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Are iodic acid measurements by chemical ionization unambiguous?

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Well-established gas-phase kinetics and thermochemistry do not indicate any straightforward route to $HOIO_2$ and oxyacid clusters (Gómez Martín et al., Nat. Commun. 2020, doi: 10.1038/s41467-020-18252-8)

- Gas-phase reactions of iodine oxides with water forming oxyacids are very slow ($k \leq 5 \times 10^{19}$ cm^3 s^{-1} molecule^{-1}).
- The formation rate of oxyacids from the composite reaction I + H_2O + O_3 is even slower ($k \leq 10^{-22}$ cm^3 s^{-1} molecule^{-1})
- This is consistent with ab initio thermochemistry, showing barriers for water reactions, and weakly bound iodine oxide-water adducts.
- Iodine oxyacid adducts are relatively weakly bound, which is a hinderance to fast iodine oxyacid nucleation.
- For such low reaction rates, iodine oxides will -at least- compete and/or interact with oxyacids
- I_2O_5 formation and water evaporation from $HOIO_2$ + $HOIO_2$ (Sipila et al, 2016) is precluded by a large barrier (Khanniche et al., 2016).

Other considerations regarding previous work on iodine oxide particle formation:

- $HOIO_2$ + HOIO (He et al, 2016) is <u>not needed to explain I_2O_4 formation</u>. OIO + OIO is known to form I_2O_4 (Gómez Martín et al., 2013).
- "Dry" iodine oxide nucleation has been observed in the lab for many years. Particle composition I_2O_5 (Saunders et al., 2010)
- The hydrated form of I_2O_5, i.e. iodic acid or $HOIO_2$, has been known for a long time to be the composition of atmospheric iodine oxide particles (Kumar et al., 2010). Gas-phase $HOIO_2$ is not needed to form $HOIO_2$ clusters: $HOIO_2$ is the liquid-phase form of I_2O_5 (Selte & Kjekshus, 1968) and other hydrated solid-phase iodine oxides like I_2O_4 rearrange to yield $HOIO_2$ (Dæhlie & Kjekshus, 1964).
- Field measurements show that the probability of iodine-driven nucleation is lower at higher RH (de Leuw et al., 2002)

It is plausible that the interpretation of the ion signals observed by CIMS (Sipilä et al, 2016; He et al. 2021; Wang et al., 2021; Pfeifer et al., 2020; Baccarini et al., 2020) is obscured by:

a) Reactions of iodine oxides with the CIMS reagent ions making ions which are wrongly interpreted as oxyacid daughter ions
b) Reaction of hydrated I_xO_y clusters with the reagent ions which are wrongly interpreted as oxyacid cluster daughter ions
c) Collisional fragmentation of hydrated I_xO_y clusters within the CIMS atmospheric pressure interface (Passananti et al., 2019)

We have performed ab initio calculations on some ion-molecule reactions to test hypotheses (a) and (b) (Gómez Martín et al., 2020). In some cases, enthalpies of reaction from evaluated thermochemical data are also available. Additional calculations have been carried out for this presentation.

Reaction enthalpies (kJ mol^{-1}) for four chemical ionization sources (E^- = main ionic reagent)

	Reagent	$E^- = NO_3^-$	$E^- = Br^-$	$E^- = CH_3COO^-$	H_3O^+		
Analyte	**Ion detected**	**IO_3^-**	**IO_3^-**	**IO_3^-**	**$H_2IO_2^+$**	**$H_2IO_3^+$**	**$H_4IO_4^+$**
HOIO	*ab initio*[a]				-164		
$HOIO_2$	Evaluated	-35 ± 10	-30 ± 10	-132 ± 11			
	ab initio[a, b]	**-23**				-90	
OIO	Evaluated	-85 ± 11		72 ± 11			
	ab initio[c]	*12*		*156*			
I_2O_2	evaluated	-95 ± 19					
I_2O_3	evaluated	-32 ± 16	-121 ± 14				
	ab initio[a]	-10	-101	-112	-48	-83	
I_2O_4	evaluated		-109 ± 18				
	ab initio[a,d]	2.1	-76	-101	-155	-81	-40

