# CH<sub>2</sub>OO Criegee Biradical Yields Following Photolysis of CH<sub>2</sub>I<sub>2</sub> in O<sub>2</sub>

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# **Supplementary Information**

Note that reactions and equations are numbered to correspond with those given in the main text.

### **Experimental Details**

We report observations of the yields of  $CH_2OO$  and  $CH_2IO_2$  from  $CH_2I + O_2$  following laser flash photolysis of  $CH_2I_2/N_2/O_2$  gas mixtures as a function of  $[N_2]$ ,  $[O_2]$  and total pressure using several complementary methods.

$$CH_2I_2 + hv \rightarrow CH_2I + I$$
 (R1)

Experiments were initially performed to monitor I atom fluorescence, thus enabling inference of the yields of CH<sub>2</sub>OO and CH<sub>2</sub>IO<sub>2</sub> in the manner described by Huang *et al.*<sup>1</sup> Subsequent experiments monitored the yields of HCHO from reactions of CH<sub>2</sub>OO/CH<sub>2</sub>IO<sub>2</sub> in the presence of excess SO<sub>2</sub> or NO. SO<sub>2</sub> concentrations were used in the range  $2.4 \times 10^{14}$  cm<sup>-3</sup> to  $1.6 \times 10^{15}$  cm<sup>-3</sup>, giving pseudo-first-order rate coefficients in the range ~6,000–60,000 s<sup>-1</sup>. NO concentrations were used in the range  $3.6 \times 10^{14}$  cm<sup>-3</sup> to  $1.7 \times 10^{15}$  cm<sup>-3</sup>, giving pseudo-first-order rate coefficients in the range ~6,000–60,000 s<sup>-1</sup>.

CH<sub>2</sub>I<sub>2</sub> (Sigma-Aldrich, 99 %) was used as a dilute gas in N<sub>2</sub> either by filling a glass bulb containing liquid CH<sub>2</sub>I<sub>2</sub> with N<sub>2</sub> or by bubbling a slow flow of N<sub>2</sub> through liquid CH<sub>2</sub>I<sub>2</sub>. Reagent gases (SO<sub>2</sub>, NO) were prepared at known concentrations in N<sub>2</sub> and stored in glass bulbs. SO<sub>2</sub> (Sigma-Aldrich, 99.9 %), N<sub>2</sub> (BOC, 99.99 %) and O<sub>2</sub> (BOC, 99.999 %) were used as supplied. NO (BOC Special Gases, 99.5 %) was purified prior to use by a series of freeze-pump-thaw cycles. Gases were mixed in a gas manifold and passed into a six-way cross reaction cell at known flow rates (determined by calibrated mass flow controllers). The pressure in the reaction cell was monitored by a capacitance manometer (MKS Instruments, 626A) and controlled by throttling the exit valve to the reaction cell. The total gas flow rate through the reaction cell

was adjusted with total pressure to maintain an approximately constant gas residence time in the cell. All experiments were performed at T = 295 K unless stated otherwise.

For the I atom experiments, and those using NO as co-reagent, initiation of chemistry within the cell was achieved using an excimer laser (KrF, Tui ExciStar M) operating at  $\lambda = 248$  nm with typical laser fluence in the range 30 – 80 mJ cm<sup>-2</sup>. Experiments in which SO<sub>2</sub> was present as the co-reagent were performed at a photolysis wavelength of 355 nm (typical fluence ~ 150 mJ cm<sup>-2</sup>), generated by frequency tripling the output of a Nd:YAG laser (Spectron Laser Systems) to avoid potential multi-photon photolysis of SO<sub>2</sub> at lower wavelengths.<sup>2-5</sup>

