Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

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

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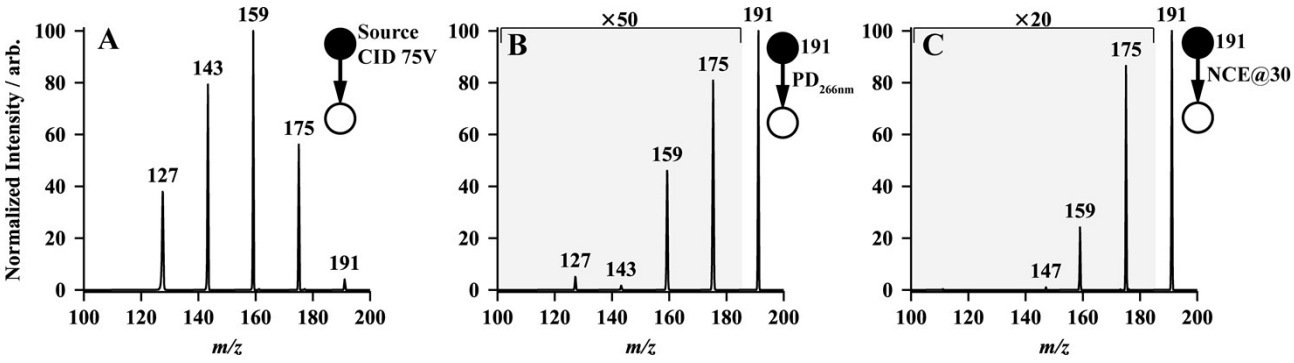

Figure S1: Comparison of three methods for synthesising IO_x^- intermediates from a solution of $NaIO_4$ in methanol: (A) Source-based collisional activation with 75 eV activation energy; (B) photodissociation of mass selected IO_4^- (m/z 191) with a single pulse of 266 nm laser radiation; (C) ion-trap collisional activation of mass selected IO_4^- (m/z 191) with a Normalised Collision Energy of 30 (arb. units).

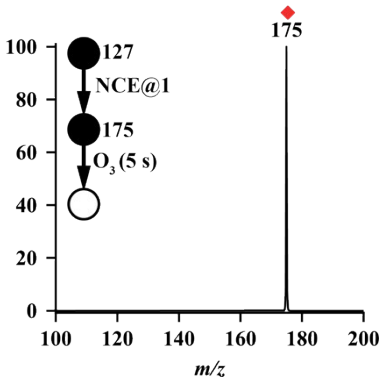

Figure S2: Reaction of IO_3^- (m/z 175) with ozone for 5 s. No reaction products are observed that correspond to further oxidation to form IO_4^- (m/z 191), nor back reactions to lower oxides.

