

Supporting Information for “Formation of Secondary Organic Aerosol from the Direct Photolytic Generation of Organic Radicals”

In order to examine the relative importance of various reaction pathways in the reactive systems studied in this work, we have performed a kinetic simulation of such reactions under the relevant experimental conditions. All reactions (and corresponding rate coefficients) used in this kinetic model are listed in Table S-I. Self-reaction of RO_2 radicals leads to the production of alcohols, carbonyls, peroxides of the form ROOR , and alkoxy radicals, RO . The alkoxy radical rapidly isomerizes and reacts with oxygen to form the hydroxy-alkylperoxy radical, which again engages in RO_2 self-reaction. Reaction of the hydroxy-alkoxy radical with oxygen yields a hydroxycarbonyl compound and HO_2 ; this radical will react with RO_2 to form hydroperoxides.

Secondary reactions, which may complicate the reactions described above, are also included in this kinetic model. These focus on the radical abstraction of the hydrogen atom from the parent iodide compound, RI , by alkyl, alkylperoxy, alkoxy, and hydroxyl radicals. The hydroxyl radical may be formed by the photolysis of either organic hydroperoxides (ROOH) or hydrogen peroxide (H_2O_2). Conservatively high rate coefficients for these side reactions are used as upper limits.

The final concentration values of stable (non-radical) products after a 37-second simulation (consistent with the residence time of the reactor) are shown in Table S-II. Species formed by the RO_2 self-reaction and RO_2+HO_2 channels are present at levels at least two orders of magnitude greater than those formed by reactions of the parent molecule with other radicals, which account for <1% of all reactions of RI . We are therefore confident that the observed

chemistry arises from the $R+O_2$ reaction to form RO_2 radicals, followed by RO_2+RO_2 and RO_2+HO_2 reactions, with negligible influence from secondary chemistry.

#	Reaction	Rate Coefficient	Source
1	$RI \rightarrow R\cdot + I$	1.56×10^{-2}	(1, 2) ^a
2	$R\cdot (+ O_2) \rightarrow RO_2\cdot$	1.87×10^4	(3)
3	$RO_2 + R'O_2 \rightarrow ROOR' (+ O_2)$	3.84×10^{-15}	(3)
4	$RO_2 + RO_2 \rightarrow RO\cdot + RO\cdot (+ O_2)$	3.97×10^{-14}	(3)
5	$RO_2 + RO_2 \rightarrow ROH + R=O (+ O_2)$	2.04×10^{-14}	(3)
6	$(H-)RI + R\cdot \rightarrow \cdot RI + RH$	1.5×10^{-13}	(4)
7	$\cdot RI (+ O_2) \rightarrow RIO_2\cdot$	1.87×10^4	(3)
8	$R\cdot + R'\cdot \rightarrow R-R'$	5.0×10^{-12}	(5) ^b
9	$RO_2\cdot + (H-)RI \rightarrow ROOH + \cdot RI$	3.90×10^{-19}	(5) ^b
10 ^c	$RO\cdot (+ O_2) \rightarrow R'(OH)R''O_2\cdot$	1.5×10^7	(6)
11	$R'(OH)R''O\cdot + (O_2) \rightarrow R'(OH)R''(O) + HO_2\cdot$	4.7×10^4	(3)
12	$RO_2\cdot + HO_2\cdot \rightarrow ROOH (+ O_2)$	7.7×10^{-12}	(3)
13	$ROOH \rightarrow RO\cdot + \cdot OH$	4.53×10^{-4}	(1, 7) ^a
14	$HO_2\cdot + HO_2\cdot \rightarrow HOOH (+ O_2)$	2.84×10^{-12}	(8)
15	$HOOH \rightarrow \cdot OH + \cdot OH$	1.16×10^{-3}	(1, 9) ^a
16	$\cdot OH + \cdot OH \rightarrow HOOH$	4.7×10^{-25}	(8)
17	$\cdot OH + HO_2\cdot \rightarrow (H_2O + O_2)$	1.1×10^{-16}	(8)
18	$\cdot OH + (H-)RI \rightarrow \cdot RI + H_2O$	1.1×10^{-18}	(3)

Table S-I. Reactions and rate coefficients used in a simplified photolytic oxidation scheme. (Pseudo-)First-order rate constants (reactions 1, 2, 7, 10, 11, 13, and 15) are in units of s^{-1} , while all other rate constants have units of $cm^3 \text{ molecule}^{-1} s^{-1}$. ^aPhotolysis rates are estimated by comparing the absorption cross-sections of ozone ($1.13 \times 10^{-17} \text{ cm}^2$ (1)) with those of methyl iodide ($1.11 \times 10^{-18} \text{ cm}^2$ (2)), methyl hydroperoxide ($3.23 \times 10^{-20} \text{ cm}^2$ (7)), and hydrogen peroxide ($6.7 \times 10^{-20} \text{ cm}^2$ (9)), as well as a previously-estimated photolysis rate coefficient of ozone of $0.159 s^{-1}$ in the flow reactor. Quantum yields in all cases are assumed to be unity. ^bRate coefficients for the self-reaction of alkyl radicals and for H-abstraction by the peroxy radical are estimated from condensed-phase studies (5), adjusted upwards by a factor of 50 as an upper limit for the calculated rate. ^cThe hydroxyalkyl radical formed by isomerization in reaction 10 is assumed to immediately form an alkylperoxy radical by reacting with abundant O_2 . Subsequent reactions with other radical species are as described in reactions 3, 4, 5, and 12.

#	Species	Final Concentration (Fraction of Initial RI)
1	RI	0.011
2	RH	5.4×10^{-12}
3	ROOR'	0.037
4	ROH	0.196
5	R=O	0.196
6	R-R'	2.3×10^{-25}
7	R(OH)R(=O)	0.252
8	ROOH	0.152
9	R(OH)ROOH	0.096
10	H ₂ O ₂	2.8×10^{-4}

Table S-II. Final concentration values of stable (non-radical) species, as a fraction of the initial concentration of RI, for a simulation of the kinetics described in Table S-I. The reaction time is estimated to be ~37 s (the residence time of the flow reactor used here), and the initial concentration of species RI is given as 6×10^{13} molecule cm⁻³.

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