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The reaction of isotope substituted hydrated iodide $I(H_2^{18}O)^-$ with ozone: the reactive influence of the solvent water molecule

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1 Supplementary information

The following explicit rate equations were used to model the data displayed in Fig. 6 of the paper. The model is schematically presented in Fig. 7.

$$\begin{aligned}\dot{N}_{I^-} = \quad & g_1^{16}[O_2]N_{I(H_2^{16}O)^-} \\ & + g_1^{18}[O_2]N_{I(H_2^{18}O)^-} \\ & + b_1^{16}[O_3]N_{I(H_2^{16}O)^-} \\ & + b_1^{18}[O_3]N_{I(H_2^{18}O)^-} \\ & - k_1^{16}[O_3]N_{I(H_2^{18}O)^-} \\ & - k_R N_{I^-} \end{aligned} \quad (1)$$

$$\begin{aligned}\dot{N}_{IO^-} = \quad & k_1^{16}[O_3]N_{I^-} \\ & - k_2^{16}[O_3]N_{IO^-} \\ & + b_2^{16}[O_3]N_{I(H_2^{16}O)^-} \\ & + b_2^{18}[O_3]N_{I(H_2^{18}O)^-} \\ & - k_R N_{IO^-} \end{aligned} \quad (2)$$

$$\begin{aligned}\dot{N}_{I(H_2^{16}O)^-} = \quad & - g_1^{16}[O_2]N_{I(H_2^{16}O)^-} \\ & + h_1[H_2O]N_{I(H_2^{18}O)^-} \\ & - b_1^{16}[O_3]N_{I(H_2^{16}O)^-} \\ & - b_2^{16}[O_3]N_{I(H_2^{16}O)^-} \\ & - b_3^{16}[O_3]N_{I(H_2^{16}O)^-} \\ & - b_4^{16}[O_3]N_{I(H_2^{16}O)^-} \\ & - k_R N_{I(H_2^{16}O)^-} \end{aligned} \quad (3)$$

$$\begin{aligned}\dot{N}_{I^{18}O^-} = \quad & \tilde{b}_2^{18}[O_3]N_{I(H_2^{18}O)^-} \\ & - k_2^{18}[O_3]N_{I^{18}O^-} \\ & - c_2^{18}[O_3]N_{I^{18}O^-} \\ & - k_R N_{I^{18}O^-} \end{aligned} \quad (4)$$

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$$\begin{aligned}\dot{N}_{\mathrm{I}(\mathrm{H_2^{18}O})^-} = & -g_1^{18}[\mathrm{O_2}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & -h_1[\mathrm{H_2O}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & -b_1^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & -b_2^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & -b_3^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & -b_4^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & -\tilde{b}_2^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & -\tilde{b}_3^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & -\tilde{b}_4^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & -k_R N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \end{aligned} \quad (5)$$

$$\begin{aligned}\dot{N}_{\mathrm{IO_2^-}} = & k_2^{16}[\mathrm{O_3}]N_{\mathrm{IO^-}} \\ & +b_3^{16}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{16}O})^-} \\ & +b_3^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & +c_2^{18}[\mathrm{O_3}]N_{\mathrm{I^{18}O^-}} \\ & -k_3^{16}[\mathrm{O_3}]N_{\mathrm{IO_2^-}} \\ & -k_R N_{\mathrm{IO_2^-}} \end{aligned} \quad (6)$$

$$\begin{aligned}\dot{N}_{\mathrm{IO^{18}O^-}} = & \tilde{b}_3^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & +k_2^{18}[\mathrm{O_3}]N_{\mathrm{I^{18}O^-}} \\ & -k_3^{18}[\mathrm{O_3}]N_{\mathrm{IO^{18}O^-}} \\ & -c_3^{18}[\mathrm{O_3}]N_{\mathrm{IO^{18}O^-}} \\ & -k_R N_{\mathrm{IO^{18}O^-}} \end{aligned} \quad (7)$$

$$\begin{aligned}\dot{N}_{\mathrm{IO_3^-}} = & b_4^{16}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{16}O})^-} \\ & +b_4^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & +k_3^{16}[\mathrm{O_3}]N_{\mathrm{IO_2^-}} \\ & +c_3^{18}[\mathrm{O_3}]N_{\mathrm{IO^{18}O^-}} \\ & -k_R N_{\mathrm{IO_3^-}} \end{aligned} \quad (8)$$

$$\begin{aligned}\dot{N}_{\mathrm{IO_2^{18}O^-}} = & \tilde{b}_4^{18}[\mathrm{O_3}]N_{\mathrm{I}(\mathrm{H_2^{18}O})^-} \\ & +k_3^{18}[\mathrm{O_3}]N_{\mathrm{IO^{18}O^-}} \\ & -k_R N_{\mathrm{IO_2^{18}O^-}} \end{aligned} \quad (9)$$

Table S1 Conditions for the reduced model of the data obtained with trapping of $I(H_2^{18}O)^-$ in the presence of O_2, O_3 and trace amounts of water (H_2O) in the ion trap, i.e. data displayed in Fig. 6. The experimental values are from the present work (g_1^{16} and g_1^{18}) and from Teiwes *et al.*.[1]. The stated errors on the fit results represents 68% confidence intervals from the fitting alone. It should be emphasized that the values displayed as *Fit result* represent values obtained with this reduced model and hence they cannot be used as absolute reaction rate constants in other contexts.