$$HIO_3 + E^- \rightarrow IO_3^- + HE$$

$$HIO_y\ (y = 2, 3) + H_3O^+ \rightarrow H_2IO_y^+ + H_2O \text{ or } H_4IO_{y+1}^+$$

$$\mathbf{I_2O_y\ (y = 2, 3, 4) + E^- \rightarrow IO_3^- + IO_{y-3}X}$$

$$\mathbf{I_2O_y\ (y = 3, 4) + H_3O^+ \rightarrow H_2IO_z^+\ (z = 2, 3, 4) + HIO_{y+1-z}}$$

	Reagent	$HNO_3.NO_3^-$	$H_2O.Br^-$
Analyte	**Ion detected**	**$HNO_3.IO_3^-$ (same m/z as $HIO_3.NO_3^-$)**	**$HIO_3.Br^-$**
I_2O_3	*ab initio*[d]	-12	-45

$$HIO_3 + E^- \rightarrow HIO_3.E^-$$

$$\mathbf{I_2O_3 + HNO_3.NO_3^- \rightarrow HNO_3.IO_3^- + IONO_2}$$

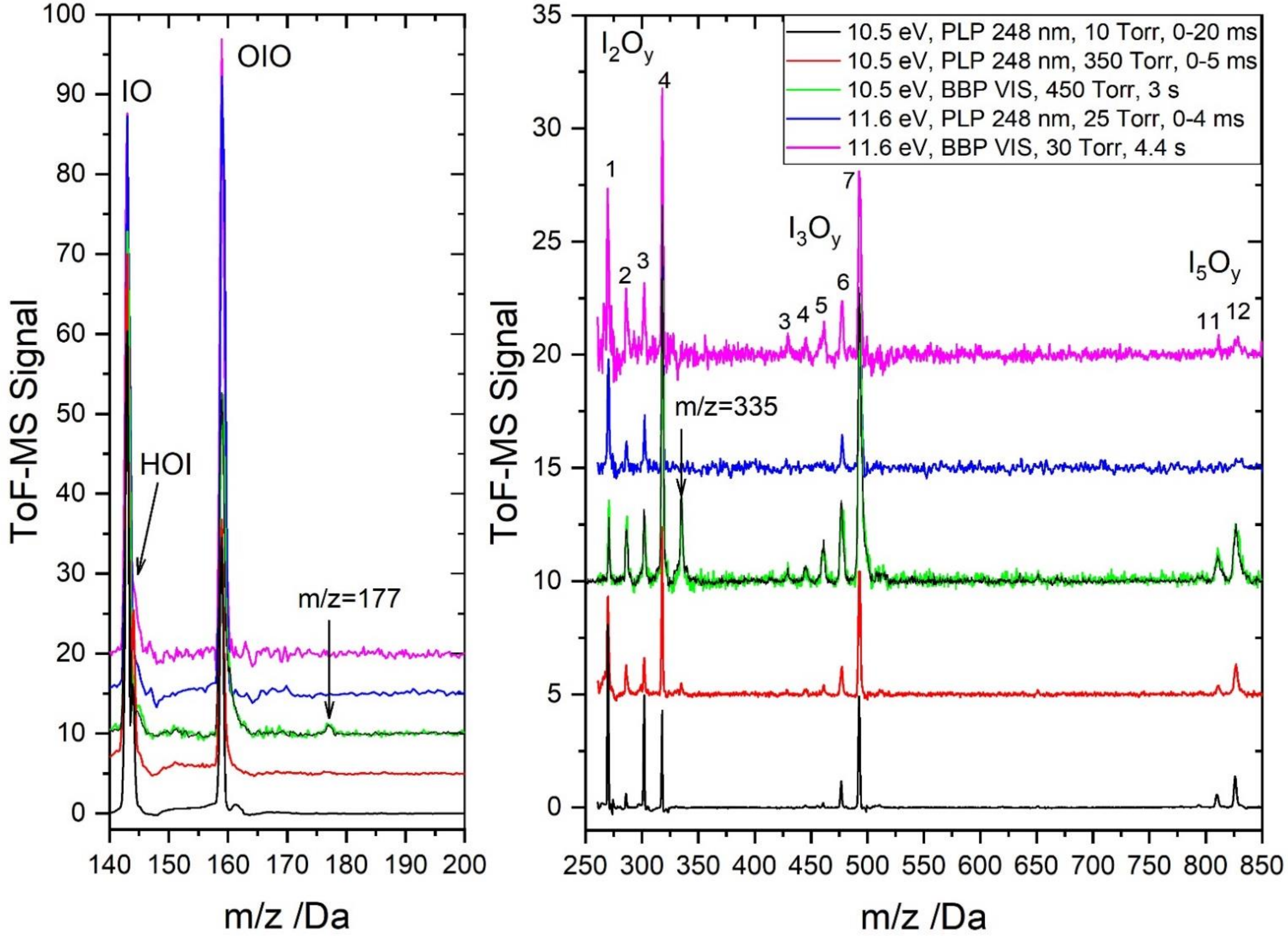
$$\mathbf{I_2O_3 + H_2O.Br^- \rightarrow HIO_3.Br^- + HOI}$$

