Supplementary material

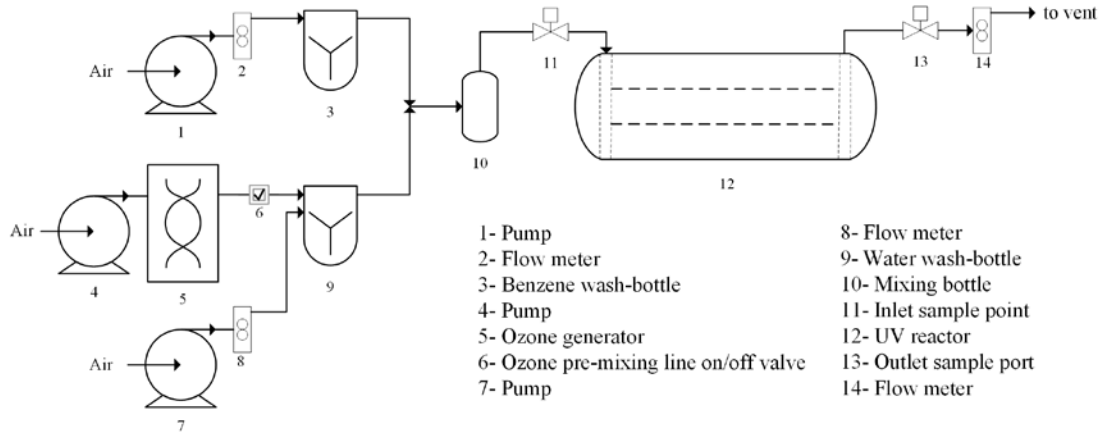

Fig. S1 Schematic diagram of the experimental setup

Table S1 Chemical mechanism of the simulation model

reaction number	reaction
1	$C_6H_6 + h\nu + 3.75O_2 \rightarrow OC{=}CHCHO + 0.5CO + 0.5OC{=}CHCH{=}CHCHO + 2HO_2$
2	$O + OH \rightarrow H + O_2$
3	$O + HO_2 \rightarrow OH + O_2$
4	$O + H_2O_2 \rightarrow OH + HO_2$
5	$O + O_2 + M \rightarrow O_3 + M$
6	$2O + M \rightarrow O_2 + M$
7	$O + O_3 \rightarrow 2O_2$
8	$2OH \rightarrow O + H_2O$
9	$OH + H_2O_2 \rightarrow HO_2 + H_2O$
10	$OH + O_3 \rightarrow HO_2 + O_2$
11	$HO_2 + O_3 \rightarrow OH + 2O_2$
12	$OH + HO_2 \rightarrow H_2O + O_2$
13	$2HO_2 + M \rightarrow H_2O_2 + O_2 + M$
14	$2OH + M \rightarrow H_2O_2 + M$
15 [a]	$C_6H_6 + OH + 1.59O_2 \rightarrow 0.57C_6H_5OH + 0.31OCHCHO + 0.1OCHCH{=}CHCHO + 0.08OCHCH{=}CHCH{=}CHCHO + 0.09OCHCH{=}CHCH\text{-}(\text{-}O\text{-})\text{-}CHCHO^{a} + 0.09C_6H_6O_3{}^{b} + HO_2$
16	$H_2O + h\nu \rightarrow HO_2 + OH$
17	$O_3 + h\nu \rightarrow O + O_2$
18	$HO_2 + h\nu \rightarrow OH + O$
19	$H_2O_2 + h\nu \rightarrow 2OH$
20	$H_2O_2 + h\nu \rightarrow H_2O + O$
21	$O(^1D) + H_2O \rightarrow 2OH$
22	$O(^1D) + O_2 \rightarrow O(^3P) + O_2$
23	$O(^1D) + N_2 \rightarrow O(^3P) + N_2$
24	$OCHCHO + OH + 1.5O_2 \rightarrow CO + CO_2 + HO_2 + H_2O$
25	$OCHCHO + OH + O_2 \rightarrow CO_2 + CO + HO_2$
26	$CO + OH + O_2 \rightarrow CO_2 + HO_2$

