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

Supplementary Information

Role of the Reaction of Stabilized Criegee Intermediates with Peroxy Radicals in Particle Formation and Growth in Air

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1. Box model description

Table S1 lists the mechanisms of the ozonolysis of *trans*-3-hexene used in the box model. It is known that the production of OH radicals in alkene ozonolysis includes prompt OH formation by fast decomposition of excited Criegee intermediates (CI) and secondary OH formation from relatively slow thermal decomposition of stabilized CI (SCI). Experimental and theoretical studies have shown that ozonolysis of *trans*-3-hexene has a very low prompt OH yield (near zero) but high SCI yields at atmospheric pressure.[1,2] However, the rate constant of thermal decomposition ($k_{thermal}$) of *trans*-3-hexene SCI is not known. The $k_{thermal}$ has been reported for a few small alkenes including ethene, 2,3-dimethyl-2-butene, and *trans*-2-butene, but the values differ widely, ranging from 2.5 to 250 s^{-1}.[2-6] In the model, a prompt OH yield of 0.05, SCI yield of 0.8, and $k_{thermal}$ of 30 s^{-1} were used. The rate constants of all ROOH + SCI reactions are assumed to be the same as that of RO_2 + SCI as recommended by Vereecken *et al.*,[7] *i.e.*, 5×10^{-12} cm^3 $molecules^{-1}$ s^{-1}.

Table S1 Mechanisms of *trans*-3-hexene ozonolysis in the box model

#	Reaction	$k_{(298K)}$ (s^{-1} or cm^3 $molecule^{-1}$ s^{-1})	Reference
1	$C_6H_{12} + O_3 \rightarrow C_2H_5CHO + C_3H_6OOE$	1.6×10^{-16}	8
2	$C_3H_6OOE \rightarrow C_3H_6OO$	$0.8*1.0\times10^{6}$	MCM v3.2
3	$C_3H_6OOE \rightarrow C_2H_5O_2 + CO + OH$	$0.05*1.0\times10^{6}$	MCM v3.2
4	$C_3H_6OOE \rightarrow C_2H_5O_2 + HO_2$	$0.05*1.0\times10^{6}$	MCM v3.2
5	$C_3H_6OOE \rightarrow C_2H_6 + CO_2$	$0.05*1.0\times10^{6}$	MCM v3.2
6	$C_3H_6OOE \rightarrow C_2H_5C(O)OH$	$0.05*1.0\times10^{6}$	MCM v3.2
7	$C_3H_6OO \rightarrow C_2H_5O_2 + CO + OH$	30	—
8	$C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH$	7.8×10^{-12}	MCMv3.2
9	$C_2H_5O_2 + RO_2 \rightarrow C_2H_5OH$	$0.2*3.4\times10^{-13}$	MCMv3.2
10	$C_2H_5O_2 + RO_2 \rightarrow CH_3CHO$	$0.2*3.4\times10^{-13}$	MCMv3.2
11	$C_2H_5O_2 + RO_2 \rightarrow C_2H_5O$	$0.6*3.4\times10^{-13}$	MCMv3.2
12	$C_2H_5OOH + OH \rightarrow C_2H_5O_2$	3.6×10^{-12}	MCMv3.2
13	$C_2H_5OOH + OH \rightarrow CH_3CHO + OH$	8.0×10^{-12}	MCM v3.2
14	$C_2H_5O \rightarrow CH_3CHO + HO_2$	3.5×10^{4}	MCM v3.2
15	$CH3CHO + OH \rightarrow CH3C(O)O_2$	1.5×10^{-11}	MCM v3.2
16	$CH_3C(O)O_2 + HO_2 \rightarrow CH_3O_2 + OH$	$0.44*1.4\times10^{-11}$	MCM v3.2
17	$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH$	$0.41*1.4\times10^{-11}$	MCMv3.2
18	$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OH + O_3$	$0.15*1.4\times10^{-11}$	MCM v3.2
19	$CH_3C(O)O_2 + RO_2 \rightarrow CH_3O_2$	$0.7*2.6\times10^{-12}$	MCM v3.2