A resonance lamp orthogonal to the excimer laser was used to probe the iodine atoms in the reaction cell with  $> 10^9$  atom cm<sup>-3</sup> sensitivity, with subsequent I atom fluorescence detected by a nitrogen purged solar blind channel photomultiplier (CPM, Perkin-Elmer C1311P) orthogonal to both the resonance lamp and the excimer laser. The signal from the CPM was captured and processed using a multichannel scalar (Ortec MCS-pci). Although reaction R1 produces both ground state ( ${}^{2}P_{3/2}$ ) and excited state ( ${}^{2}P_{1/2}$ ) iodine atoms in approximately equal yield at 248 nm,<sup>6</sup> the excited state iodine atoms are quenched by O<sub>2</sub> to the ground state  $\sim 20$  times faster than reaction R2 and will thus not influence the observed kinetics or yields.<sup>7</sup>

Production of HCHO from reactions of CH<sub>2</sub>OO and CH<sub>2</sub>IO<sub>2</sub> was monitored by laser-induced fluorescence (LIF) of HCHO at  $\lambda \sim 353.1$  nm.<sup>8</sup> Approximately 2 to 4 mJ pulse<sup>-1</sup> of laser light at ~ 353.1 nm was generated by a dye laser (Lambda Physik, FL3002) operating on DMQ/dioxirane dye and pumped by a 308 nm excimer laser generating ~ 50 mJ pulse<sup>-1</sup> (XeCl, Lambda Physik LPX100). The output of the dye laser was passed through the reaction cell in an orthogonal axis to the 248 nm/355 nm photolysis laser output, with HCHO fluorescence detected by a channel photomultiplier (CPM, Perkin-Elmer C1943P). A Perspex filter was used to prevent scattered laser light from the photolysis laser and the LIF excitation laser reaching the CPM. The HCHO fluorescence signal was monitored as a function of time following photolysis of CH<sub>2</sub>I<sub>2</sub> by varying the time delay between firing the photolysis laser and the LIF excitation laser through use of a delay generator (SRS DG535). Results from between 5 and 20 photolysis shots were typically averaged prior to analysis.

## **Kinetic Equations**

The production of iodine atoms in R1 and R2, combined with a first-order loss through a combination of reaction and diffusion out of the probe region, can be described by Equation 1, as discussed by Huang *et al.*<sup>1</sup>:

$$[\mathbf{I}]_{t} = S_{0} [\exp(-k_{\text{loss}}t)] + \frac{S_{1}k_{2}}{k_{2} - k_{\text{loss}}} [\exp(-k_{\text{loss}}t) - \exp(-k_{2}t)]$$
(Equation 1)

where  $[I]_t$  is the iodine atom signal at time *t*,  $S_0$  is the amplitude of the instant photolytic signal resulting from R1,  $S_1$  is the amplitude of the iodine atom signal resulting from the slower growth process occurring after photolysis,  $k'_2$  is the pseudo-first-order rate coefficient for R2 (i.e.  $k'_2 = k_2[O_2]$ ), and  $k_{loss}$  is the rate coefficient representing the slow loss of iodine atoms from the detection region *via* reaction or diffusion. Iodine atom production is thus described by an instant photolytic process, followed by a first-order exponential growth process, with a subsequent first-order exponential loss from the system. Figure S1 shows a schematic demonstrating the determination of the CH<sub>2</sub>OO yield from the iodine atom signal.



Figure S1: Schematic showing the determination of  $CH_2OO$  and  $CH_2IO_2$  yields from the reaction of  $CH_2I$  with  $O_2$  (R2) by monitoring the iodine atom production following photolysis of  $CH_2I_2/O_2/N_2$  gas mixtures.