[a] b3lyp/6-311+G(2d,p) with All electron iodine basis set . Gómez Martín et al., 2020 (normal typescript).
[b] CCSD(T)/aug-cc-pV5Z//PBE0/aug-cc-pVQZ with ECP28MDF effective core for iodine. Sipilä et al. 2016 (bold)
[c] wB97xd/6-311+G(2df,2p) Sipilä et al. 2016 (Italics)
[d] b3lyp/aug-cc-pvqz with All electron iodine basis set. This work (underscored).

Alternative Assignment of nitrate CIMS peaks in He et al. 2021 (Figures 2B and S4, and Table S2)

n I	n H	n peaks	Peak assignment according to He et al., 2021	Ionization process according to He et al., 2021	Strongest peak	S /cps	Alternative peak assignment	Alternative ionization process
1	0	1	$IO.NO_3^-$	**IO** + NO_3^- cluster		0.7	=	**=**
1	0, 1	2	$IO_2(HNO_3)_m.NO_3^-$	**OIO** + NO_3^- cluster	$OIO.NO_3^-$	145	=	**=**
1	1, 2	2	$HIO_2(HNO_3)_m.NO_3^-$	**HOIO** + $(HNO_3)_m.NO_3^-$ cluster	$HIO_2HNO_3NO_3^-$	38	$(HNO_3)_{m+1}.IO_2^-$	Fragment?
1	0	1	IO_3^-	**$HOIO_2$** + NO_3^- transfer		194	=	**I_xO_y**+$E.NO_3^- \rightarrow E.IO_3^-+I_{x-1}O_{y-2}NO_2$ $x=1, 2; y = 2,3,4$
1	1+2n+m	30	$HIO_3(H_2O)_n(HNO_3)_m.NO_3^-$	**$HOIO_2$** + $(H_2O)_n(HNO_3)_m.NO_3^-$ cluster	$HIO_3.NO_3^-$	2472	$(H_2O)_n.(HNO_3)_{m+1}.IO_3^-$	
2	0	1	$I_2O_2.NO_3^-$	**I_2O_2** + NO_3^- cluster		4	=	**=**
2	0	1	$I_2O_3.NO_3^-$	**I_2O_3** + NO_3^- cluster		6	=	**=**
2	0	2	$I_2O_4.(HNO_3)_m.NO_3^-$	**I_2O_4** + $(HNO_3)_m.NO_3^-$ cluster	$I_2O_4.HNO_3.NO_3^-$	35	=	**$(H_2O)_{n-1}.I_2O_4$** + $E.NO_3^-$ cluster $n=1, 2$
2	2+2n+m	12	$HIO_2HIO_3(H_2O)_n(HNO_3)_m.NO_3^-$	**$HIO_2.HIO_3$**+$(H_2O)_n(HNO_3)_m.NO_3^-$ cluster	$HIO_2HIO_3.NO_3^-$	80	$I_2O_4(H_2O)_p(HNO_3)_mNO_3^-$	
2	0	1	$I_2O_5.NO_3^-$	**I_2O_5** + NO_3^- cluster		6	=	Fragments (barrier and weak bonding)
2	2	1	$2HIO_3.NO_3^-$	**$HIO_3.HIO_3$** + NO_3^- cluster		4	$I_2O_5.(H_2O)_n.NO_3^-$	