27	$OCHCHO + h\nu + 2O_2 \rightarrow 2CO + 2HO_2$
28	$OCHCHO + h\nu + 2.5O_2 \rightarrow CO + CO_2 + 2HO_2$
29	$OCHCH{=}CHCHO + h\nu + 2O_2 \rightarrow CO + OCHCH{=}CO + 2HO_2$
30	$OCHCH{=}CHCHO + h\nu \rightarrow CO + OCHCH{=}CH_2$
31	$C_6H_5OH + OH + 1.26O_2 \rightarrow 0.8C_6H_4(OH)_2$[c] $+ 0.1OCHCH{=}CHCHO + 0.1OCHCOOH + 0.06CO +$ $0.04C_6H_4O_2$[d] $+ 0.06OCHCH{=}CHCOCHO + 0.1H_2O + HO_2$
32	$C_6H_4(OH)_2 + OH + 1.3O_2 \rightarrow 0.8C_6H_3(OH)_3 + 0.2OCHCH{=}CHCOOH + 0.2OCHCOOH + HO_2$
33	$C_6H_3(OH)_3 + OH + 1.3O_2 \rightarrow 0.8C_6H_2(OH)_4 + 0.2OCHCH_2COCOOH + 0.2OCHCOOH + HO_2$
34	$C_6H_2(OH)_4 + OH + 1.3O_2 \rightarrow 0.8C_6H(OH)_5 + 0.1OCHCOCOOH + 0.1OCHCHOHCOOH +$ $0.1OCHCOCHOH + 0.1OCHCOOH + HO_2$
35	$C_6H(OH)_5 + OH + O_2 \rightarrow C_6(OH)_6 + HO_2$
36	$C_6(OH)_6 + OH + 2.5O_2 \rightarrow OCOHCOOH + COOHCOCHOHCOOH + HO_2$
37	$OCHCH{=}CHCHO + OH + 1.5O_2 \rightarrow 2OCHCHO + HO_2$
38	$OCHCH{=}CHCH{=}CHCHO + OH + 1.5O_2 \rightarrow OCHCH{=}CHCHO + OCHCHO + HO_2$
39	$OCHCH{=}CHCH\text{-}(\text{-}O\text{-})\text{-}CHCHO$[a] $+ OH + 2O_2 \rightarrow OCHCHOHCHO + OCHCHO + CO + HO_2$
40	$C_6H_6O_3$[b] $+ OH + 1.5O_2 \rightarrow OCHCH\text{-}(\text{-}O\text{-})\text{-}CHCHOHCOCHO + HO_2$
41	$OC{=}CHCHO + OH + 1.5O_2 \rightarrow CO_2 + OCHCHO + HO_2$
42	$OC{=}CHCH{=}CHCHO + OH + 1.5O_2 \rightarrow OC{=}CHCHO + OCHCHO + HO_2$
43	$OCHCH{=}CH_2 + OH + 1.5O_2 \rightarrow OCHCHO + CH_2O + HO_2$
44	$CH_2O + OH \rightarrow CO + HO_2 + H_2O$
45	$OCHCOOH + OH + 1.5O_2 \rightarrow 2CO_2 + H_2O + HO_2$
46	$OCHCH{=}CHCOOH + OH + 1.5O_2 \rightarrow OCHCHO + OCHCOOH + HO_2$
47	$C_6H_4O_2$[d] $+ OH + 1.5O_2 \rightarrow OCHCOCH{=}CHCOCHO$
48	$OCHCH{=}CHCOCHO + OH + 1.5O_2 \rightarrow OCHCHO + OCHCOCHO + HO_2$
49	$OCHCH_2COCOOH + OH + 2O_2 \rightarrow CO_2 + H_2O + OCHCOCOOH + HO_2$
50	$OCHCOCHOHCOOH + OH + 2O_2 \rightarrow 2CO_2 + H_2O + OCHCOOH + HO_2$
51	$OCHCOCOOH + OH + 2O_2 \rightarrow 3CO_2 + HO_2 + H_2O$
52	$OCHCHOHCOOH + OH + 1.5O_2 \rightarrow CO_2 + OCHCOOH + H_2O + HO_2$
53	$OCOHCOOH + OH + O_2 \rightarrow 2CO_2 + H_2O + HO_2$
54	$OCOHCOCHOHCOOH + OH + 1.5O_2 \rightarrow 2CO_2 + H_2O + OCHCOOH + HO_2$
55 [a]	$OCHCH\text{-}(\text{-}O\text{-})\text{-}CHCHOHCOCHO + OH + 2O_2 \rightarrow 2CO_2 + H_2O + OCHCH\text{-}(\text{-}O\text{-})\text{-}CHCHO + HO_2$
56	$OCHCOCH{=}CHCOCHO + OH + 1.5O_2 \rightarrow 2OCHCOCHO + HO_2$
57	$OCHCOCHO + OH + 2O_2 \rightarrow 2CO_2 + H_2O + CO + HO_2$
58	$OCHCOCOOH + OH + 2O_2 \rightarrow 2CO_2 + H_2O + HO_2$
59	$OCHCH\text{-}(\text{-}O\text{-})\text{-}CHCHO + OH + 2O_2 \rightarrow 2CO_2 + H_2O + OCHCOCHO + HO_2$
60	$OC{=}CHCHO + OH + 2O_2 \rightarrow 2CO_2 + H_2O + OC{=}CO$
61	$OC{=}CO + OH + 1.5O_2 \rightarrow 2CO_2 + HO_2$
62	$OCHCHOHCHO + OH + 1.5O_2 \rightarrow CO_2 + H_2O + OCHCHO + HO_2$

