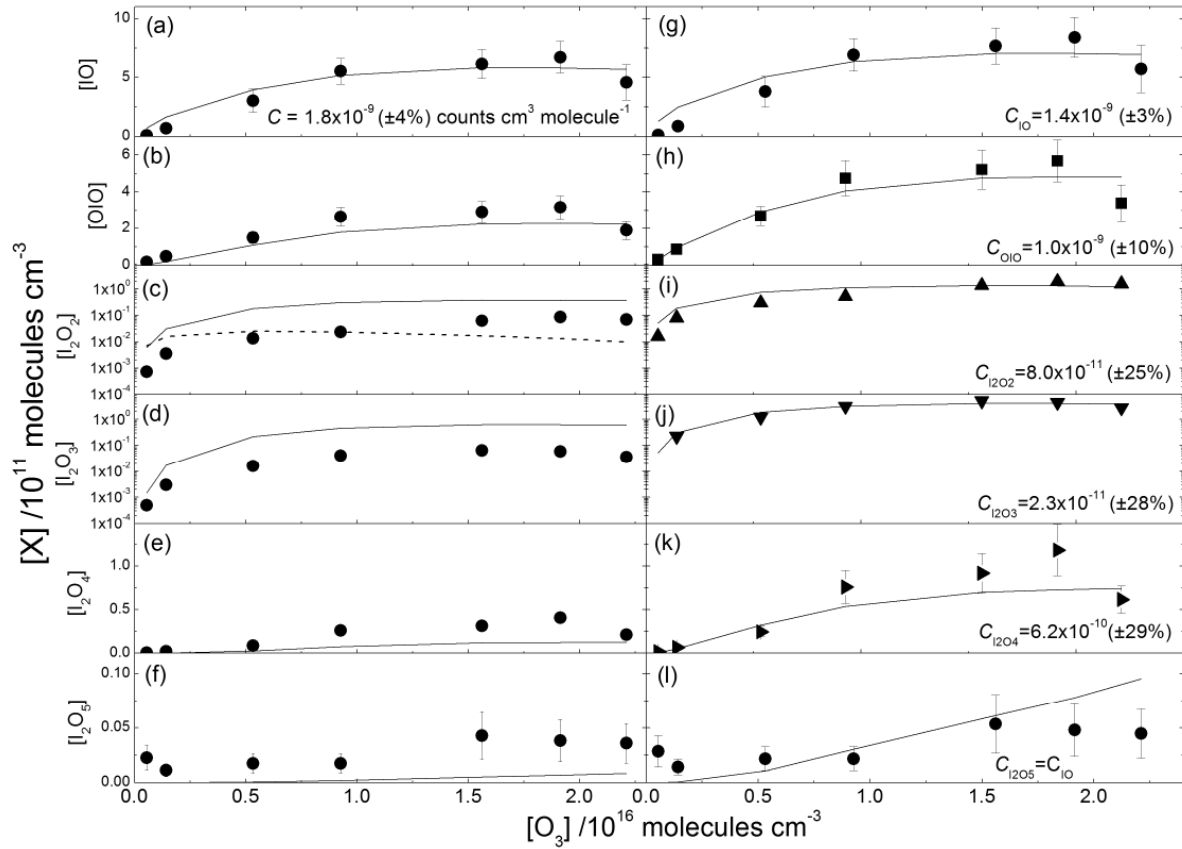
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DOI: 10.1039/C3CP51217G