~~3~~	~~0~~	~~1~~	~~$[I_2O_4.IO_3^-]$ missing~~	~~**$HIO_3.I_2O_4$** + NO_3^- transfer~~	$HIO_3.I_2O_4.NO_3^-$		$(H_2O)_n(HNO_3)_mI_3O_7^-$	**I_3O_7** + $E.NO_3^- \rightarrow E.I_3O_7^-$ + NO_3? (I_3O_{5-7} seen by PI-TOF-MS, Gómez Martín et al. 2020, see below)
3	1	1	$HIO_3.I_2O_4.NO_3^-$	**$HIO_3.I_2O_4$** + NO_3^- cluster		2		
3	2	1	$HIO_2.HIO_3.IO_3^-$	**$HIO_2.(HIO_3)_2$** + NO_3^- transfer		0.5		
3	3	1	$2HIO_3.HIO_2.NO_3^-$	**$HIO_2.(HIO_3)_2$** + NO_3^- cluster		0.3		
3	0	1	$I_2O_5.IO_3^-$	**$I_2O_5.HIO_3$** + NO_3^- transfer		0.4		Fragment (weak bonding)
4	0	1	$2I_2O_4.NO_3^-$	**$2I_2O_4$** + NO_3^- cluster	$HIO_2.HIO_3.I_2O_4.NO_3^-$	0.4	$I_4O_8.(H_2O)_n.NO_3^-$	**$(H_2O)_{n-2}.I_4O_8$** + $E.NO_3^-$ cluster ($I_4O_{7,9}$ seen by PI-TOF-MS, Gómez Martín et al. 2020, see below)
~~4~~	~~1~~	~~1~~	~~$[HIO_2.I_2O_4.IO_3^-]$ missing~~	~~**$HIO_3.HIO_2.I_2O_4$** + NO_3^- transfer~~				
4	2	1	$HIO_3.HIO_2.I_2O_4.NO_3^-$	**$HIO_3.HIO_2.I_2O_4$** + NO_3^- cluster		1.6		
~~4~~	~~3~~	~~1~~	~~$[HIO_3.2HIO_2.IO_3^-]$ missing~~	~~**$2HIO_3.2HIO_2$** + NO_3^- transfer~~				
4	4	1	$2HIO_3.2HIO_2.NO_3^-$	**$2HIO_3.2HIO_2$** + NO_3^- cluster		0.5		
5	0	1	$2I_2O_4.IO_3^-$	**$HIO_3.(I_2O_4)_2$**+ NO_3^- transfer	$HIO_2.HIO_3.I_2O_4.IO_3^-$	0.4	$(HNO_3)_n(H_2O)_m.I_5O_{11}^-$	**I_5O_{11}**+$E.NO_3^- \rightarrow E.I_5O_{11}^-$ + NO_3? (I_5O_{10-12} seen by PI-TOF-MS, Gómez Martín et al. 2020, see below)
5	1	1	$HIO_3.2I_2O_4.NO_3^-$	**$HIO_3.(I_2O_4)_2$** + NO_3^- cluster		0.3		
5	2	1	$HIO_3.HIO_2.I_2O_4.IO_3^-$	**$HIO_2.HIO_3.I_2O_4$** + NO_3^- transfer		2		
5	3	1	$2HIO_3.HIO_2.I_2O_4.NO_3^-$	**$HIO_2.HIO_3.I_2O_4$** + NO_3^- cluster		0.3		
5	4	1	$2HIO_3.2HIO_2.IO_3^-$	**$(HIO_2)_2.(HIO_3)_3$** + NO_3^- transfer		1.6		
5	5	1	$3HIO_3.2HIO_2.NO_3^-$	**$(HIO_2)_2.(HIO_3)_3$** + NO_3^- cluster		0.3		