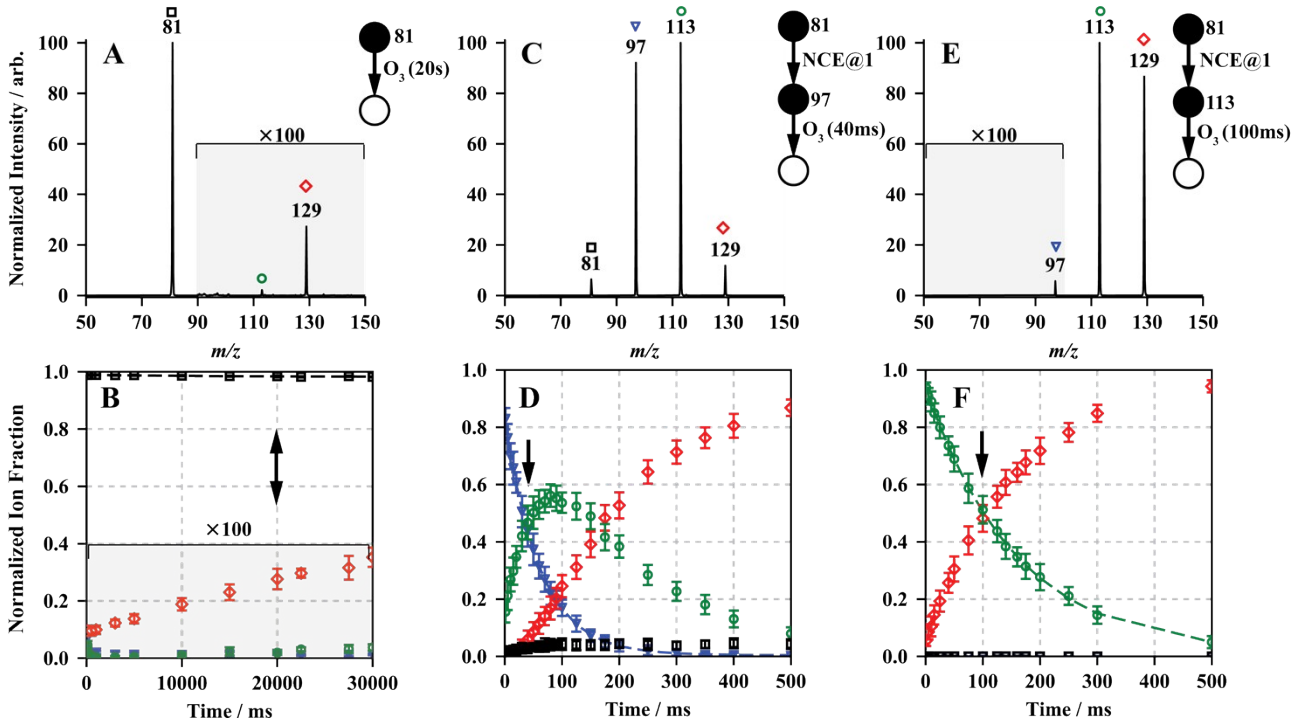

Figure S3: Mass spectra and kinetic traces for the companion bromide isotope $^{81}Br^-$ reacting with ozone. **A)** Mass spectrum of $^{81}Br^-$ (m/z 81) reacting with ozone at 20 s reaction time, (**B**) kinetic plot showing decay of $^{81}Br^-$ and growth of BrO_3^- (m/z 129), (**C**) Mass spectrum of $^{81}BrO^-$ (m/z 97) reacting with ozone for 40 ms, (**D**) associated kinetic plot showing decay of m/z 97, growth and subsequent decay of m/z 113 and ultimate growth of m/z 129, (**E**) Mass spectrum of $^{81}BrO_2^-$ (m/z 113) reacting with ozone for 100 ms, (**F**) associated kinetic plot showing decay of m/z 113 and growth of m/z 129. Arrows in the lower panels indicate the time points mass spectra are taken from.