A Stern-Volmer analysis of the iodine atom yield ( $\Phi_I$ ) from R2 (i.e.  $S_1/S_0$ ) gives Equation 2:

$$\frac{1}{\Phi_{I(R2)}} = 1 + \frac{k_{2b}}{k_{2a}} [M]$$
 (Equation 2)

The evolution of HCHO following photolysis of  $CH_2I_2/O_2/N_2$  gas mixtures was investigated by Gravestock *et al.*<sup>9</sup>, and it was shown that the production could be approximated to a pseudo-first-order process and, on inclusion of a loss term representing diffusion out of the probe region, could be described by Equation 3:

$$[\text{HCHO}]_t = S_0 [\exp(-k_{\text{loss}}t)] + \frac{S_1 k_g}{k_g - k_{\text{loss}}} [\exp(-k_{\text{loss}}t) - \exp(-k_g t)] \quad \text{(Equation 3)}$$

where  $[\text{HCHO}]_t$  is the HCHO signal at time *t*,  $S_0$  is the amplitude of the HCHO signal at time zero,  $S_1$  is the maximum HCHO signal,  $k'_g$  is the pseudo-first-order rate coefficient for HCHO growth, and  $k_{\text{loss}}$  is the rate

coefficient representing the slow loss of HCHO from the detection region *via* diffusion. The  $S_0$  term in Equation 3 accounts for any potential instantaneous production of HCHO following multi-photon dissociation of CH<sub>2</sub>I<sub>2</sub>, resulting in production <sup>3</sup>CH<sub>2</sub> which generates HCHO through reaction with O<sub>2</sub>.<sup>10-13</sup> The HCHO yield from multi-photon dissociation of CH<sub>2</sub>I<sub>2</sub> (the  $S_0$  term) is typically no greater than 5 – 10 % of the total HCHO yield. Although the production of HCHO through reactions of CH<sub>2</sub>OO and CH<sub>2</sub>I<sub>2</sub> is not strictly pseudo-first-order, Gravestock *et al.*<sup>9</sup> demonstrated that the HCHO signal in this system could be well-described by a single exponential first-order growth process. In order to demonstrate that the yields of HCHO in the CH<sub>2</sub>I<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> system could be established using Equation 3 we used the numerical integration package Kintecus<sup>14</sup> to simulate HCHO production in the system explicitly, with initial conditions, reactions and rate coefficients as listed in Table S1, and then fitted the simulated data with Equation 3. As shown in Figure S2 and Table S2, the fits to the simulated data faithfully reproduce the yields of HCHO.

Reaction	$k / \text{cm}^3 \text{ s}^{-1}$	Reference
$\mathbf{CH}_{2}\mathbf{I} + \mathbf{O}_{2} \rightarrow \boldsymbol{\beta}(\mathbf{CH}_{2}\mathbf{OO} + \mathbf{I}) + (1\text{-}\boldsymbol{\beta}) \ \mathbf{CH}_{2}\mathbf{IO}_{2}$	$1.5 \times 10^{-12}$	This work, Gravestock <i>et al.</i> <sup>9</sup> , Masaki <i>et al.</i> <sup>15</sup> ,
		Eskola <i>et al.</i> <sup>16</sup>
$\mathbf{CH_2OO} + \mathbf{I} \rightarrow \mathbf{HCHO} + \mathbf{IO}$	$9.3 \times 10^{-11}$	Estimated <sup>a</sup>
$CH_2IO_2 + CH_2IO_2 \rightarrow 2 \ CH_2IO + O_2$	$9.0  imes 10^{-11}$	Gravestock <i>et al.</i> <sup>9</sup>
$\mathbf{CH}_{2}\mathbf{IO}_{2}+\mathbf{I}\rightarrow\mathbf{CH}_{2}\mathbf{IO}+\mathbf{IO}$	$3.5 \times 10^{-11}$	Gravestock <i>et al.</i> <sup>9</sup>
$CH_2IO \rightarrow HCHO + I$	$1.0  imes 10^{5}$	Gravestock <i>et al.</i> <sup>9</sup>