Notes: [a] -(-O-)- refers to an epoxide

[b] Cyclic epoxide

[c] catechol

[d] *p*-benzoquinone

Table S2 Rates of chemical reactions in the model

reaction number	rate constant/($cm^3 \cdot mol^{-1} \cdot s^{-1}$)	reference/comments
2	$2.4\times10^{-11}\ \exp(110/T)$	[28]
3	$2.7\times10^{-11}\ \exp(224/T)$	[28]
4	$1.4\times10^{-12}\ \exp(-2000/T)$	[28]
5	$k_0 = 6.0\times10^{-34}\ (T/300)^{-2.6}\ [O_2] + 5.6\times10^{-34}\ (T/300)^{-2.6}\ [N_2]$	[28]
6	$k_0 = 2.7\times10^{-34}\ T^{-0.41}\ [M]$	[31]
7	$8.0\times10^{-12}\ \exp(-2060/T)$	[28]
8	$6.2\times10^{-14}\ (T/298)^{2.6}\ \exp(945/T)$	[28]
9	$2.9\times10^{-12}\ \exp(-160/T)$	[28]
10	$1.7\times10^{-12}\ \exp(-940/T)$	[28]
11	$2.03\times10^{-16}\ (T/300)^{4.57}\ \exp(693/T)$	[28]
12	$4.8\times10^{-11}\ \exp(250/T)$	[28]
13	$2.2\times10^{-13}\ \exp(600/T) + (1.9\times10^{-33}\ \exp(980/T)[N_2] + 1.6\times10^{-33}\ \exp(980/T)[O_2]) \times (1 + 1.4\times10^{-21}\ \exp(2200/T)\ [H_2O])$	[28]
14	$k_0 = 6.9\times10^{-31}\ (T/300)^{-0.8}\ [M]$ $k_\infty = 2.6\times10^{-11}$ $F_c = 0.5$	[28]
15	$2.33\times10^{-12}\ \exp(-193/T)$	[28]
21	2.2×10^{-10}	[28]
22	$3.2\times10^{-11}\ \exp(67/T)$	[28]
23	$1.8\times10^{-11}\ \exp(107/T)$	[28]
24	$1.1\times10^{-11}\ \phi_1$ $\varphi_1 = \frac{5\times10^{-12}\left[O_2\right]}{10^{-11}\left[O_2\right]+1.4\times10^{-12}\exp\left(-3160/T\right)}$	[32]
25	$1.1\times10^{-11}\ \phi_2$ $\phi_2 = 1 - \phi_1$ (see reaction 24)	[32]
26	$1.3\times10^{-13}\ (1 + 0.6p)(300/T)$ (p in bar)	[29]
31	2.63×10^{-11}	[33]
32	10.4×10^{-11}	[33]
33	20.5×10^{-11}	[33]
34	20.5×10^{-11}	Estimate based on [33]
35	20.5×10^{-11}	Estimate based on [33]
36	20.5×10^{-11}	Estimate based on [33]
37	7.0×10^{-12}	Kwok and Atkinson [34] method, addition on double bond
38	16.4×10^{-12}	Kwok and Atkinson [34] method, addition on double bond
39	20.5×10^{-12}	Kwok and Atkinson [34] method, addition on double bond