20	$CH_3C(O)O_2 + RO_2 \rightarrow CH_3C(O)OH$	$0.3*2.6\times10^{-12}$	MCM v3.2
21	$C_6H_{12} + OH \rightarrow HERO_2$	6.7×10^{-11}	8
22	$HERO_2 + HO_2 \rightarrow HEOOH$	$0.75*2.4\times10^{-11}$	MCM v3.2
23	$HERO_2 + HO_2 \rightarrow HRO + OH$	$0.25*2.4\times10^{-11}$	MCM v3.2
24	$HERO_2 + RO_2 \rightarrow C_2H_5C(O)C(OH)C_2H_5$	$0.2*8.8\times10^{-13}$	MCM v3.2
25	$HERO_2 + RO_2 \rightarrow C_2H_5C(OH)C(OH)C_2H_5$	$0.2*8.8\times10^{-13}$	MCM v3.2
26	$HERO_2 + RO_2 \rightarrow HERO$	$0.6*8.8\times10^{-13}$	MCM v3.2
27	$HERO \rightarrow C_2H_5CHO + C_2H_5CHO + HO_2$	2.3×10^{7}	MCM v3.2
28	$HERO \rightarrow C_2H_5C(O)C(OH)C_2H_5 + HO_2$	1.0×10^{6}	MCM v3.2
29	$HEOOH + OH \rightarrow HERO_2$	3.6×10^{-12}	MCM v3.2
30	$HEOOH + OH \rightarrow C_2H_5C(O)C(OH)C_2H_5 + OH$	3.6×10^{-11}	MCM v3.2
31	$C_2H_5C(O)C(OH)C_2H_5 + OH \rightarrow C_2H_5C(O)C(O)C_2H_5 + HO_2$	1.0×10^{-11}	MCM v3.2
32	$C_2H_5C(OH)C(OH)C_2H_5 + OH \rightarrow C_2H_5C(O)C(OH)C_2H_5 + HO_2$	2.1×10^{-11}	MCM v3.2
33	$C_2H_5CHO + OH \rightarrow C_2H_5C(O)O_2$	2.0×10^{-11}	8
34	$C_2H_5C(O)O_2 + HO_2 \rightarrow C_2H_5O_2 + OH$	$0.44*1.4\times10^{-11}$	MCM v3.2
35	$C_2H_5C(O)O_2 + HO_2 \rightarrow C_2H_5C(O)OOH$	$0.41*1.4\times10^{-11}$	MCM v3.2
36	$C_2H_5C(O)O_2 + HO_2 \rightarrow C_2H_5C(O)OH + O_3$	$0.15*1.4\times10^{-11}$	MCM v3.2
37	$C_2H_5C(O)O_2 + RO_2 \rightarrow C_2H_5O_2$	$0.7*1.0\times10^{-11}$	MCM v3.2
38	$C_2H_5C(O)O_2 + RO_2 \rightarrow C_2H_5C(O)OH$	$0.3*1.0\times10^{-11}$	MCM v3.2
39	$C_2H_5C(O)OOH + OH \rightarrow C_2H_5C(O)O_2$	4.4×10^{-12}	MCM v3.2
40	$C_2H_5C(O)OH + OH \rightarrow C_2H_5O_2$	1.2×10^{-12}	MCM v3.2
41	$OH + O_3 \rightarrow HO_2 + O_2$	7×10^{-14}	MCM v3.2
42	$OH + CO \rightarrow CO_2 + HO_2$	2.1×10^{-13}	MCM v3.2
43	$HO_2 + HO_2 \rightarrow H_2O_2$	1.7×10^{-10}	MCM v3.2
44	$OH + H_2O_2 \rightarrow HO_2 + H_2O$	4.6×10^{-12}	MCM v3.2
45	$HO_2 + O_3 \rightarrow OH + O_2$	2.0×10^{-15}	MCM v3.2
46	$C_3H_6OO + C_2H_5CHO \rightarrow C_2H_5CHO + C_2H_5C(O)OH$	$0.04*1.7\times10^{-12}$	9
47	$C_3H_6OO + C_2H_5CHO \rightarrow SOZ1$	$0.96*1.7\times10^{-12}$	9
48	$C_3H_6OO + CH_3CHO \rightarrow C_2H_5CHO + CH_3C(O)OH$	$0.04*1.7\times10^{-12}$	9
49	$C_3H_6OO + CH_3CHO \rightarrow SOZ2$	$0.96*1.7\times10^{-12}$	9
50	$C_3H_6OO + C_2H_5C(O)OH \rightarrow PPOOH$	2.6×10^{-12}	3,10
51	$C_3H_6OO + HEOOH \rightarrow OLIOOH11$	5×10^{-12}	—
52	$C_3H_6OO + OLIOOH11 \rightarrow OLIOOH12$	5×10^{-12}	—
53	$C_3H_6OO + OLIOOH12 \rightarrow OLIOOH13$	5×10^{-12}	—
54	$C_3H_6OO + OLIOOH13 \rightarrow OLIOOH14$	5×10^{-12}	—
55	$C_3H_6OO + OLIOOH14 \rightarrow OLIOOH15$	5×10^{-12}	—
56	$C_3H_6OO + OLIOOH15 \rightarrow OLIOOH16$	5×10^{-12}	—
57	$C_3H_6OO + OLIOOH16 \rightarrow OLIOOH17$	5×10^{-12}	—
In the presence of formic acid			
58	$HCOOH + C_3H_6OO \rightarrow FPOOH$	2.1×10^{-12}	3,10
59	$HCOOH + OH \rightarrow HO_2$	4.5×10^{-13}	MCM v3.2
60	$C_3H_6OO + FPOOH \rightarrow OLIOOH21$	5×10^{-12}	—
61	$C_3H_6OO + OLIOOH21 \rightarrow OLIOOH22$	5×10^{-12}	—
62	$C_3H_6OO + OLIOOH22 \rightarrow OLIOOH23$	5×10^{-12}	—

63	C_3H_6OO + OLIOOH23 → OLIOOH24	5×10^{-12}	—
64	C_3H_6OO + OLIOOH24 → OLIOOH25	5×10^{-12}	—
65	C_3H_6OO + OLIOOH25 → OLIOOH26	5×10^{-12}	—
66	C_3H_6OO + OLIOOH26 → OLIOOH27	5×10^{-12}	—

Note:

(1) The reaction mechanisms for ozonolysis and OH oxidation of *trans*-3-hexene were based on those for *trans*-2-pentene and/or *trans*-2-hexene in the Master Chemical Mechanism (MCM v3.2, http://mcm.leeds.ac.uk/MCM/home.htt).

(2) The reactions highlighted in blue are newly added (not included in MCM v3.2). The numbers highlighted in red are reaction branching ratios.

(3) C_3H_6OOE: excited CI; C_3H_6OO: stabilized CI; HEOOH: *trans*-3-hexene derived hydroperoxide from HE-RO_2 + HO_2 reaction; FPOOH: 3-formyloxypropyl hydroperoxide from formic acid + SCI reaction; OLIOOH1n and OLIOOH2n (n = 1-7): oligomers from HEOOH + n SCI and FPOOH + n SCI, respectively.

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