Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Kinetics of CH_2OO reactions with SO_2, NO_2, NO, H_2O and CH_3CHO as a function of pressure

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Supplementary Information

Reactions and equations are numbered to correspond with those given in the main text.

$CH_2I + NO_2$

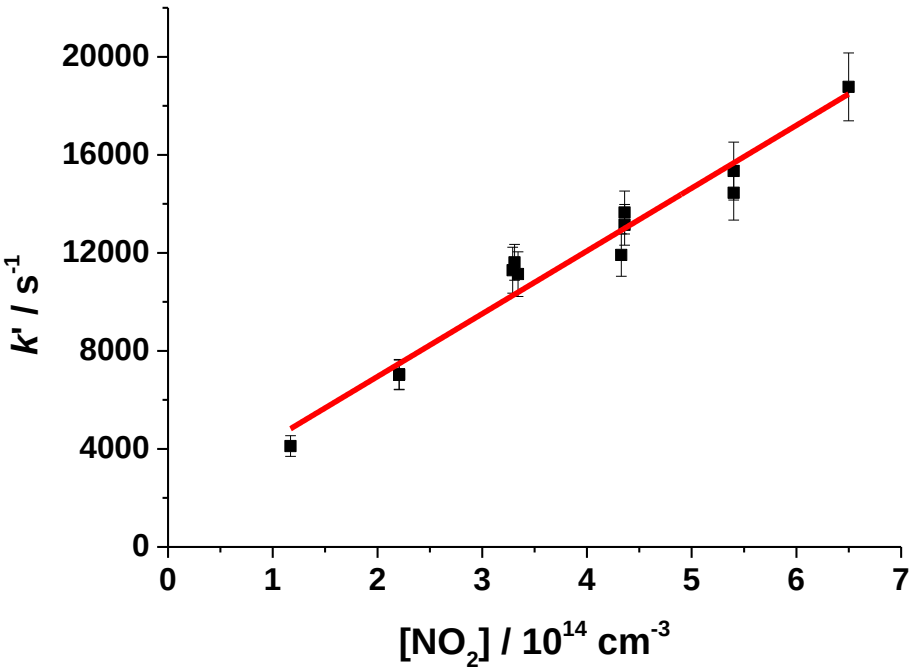

Figure S1: Pseudo-first-order rate coefficients (k') for HCHO production at 50 Torr, derived from fits to Equation 1, following photolysis of CH_2I_2/N_2 in the presence of NO_2. Error bars are 1σ. The fit to the data (shown in red) gives the bimolecular rate coefficient for $CH_2I + NO_2$ (k_8).

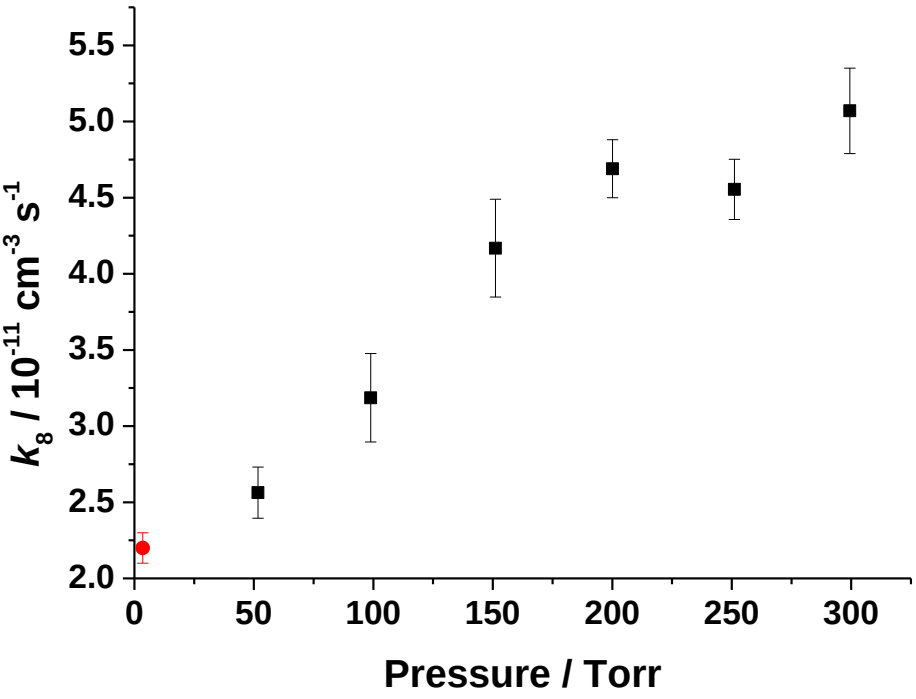

Figure S2: Bimolecular rate coefficients for $CH_2I + NO_2$ (k_8) as a function of pressure. The data point shown in red is that determined by Eskola *et al.*[1] Error bars are 1σ.