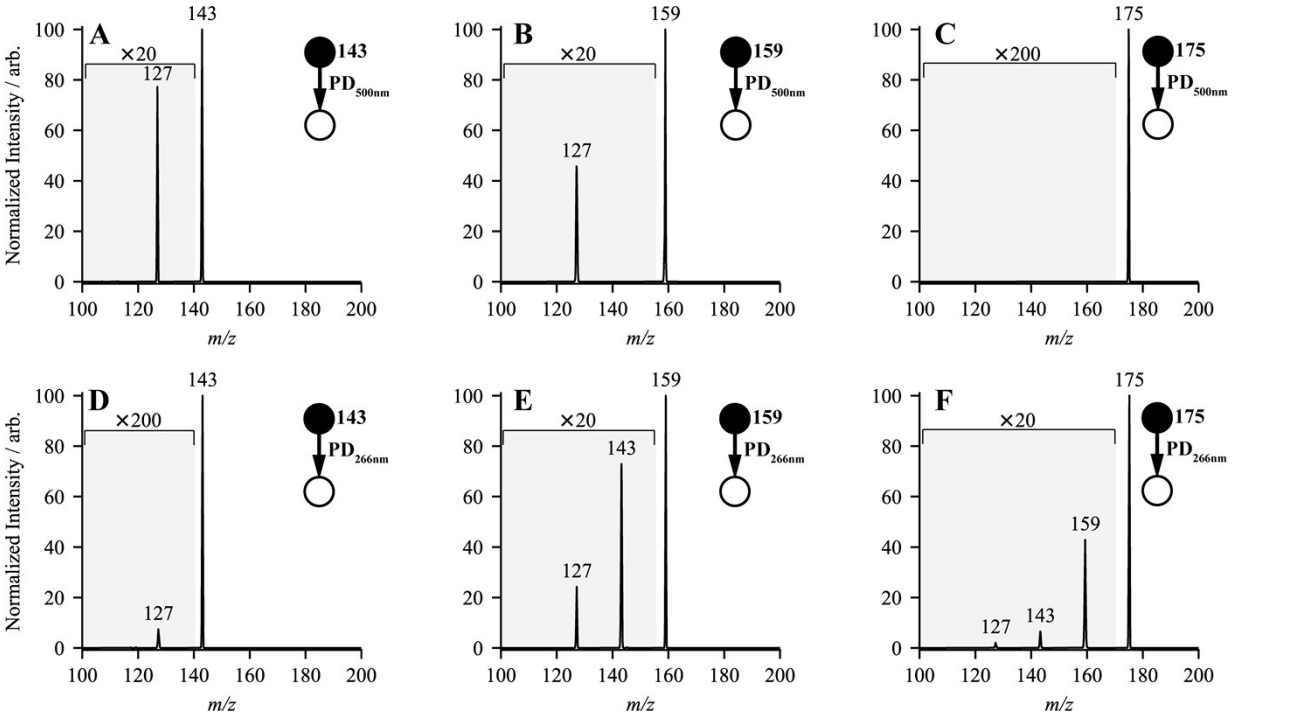

Figure S4: Comparison of the photodissociation products from a single pulse of 500 nm radiation from mass selected (A) IO^- (B) IO_2^- and (C) IO_3^- compared to 266 nm photodissociation from mass selected (D) IO^- (E) IO_2^- and (F) IO_3^-. All precursors were synthesised using Source CID set to 75 eV (see Figure S1A). Note the different magnification factors used in each spectrum.

Table S1: Comparison of two independent ion-molecule reactions for the experimental determination of ozone concentration in the ion-trap. Literature value for Ba^+ was taken from Feil et al., J. Phys. Chem. A. **2007**, 111, 13397-13402. The charge exchange reaction between phenide ($C_6H_5^-$) anion and ozone was assumed to be collision limited, and the trajectory collision rate at 320K was used.

	Ba^+	**Phenide**
m/z	138	77
k' / s^{-1}	30.8	38.2
$t_{1/2}$ / ms	20	18
Literature k_2 / cm^3 $molecule^{-1}$ s^{-1}	8.6×10^{-10}	9.2×10^{-10}
$[O_3]$ / molecules cm^{-3}	$3.6(\pm 0.1) \times 10^{10}$	4.2×10^{10}