Table S1: Reactions, rate coefficients and initial conditions used to simulate HCHO production following the reaction of CH<sub>2</sub>I with O<sub>2</sub>. Initial concentrations of CH<sub>2</sub>I and O<sub>2</sub> were set to  $2.5 \times 10^{12}$  cm<sup>-3</sup> and  $1 \times 10^{17}$  cm<sup>-3</sup>, respectively. The parameter  $\beta$  was varied to vary the relative yields of CH<sub>2</sub>OO and CH<sub>2</sub>IO<sub>2</sub> in the simulations. <sup>*a*</sup> The rate coefficient for CH<sub>2</sub>OO + I was estimated by modelling HCHO production from CH<sub>2</sub>IO<sub>2</sub> + I and CH<sub>2</sub>IO<sub>2</sub> + CH<sub>2</sub>IO<sub>2</sub> (using the rate coefficients shown in the table from Gravestock *et al.*<sup>9</sup>), followed by re-fitting the simulated data with the HCHO production occurring due to CH<sub>2</sub>OO + I and optimising  $k_{CH2OO+I}$  to fit to the original simulation.



Figure S2: Simulation of HCHO production following the reaction of CH<sub>2</sub>I radicals with O<sub>2</sub> (blue), using parameters in Table S1 for  $\beta = 0.75$  (the ratio of CH<sub>2</sub>OO to CH<sub>2</sub>IO<sub>2</sub>) with the fits to Equation 3 shown in red. The HCHO yield is shown relative to the initial CH<sub>2</sub>I concentration ( $2.5 \times 10^{12}$  cm<sup>-3</sup>). Approximation of the kinetic scheme to pseudo-first-order production of HCHO provides a faithful reproduction of the HCHO yield in the system.

β	Simulated HCHO yield / %	HCHO yield from fits to Equation 3 / %
0	100	99.9
0.25	100	98.3
0.50	100	97.9
0.75	100	98.2
1	100	99.0

Table S2: Yields of HCHO following the reaction of CH<sub>2</sub>I radicals with O<sub>2</sub> from simulations, using parameters in Table S1, with those determined from the fits to Equation 3, showing that the yields of HCHO in the system are well-described by Equation 3.  $\beta$  defines the ratio between CH<sub>2</sub>OO and CH<sub>2</sub>IO<sub>2</sub> produced by CH<sub>2</sub>I + O<sub>2</sub>.

In the presence of excess SO<sub>2</sub>, HCHO production occurs through the rapid reaction of CH<sub>2</sub>OO with SO<sub>2</sub> (R7), and the slower growth through reactions of CH<sub>2</sub>IO<sub>2</sub>, with the rates of the CH<sub>2</sub>OO and CH<sub>2</sub>IO<sub>2</sub> reactions sufficiently different that biexponential growth is observed. In the presence of excess NO, the situation is reversed, with the rapid growth process occurring as a result of CH<sub>2</sub>IO<sub>2</sub> + NO (R8) and the slower growth through the reaction of CH<sub>2</sub>OO with iodine atoms. Comparison of the total HCHO yields

with and without co-reagent show that the total yield of HCHO is not influenced by the addition of the coreagent, indicating complete titration of  $CH_2OO$  and  $CH_2IO_2$  to HCHO on addition of excess  $SO_2$  or NO. This is shown in Figure S3.



Figure S3: Formation of HCHO in back-to-back experiments in a) the absence of any co-reagent and b) the presence of excess  $SO_2$ . The results indicate that the total HCHO yield is unaffected by the addition of the co-reagent and 100 % of the  $CH_2I$  radicals are titrated to HCHO through the reactions of  $CH_2OO$  and  $CH_2IO_2$ .