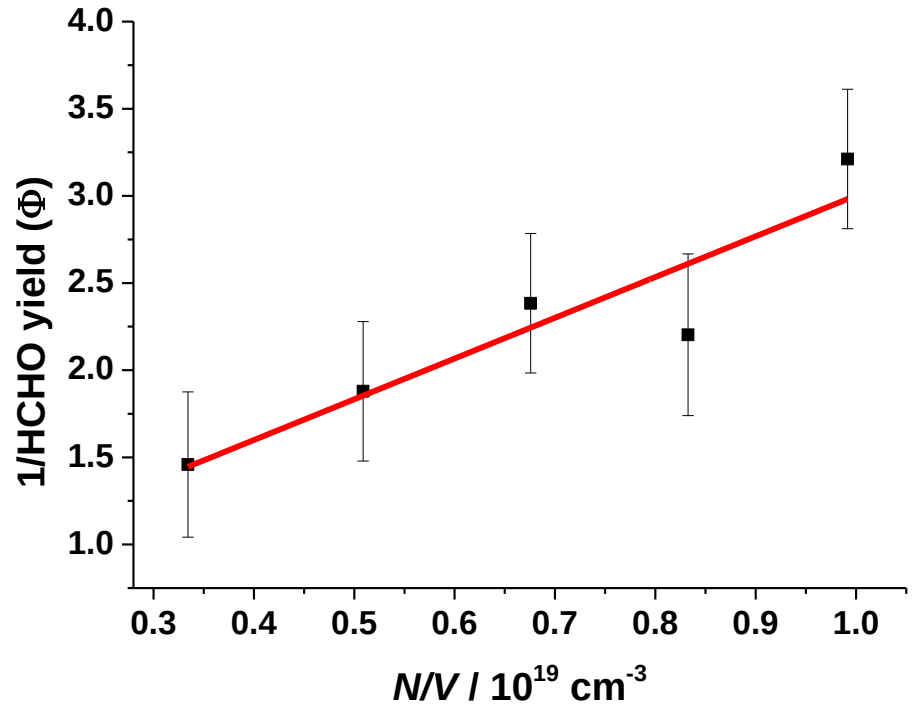

Figure S3: Stern-Volmer analysis for HCHO yields from $CH_2I + NO_2$ (R8) as a function of total pressure, with the fit to the data (red). Error bars are 1σ.

Pressure / Torr	k_8 / 10^{-11} cm^3 s^{-1}	Reference
2-5	2.2 ± 0.1	Eskola *et al.*[1]
50	2.56 ± 0.17	This work
100	3.19 ± 0.29	This work
150	4.17 ± 0.32	This work
200	4.69 ± 0.19	This work
250	4.55 ± 0.20	This work
300	5.07 ± 0.28	This work

Table S1: Bimolecular rate coefficients for $CH_2I + NO_2$ (k_8) as a function of pressure. Errors are 1σ.