40	50.76×10^{-12}	Kwok and Atkinson [34] method, addition on double bond
41	38.41×10^{-12}	Kwok and Atkinson [34] method, addition on double bond
42	83.98×10^{-12}	Kwok and Atkinson [34] method, addition on double bond
43	8.94×10^{-12}	Kwok and Atkinson [34] method, addition on double bond
44	$5.4\times10^{-12}\exp(135/T)$	[29]
45	12.49×10^{-12}	Kwok and Atkinson [34] method, abstraction of H from C
46	11.13×10^{-12}	Kwok and Atkinson [34] method, addition on double bond
47	4.6×10^{-12}	[33]
48	18.42×10^{-12}	Kwok and Atkinson [34] method, addition on double bond
49	$5.1\times10^{-12}\exp(405/T)$	Same as propionaldehyde, [29]
50	1.5×10^{-11}	Same as CH_3COCHO, [29]
51	1.5×10^{-11}	Same as CH_3COCHO, [29]
52	$3.1\times10^{-12}\exp(405/T)$	40 % less than reaction 46[c], [29]
53	$8.4\times10^{-14}\exp(855/T)$	Twice the value of acetic acid, [29]
54	$8.4\times10^{-14}\exp(855/T)$	Twice the value of acetic acid, [29]
55	3.0×10^{-11}	Twice the value of reaction 47
56	7.0×10^{-12}	Kwok and Atkinson [34] method, addition on double bond
57	3.0×10^{-11}	Twice the value of reaction 47
58	1.5×10^{-11}	Same as CH_3COCHO, [29]
59	3.0×10^{-11}	Twice the value of reaction 47
60	1.5×10^{-11}	Same as CH_3COCHO, [29]

61	4.5×10^{-11}	Kwok and Atkinson [34] method, addition on double bond
62	3.0×10^{-11}	Twice the value of reaction 47

Notes: [a] Assuming that the effect of an epoxide in beta position on the rate constant is negligible

[b] Based on the reactivity of $O=C=CH_2$, [34] the effect of carbonyl in alpha position on the reactivity of the C=C bond is estimated at 0.64

[c] Based on a comparison of $HOCH_2CHO$ and CH_3CHO

Table S3 Quantum yields and absorption cross-sections at 185 nm and 254 nm of photochemical reactions in the model

reaction number	λ/nm	ϕ	σ/cm^2	comments/references
1	185	$(6.705(p_i + 340.06p_b) + 1)^{-1}$ [a]	1.24×10^{-17}	see text; NIST [b]
	254	0	3×10^{-19}	assumed; NIST [b]
16	185	1	5.5×10^{-20}	[36]
	254	0	0	[36]
17	185	$O(^1D)$: 0.9; $O(^3P)$: 0.1	66.1×10^{-20}	[36]
	254	$O(^1D)$: 0.9; $O(^3P)$: 0.1	1148×10^{-20}	[36]
18	185	1	324.8×10^{-20}	[36]
	254	1	29.9×10^{-20}	[36]
19, 20	185	OH: 0.75; O: 0.16; H_2O: 0.16	80.1×10^{-20}	[36]
	254	1	6.99×10^{-20}	[36]
27	185		0	assumed
	254	$\phi_1 = \frac{5\times10^{-12}[O_2]}{10^{-11}[O_2]+1.4\times10^{-12}\exp(-3160/T)}$	1.596×10^{-20}	[37]
28	185		0	assumed
	254	$\phi_2 = 1 - \phi_1$ (see reaction 27)	1.596×10^{-20}	[37]
29	185	0.55	6.88×10^{-18}	[38]
	254	0.12	3.62×10^{-19}	[38]
30	185	0.011	6.88×10^{-18}	[38]
	254	0.037	3.62×10^{-19}	[38]

Notes: [a] p_i = inert partial pressure in atm; p_b = benzene partial pressure in atm

[b] NIST Chemistry Webbook, http://webbook.nist.gov/chemistry