The evolution of HCHO in the  $SO_2$  and NO experiments, incorporating first-order loss of HCHO through diffusion out of the probe region and potential for instantaneous production related to multi-photon dissociation of  $CH_2I_2$ , can be described by Equation 4:

$$[\text{HCHO}]_{t} = S_{0}[\exp(-k_{\text{loss}}t)] + \frac{S_{1}fk_{g1}}{k_{g1}-k_{\text{loss}}}[\exp(-k_{\text{loss}}t) - \exp(-k_{g1}t)]$$
(Equation 4)
$$+ \frac{S_{1}(1-f)k_{g2}}{k_{g2}-k_{\text{loss}}}[\exp(-k_{\text{loss}}t) - \exp(-k_{g2}t)]$$

where [HCHO]<sub>*t*</sub> is the HCHO signal at time *t*,  $S_0$  is the amplitude of the HCHO signal at time zero,  $S_1$  is the maximum HCHO signal,  $k'_{g1}$  is the pseudo-first-order rate coefficient for the fast HCHO growth,  $k'_{g2}$  is the pseudo-first-order rate coefficient for the slower HCHO growth, *f* is the fractional contribution of the fast growth process to the total HCHO yield (and hence (1-*f*) is the fractional contribution of the slower growth process to the total HCHO yield), and  $k_{loss}$  is the rate coefficient representing the slow loss of HCHO from the detection region *via* diffusion. In the SO<sub>2</sub> experiments the CH<sub>2</sub>OO yield is given by *f* and  $k'_{g1} = k_7$ [SO<sub>2</sub>], while in the NO experiments, the yield of CH<sub>2</sub>OO is thus given by (1-*f*) and  $k'_{g1} = k_8$ [NO], representing the reaction of CH<sub>2</sub>IO<sub>2</sub> with NO. Figures S4 and S5 display this schematically.



Figure S4: Schematic showing the determination of  $CH_2OO$  and  $CH_2IO_2$  yields from the reaction of  $CH_2I$  with  $O_2$  (R2) by monitoring HCHO production in the presence of excess SO<sub>2</sub>. The rapid production of HCHO results from  $CH_2OO + SO_2$ , while the slower HCHO production results from  $CH_2IO_2 + I$  and  $CH_2IO_2 + CH_2IO_2$ .



Figure S5: Schematic showing the determination of  $CH_2OO$  and  $CH_2IO_2$  yields from the reaction of  $CH_2I$  with  $O_2$  (R2) by monitoring HCHO production in the presence of excess NO. The rapid production of HCHO results from  $CH_2IO_2$  + NO, while the slower HCHO production results from  $CH_2OO$  + I.

Since the slower growth process in the presence of  $SO_2$  and NO, described by  $k'_{g2}$  in Equation 4, is not strictly pseudo-first-order we present a number of simulations made using the numerical integration package Kintecus to demonstrate that the approximation of the slower growth process to first-order kinetics does not influence the HCHO yields or kinetics of the fast growth process determined by Equation 4. Initial conditions, reactions and rate coefficients are as given in Table S1, with an additional reaction between

CH<sub>2</sub>OO and SO<sub>2</sub>, with a rate coefficient of  $4 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. The range of [SO<sub>2</sub>] in the simulation was varied to give pseudo-first-order rate coefficients (i.e.  $k'_{g1}$  in Equation 4) in the range 5,000 to 60,000 s<sup>-1</sup>, as was observed experimentally in this work. The simulations were fitted with Equation 4, and the fitted parameters compared to the parameters defined in the model. Results are shown in Table S3, demonstrating that the yields of HCHO from the two growth processes (i.e.  $S_1$  and f) and the kinetics of the fast growth process (i.e.  $k'_{g1}$ ) are faithfully reproduced by fitting with Equation 4. An example plot (for the case with 75 % yield of CH<sub>2</sub>OO from CH<sub>2</sub>I + O<sub>2</sub> and  $k'_{CH2OO+SO2} = 60,000 \text{ s}^{-1}$ ) is shown in Figure S6. Results from these simulations can be applied analogously to the case where NO is added as co-reagent, reacting with CH<sub>2</sub>IO<sub>2</sub> and not CH<sub>2</sub>OO as for SO<sub>2</sub>. Thus, since the fast HCHO growth processes are significantly faster than the slower growth process (5,000 – 60,000 s<sup>-1</sup> compared to ~300 – 500 s<sup>-1</sup>), the two processes are sufficiently decoupled to enable faithful determination of the HCHO yields and kinetics of the fast growth process.