Near-threshold Photo-ionization Mass Spectra under different conditions in the presence of water (Gómez Martín et al. 2020)



TOF Mass Spectra of iodine oxides in the presence of water vapor from Gómez Martín et al., 2020. Acquired under high water mixing ratios (2%) but otherwise different flow tube conditions, photolysis source (PLP 248 nm: pulsed UV laser photolysis ; BBP VIS: broad band photolysis in the visible) and photoionization energy (10.5 eV and 11.6 eV). The photoionization energy 10.5 eV is below the I_2O_5 and $HOIO_2$ photoionization thresholds. The spectra are displayed in two separated m/z ranges for clarity. Except for the changes in the relative differences between the I_2O_y peaks with pressure, and the poorer signal to noise ratio at 11.6 eV, the spectra look very similar under all conditions. The only instances where some new peaks emerge (red and green lines) are for high pressure (350 and 450 Torr) at 10.5 eV. 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 = 335. At 10.5 eV, they cannot be assigned to $HOIO_2^+$ (m/z = 176) nor $I_2O_5^+$ (m/z = 334) and they were also observed in a previous study under dry conditions (Gómez Martín et al., 2013).

Conclusions and outlook

- The interpretation of CIMS observations needs to be revisited.
- The identification of IO_3^- as iodic acid and the calibration of the nitrate CIMS is only based on a calculation of the proton affinities of IO_3^- and NO_3^-. However, I_xO_y can also generate a IO_3^- signal in a negative ion CIMS. We know I_xO_y are formed, because they are detected by the reference nitrate CIMS in the form of $I_xO_y.NO_3^-$ ion clusters. This puts a question mark on the calibration of the NO_3^- CIMS, which is relative to H_2SO_4. Does it quantify $HOIO_2$, or rather the sum of $HOIO_2$ and I_2O_y?
- In the hydronium CIMS, the interpretation of $H_2IO_3^+$ and $H_4IO_4^+$ is also consistent with both $HOIO_y + H_3O^+$ and $I_2O_y + H_3O^+$
- The nitrate CIMS instrument is not calibrated for I_2O_y and therefore it cannot be used to estimate the I_2O_y concentration from the $I_2O_y.NO_3^-$ signals. Comparing $HIO_3.NO_3^-$ and $I_2O_y.NO_3^-$ signals is not the same as comparing concentrations.
- Other signals interpreted as ion clusters formed by $HOIO_2$ and the source ions may also originate from the reaction of I_xO_y or $(H_2O)_n.I_xO_y$ with source ion clusters, e.g. $(H_2O)_n.HNO_3.NO_3^-$
- The other large group of ions besides the $HIO_3.E.NO_3^-$ group is $HIO_3.HIO_2.E.NO_3^-$, which can also be interpreted as $I_2O_4.H_2O.E.NO_3^-$
- A different assignment of the nitrate CIMS peaks (He et al., 2021) may bring these observations into better agreement with the positive PI-ToF-MS spectra reported by Gómez Martín et al., 2020.
- Kinetic experiments and further quantum calculations on ion-molecule and ion-cluster reactions are required to ascertain the identity of the observed CIMS signals. We are planning lab kinetic experiments with an NO_3^- source plugged into an I_2+O_3 system, were products are followed with a negative ion mass spectrometer.
- Atmospheric iodine-driven particle formation is likely started by iodine oxides, while exposure of iodine oxide particles to ambient humidity leads to the formation of iodic acid particles. This would still be consistent with CIMS observations.