Figure 5

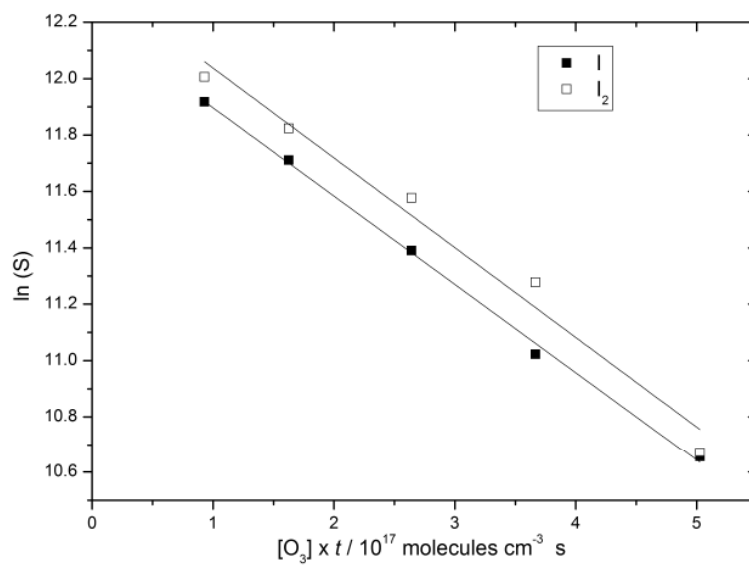
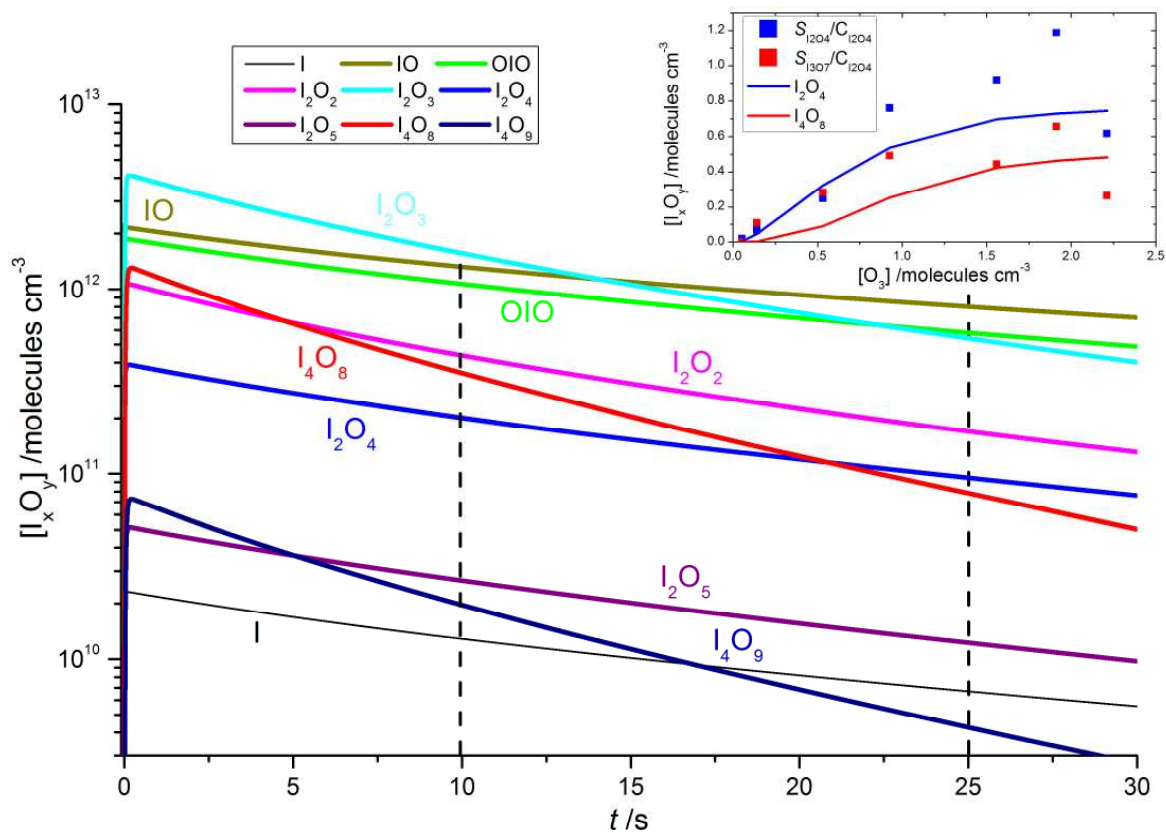




Figure 6



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DOI: 10.1039/C3CP51217G

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