Simulated $\beta$	$k' / s^{-1}$	Simulated total	Total HCHO yield	k' derived from	$\beta$ derived from
		HCHO yield / %	derived from fitting to	fitting to	fitting to
			Equation 4 / %	Equation $4 / s^{-1}$	<b>Equation 4</b>
0		100	101.0		0
U	-	100	101.8	-	0
0.25	5000	100	96.1	5500	0.26
0.25	60,000	100	99.1	60,000	0.26
0.50	5000	100	99.7	4827	0.54
0.50	60,000	100	99.1	60,000	0.52
0.75	5000	100	99.9	5030	0.77
0.75	60,000	100	99.9	60,000	0.75
1	5000	100	100	5224	1.00
1	60,000	100	100	59,998	1.00

Table S3: Yields of HCHO following the reaction of CH<sub>2</sub>I radicals with O<sub>2</sub> in the presence of excess SO<sub>2</sub> from simulations using parameters in Table S1 with the addition of a reaction between CH<sub>2</sub>OO and SO<sub>2</sub> ( $k = 4 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>) and [SO<sub>2</sub>] varied to give pseudo-first-order rate coefficients for CH<sub>2</sub>OO + SO<sub>2</sub> (k', where  $k' = k[SO_2]$ ) as shown, with the parameters derived from fitting to Equation 4. The HCHO yield is shown relative to the initial CH<sub>2</sub>I concentrations ( $2.5 \times 10^{12}$  cm<sup>-3</sup>).  $\beta$  defines the ratio between CH<sub>2</sub>OO and CH<sub>2</sub>IO<sub>2</sub> produced by CH<sub>2</sub>I + O<sub>2</sub> ( $\beta = 1$  gives 100 % CH<sub>2</sub>OO + I), thus the fitted value for  $\beta$  is given by *f* in Equation 4.



Figure S6: Simulated HCHO production (black line) in the presence of SO<sub>2</sub> (using  $k' = 60,000 \text{ s}^{-1}$  for a 75 % yield of CH<sub>2</sub>OO from CH<sub>2</sub>I + O<sub>2</sub>) with the results from the fit to Equation 4 (broken red line). The results from the fit are given in Table S3.

#### **Additional Figures**



Figure S7: Plot of  $k'_2$  versus [O<sub>2</sub>] at 10 Torr total pressure, nitrogen. The slope yields the bimolecular rate constant for reaction between CH<sub>2</sub>I and O<sub>2</sub> (R2), equal to  $(1.67 \pm 0.04) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, 2 $\sigma$  error.



Figure S8: Stern-Volmer analyses for CH<sub>2</sub>OO yields from CH<sub>2</sub>I + O<sub>2</sub> as a function of total pressure from a) iodine atom experiments (intercept =  $1.08 \pm 0.12$ ; slope =  $(2.28 \pm 0.11) \times 10^{-19}$  cm<sup>3</sup>); b) SO<sub>2</sub> experiments (intercept =  $1.46 \pm 0.25$ ; slope =  $(0.95 \pm 0.24) \times 10^{-19}$  cm<sup>3</sup>); c) NO experiments (intercept =  $1.41 \pm 0.30$ ; slope =  $(1.33 \pm 0.31) \times 10^{-19}$  cm<sup>3</sup>). Best fit lines are shown in red. Constraining the intercepts to unity for fits to SO<sub>2</sub> and NO data gives slopes of  $(1.37 \pm 0.10) \times 10^{-19}$  cm<sup>3</sup> and  $(1.71 \pm 0.16) \times 10^{-19}$  cm<sup>3</sup>, respectively. Data shown for SO<sub>2</sub> and NO were taken over a range of [O<sub>2</sub>] ( $(0.1 - 7.8) \times 10^{18}$  cm<sup>-3</sup>). Error bars are  $1\sigma$ , with fits weighted to the experimental errors.

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