CH_2IO_2 + NO

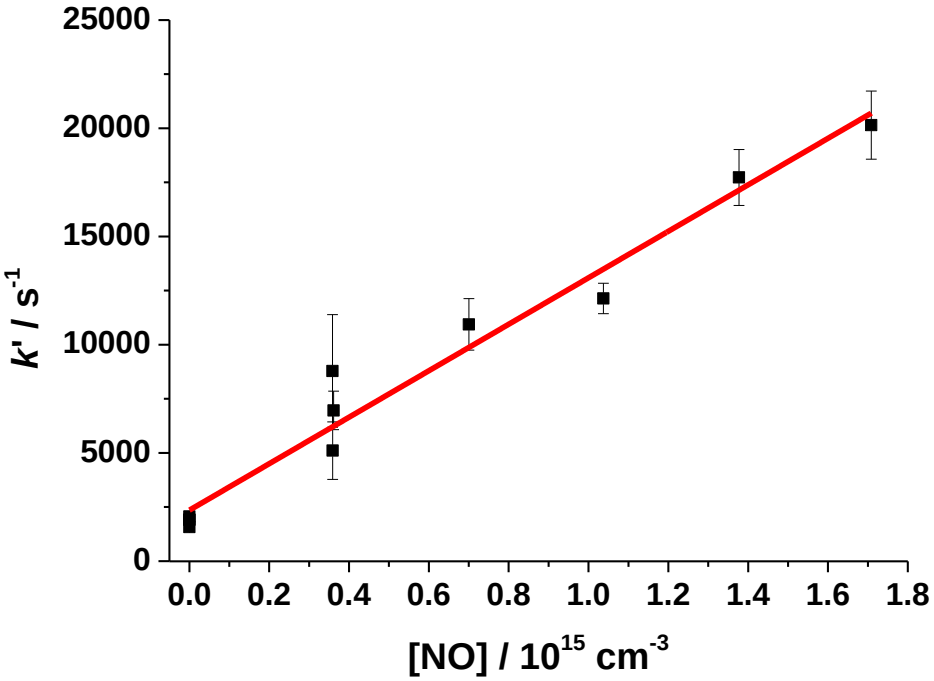

Figure S4: Pseudo-first-order rate coefficients (k') for the rapid HCHO production at 250 Torr, derived from fits to Equation 2, following photolysis of $CH_2I_2/O_2/N_2$ in the presence of NO. Error bars are 1σ. The fit to the data (shown in red) gives the bimolecular rate coefficient for CH_2IO_2 + NO (k_{10}).

$CH_2OO + NO_2$

The use of Equation 1 (main text) to describe HCHO production following photolysis of $CH_2I_2/O_2/N_2/NO_2$ mixtures was validated through simulations using the numerical integration package Kintecus.[2] Simulations were performed using the chemistry scheme described in Table S2 (below) to determine the rate coefficient for reaction of CH_2OO with NO_2 by fitting to experimental data. Rate coefficients determined in this way were typically within 10 % of those obtained by fitting to the analytical expression (Equation 1, main text). All rate coefficients described in this work were obtained from the fits to Equation 1, with errors from the fit to the bimolecular plot combined with an additional error of ± 10 %.

Reaction	***k* / cm^3 s^{-1} or s^{-1}**	**Reference**
$CH_2I + O_2 \rightarrow \beta(CH_2OO + I) + (1-\beta)\ CH_2IO_2$	1.5×10^{-12}	This work, Stone *et al.*,[3] Gravestock *et al.*,[4] Masaki *et al.*,[5] Eskola *et al.*6
$CH_2OO + I \rightarrow HCHO + IO$	9.3×10^{-11}	Estimated[a]
$CH_2IO_2 + CH_2IO_2 \rightarrow 2\ CH_2IO + O_2$	9.0×10^{-11}	Gravestock *et al.*[4]
$CH_2IO_2 + I \rightarrow CH_2IO + IO$	3.5×10^{-11}	Gravestock *et al.*[4]
$CH_2IO \rightarrow HCHO + I$	1.0×10^{5}	Gravestock *et al.*[4]
$CH_2OO + NO_2 \rightarrow HCHO + NO_3$	-	This work
$CH_2IO_2 + NO_2 \rightarrow CH_2IO_2NO_2$	3.8×10^{-12}	Estimated[b]
$CH_2IO_2NO_2 \rightarrow CH_2IO_2NO_2$	1.2	Estimated[b]

Table S2: Reactions and rate coefficients used in simulations of HCHO production in the $CH_2I_2/O_2/NO_2$ system. The parameter β was used to vary the relative yields of CH_2OO and CH_2IO_2 in the simulations, with pressure-dependent values taken from our previous work. [a] The rate coefficient for CH_2OO + I was estimated by modelling HCHO production from CH_2IO_2 + I and CH_2IO_2 + CH_2IO_2 (using the rate coefficients shown in the table from Gravestock *et al.*[4]), followed by re-fitting the simulated data with the HCHO production occurring due to CH_2OO + I and optimising $k_{CH2OO+I}$ to fit to the original simulation. Simulations were initialised with varying values for the rate coefficient describing the reaction between CH_2OO and NO_2, with the rate coefficient determined by fitting to the experimental data. [b] The rate coefficients for production and decomposition of $CH_2IO_2NO_2$ were estimated from the recommended values for the corresponding reactions $CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$ and $CH_3O_2NO_2 \rightarrow CH_3O_2 + NO_2$ (values in the table are shown for 300 Torr, 298 K).