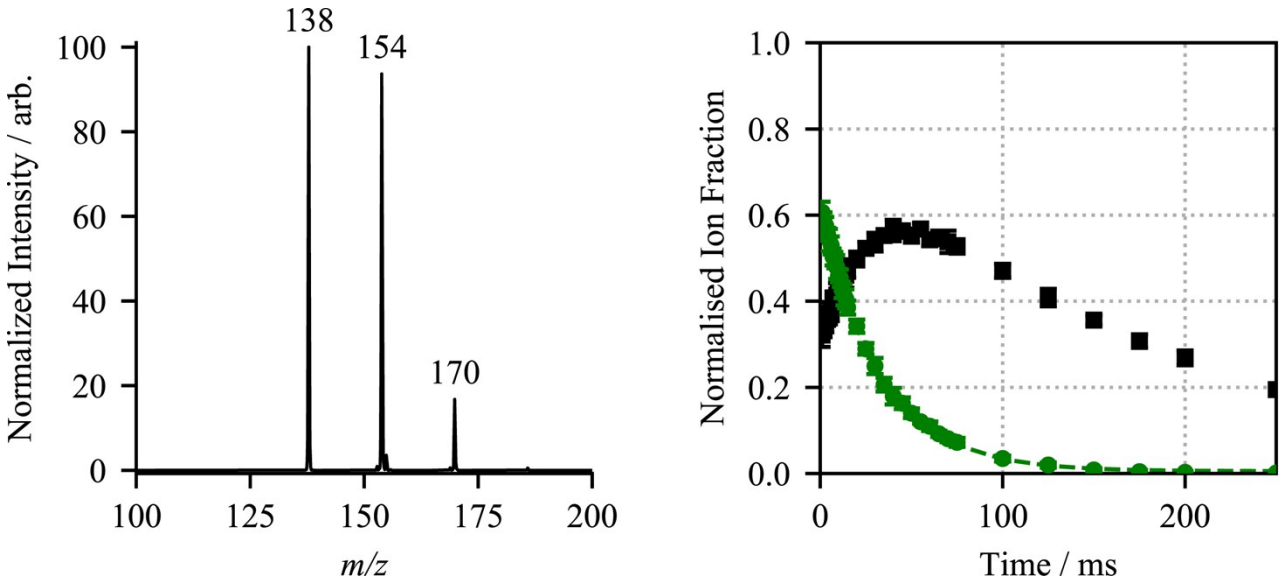

Figure S5: Mass spectrum and kinetic trace for the reaction of barium cation (Ba+; m/z 138 green circles in kinetc trace) with ozone, producing charged products BaO^+ (m/z 154; black squares in kinetic trace) and BaO_2^+ (m/z 170)

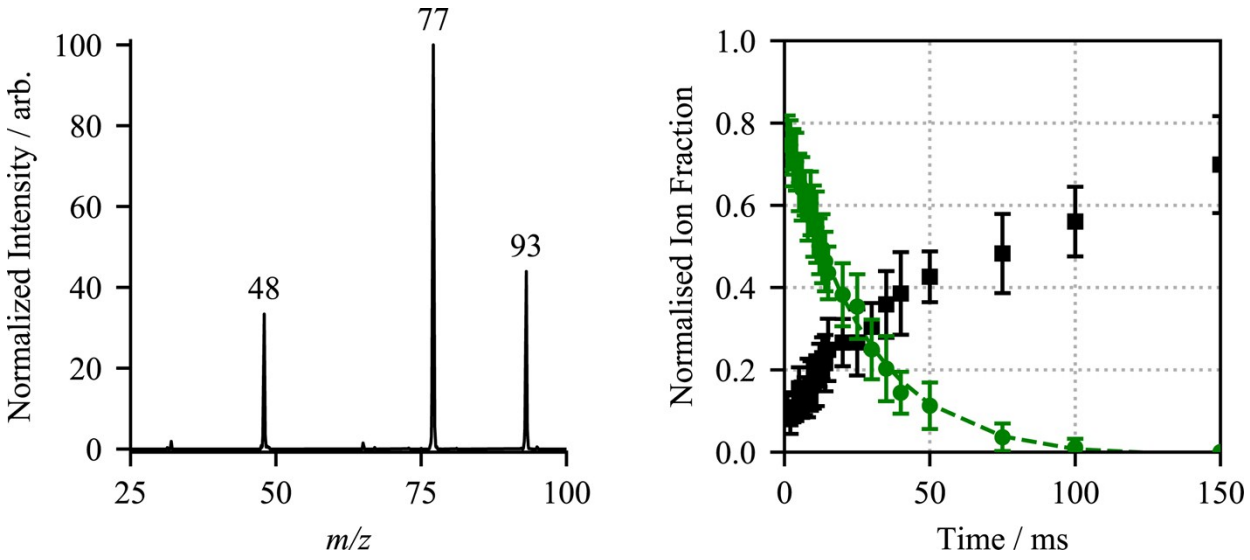

Figure S6: Mass spectrum and kinetic trace for the charge exchange reaction between phenide anion (m/z 77) and ozone producing charged products corresponding to O_3^- (m/z 48) and $C_6H_5O^-$ (m/z 93).