Reaction		Symbol	Experimental (cm^3 $molecule^{-1}$ s^{-1})	Status in fit	Fit result (cm^3 $molecule^{-1}$ s^{-1})
$I(H_2^{18}O)^- + H_2^{16}O$	$\rightarrow I(H_2^{16}O)^- + H_2^{18}O$	h_1	$(1.3\pm0.1)\times10^{-8}$	fixed	—
$I(H_2^{16}O)^- + O_2$	$\rightarrow I^-$ + neutrals	g_1^{16}	$(1.9\pm0.2)\times10^{-12}$	fixed	—
$I(H_2^{18}O)^- + O_2$	$\rightarrow I^-$ + neutrals	g_1^{18}	$(3.2\pm0.6)\times10^{-12}$	fixed	—
$I(H_2^{16}O)^- + O_3$	$\rightarrow I^-$ + neutrals	b_1^{16}	$(2.0\pm0.3)\times10^{-10}$	fixed	—
$I(H_2^{16}O)^- + O_3$	$\rightarrow IO^-$ + neutrals	b_2^{16}	$(0.2\pm0.1)\times10^{-10}$	fixed	—
$I(H_2^{16}O)^- + O_3$	$\rightarrow IO_2^-$ + neutrals	b_3^{16}	$(2.5\pm0.3)\times10^{-10}$	free	$(8.1\pm0.1)\times10^{-10}$
$I(H_2^{16}O)^- + O_3$	$\rightarrow IO_3^-$ + neutrals	b_4^{16}	$(0.1\pm0.2)\times10^{-10}$	fixed	—
$I^- + O_3$	$\rightarrow IO_2^-$ + neutrals	k_1^{16}	$(6.0\pm3.0)\times10^{-12}$	fixed	—
$IO^- + O_3$	$\rightarrow IO_2^-$ + neutrals	k_2^{16}	$(1.3\pm0.4)\times10^{-8}$	fixed	—
$IO_2^- + O_3$	$\rightarrow IO_3^-$ + neutrals	k_3^{16}	$(1.4\pm0.1)\times10^{-8}$	fixed	—
$I(H_2^{18}O)^- + O_3$	$\rightarrow I^-$ + neutrals	b_1^{18}	—	fixed = b_1^{16}	—
$I(H_2^{18}O)^- + O_3$	$\rightarrow IO^-$ + neutrals	b_2^{18}	—	free	$(0.8\pm0.1)\times10^{-10}$
$I(H_2^{18}O)^- + O_3$	$\rightarrow IO_2^-$ + neutrals	b_3^{18}	—	free	$(5.5\pm0.1)\times10^{-10}$
$I(H_2^{18}O)^- + O_3$	$\rightarrow IO_3^-$ + neutrals	b_4^{18}	—	fixed = b_4^{16}	—
$I(H_2^{18}O)^- + O_3$	$\rightarrow I^{18}O^-$ + neutrals	$\tilde{b}_2^{18}$	—	fixed = 0	—
$I(H_2^{18}O)^- + O_3$	$\rightarrow IO^{18}O^-$ + neutrals	$\tilde{b}_3^{18}$	—	free	$(9.9\pm3.3)\times10^{-12}$
$I(H_2^{18}O)^- + O_3$	$\rightarrow IO_2^{18}O^-$ + neutrals	$\tilde{b}_4^{18}$	—	fixed = 0	—
$I^{18}O^- + O_3$	$\rightarrow IO^{18}O^-$ + neutrals	k_2^{18}	—	fixed = k_2^{16}	—
$IO^{18}O^- + O_3$	$\rightarrow IO_2^{18}O^-$ + neutrals	k_3^{18}	—	fixed = k_3^{16}	—
$I^{18}O^- + O_3$	$\rightarrow IO_2^-$ + neutrals	c_2^{18}	—	fixed = 0	—
$IO^{18}O^- + O_3$	$\rightarrow IO_3^-$ + neutrals	c_3^{18}	—	fixed = 0	—

Notes and references

1 R. Teiwes, J. Elm, M. Bilde and H. B. Pedersen, *Phys. Chem. Chem. Phys.*, 2019, **21**, 17546–17554.