The use of Equation 3 (main text) to describe HCHO production in the presence of SO_2 or NO was described in our previous work.[3]

$CH_2OO + CH_3CHO$

Low and high pressure limiting rate coefficients for the reaction between CH_2OO and CH_3CHO were approximated using the results of Taatjes *et al.*[7] at 4 Torr (k_{13} = (9.5 ± 0.7) × 10^{-13} cm^3 s^{-1}), combined with those obtained in this work at 25 Torr (k_{13} = (1.48 ± 0.04) × 10^{-12} cm^3 s^{-1}), 50 Torr (~2.2 × 10^{-12} cm^3 s^{-1}) and the determination of k_{13b}/k_{13a} from the Stern-Volmer plot (k_{13b}/k_{13a} = (1.09 ± 0.08) × 10^{-18} cm^3, Figure 13, main text).

Data were fitted to a simple Lindemann-Hinshelwood mechanism for chemical activation (Equations S1-S3 below), as shown in Figure S5, giving a low pressure limit ($k_{13,0}$) of ~ 1.6 × 10^{-29} cm^6 s^{-1} and a high pressure limit ($k_{13,\infty}$) of ~ 1.7 × 10^{-12} cm^3 s^{-1}.

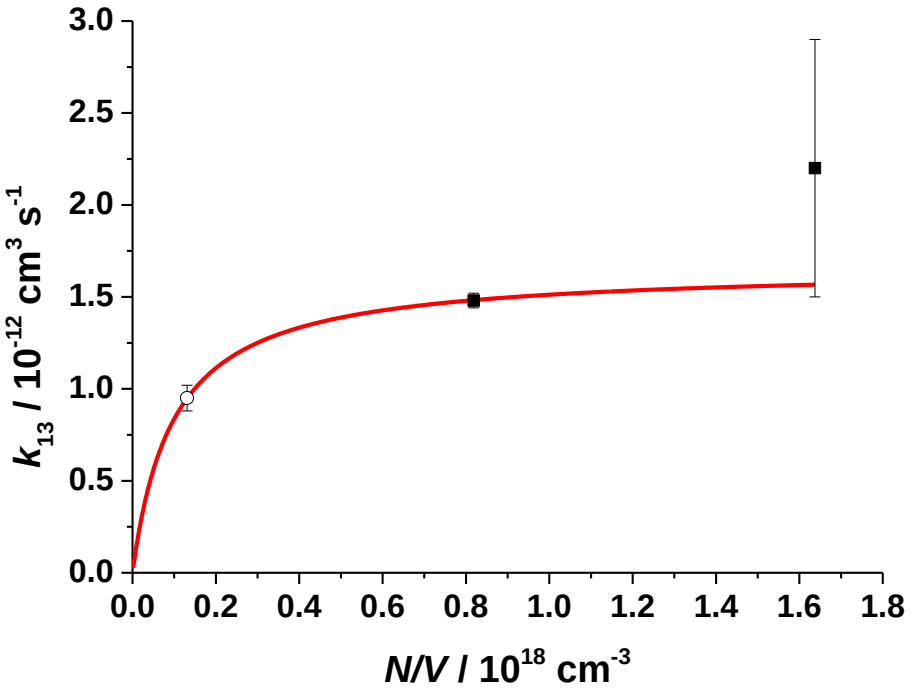

Figure S5: Data and fit to Equations S1-S3 used to estimate $k_{13,0}$ and $k_{13,\infty}$. The low pressure data point (shown by the open circle) is taken from Taatjes *et al.*[7] Data points at higher pressures (shown by the filled squares), and the value for k_{13b}/k_{13a} (k_{CA} in Equations S1-S3) are those obtained in this work.

$$k_a = 1 + \left(\frac{k_{CA}}{[M]} \right)$$ Equation S1

$$k_b = \left\{ \left(\frac{1}{k_{13,0}} \right) + \left(\frac{k_{CA}}{k_{13,\infty}} \right) \right\}^{-1}$$ Equation S2

$$k_{13} = \frac{k_a k_b k_{13,\infty} [M]}{k_{13,\infty} + k_b [M]}$$ Equation S3

where k_{CA} is the slope of the Stern-Volmer plot describing yields of HCHO from CH_2OO + CH_3CHO as a function of pressure (i.e. $k_{CA} = k_{13b}/k_{13a}$) , M is the total number density (N/V), $k_{13,0}$ is the low pressure limiting rate coefficient for CH_2OO + CH_3CHO and $k_{13,\infty}$ is the high pressure limiting rate coefficient for CH_2OO + CH_3CHO.

References

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