Chamber Simulation of Photooxidation of Dimethyl Sulfide and Isoprene in the Presence of NO$_x$

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Supplementary Materials

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The artifacts of DMSO measurement in the presence of DMS

The prediction of DMSO (not shown in the figures) is systematically much lower than the measured DMSO. However, as explained by Sorensen et al (1996), the fast reaction between DMSO and OH· should lead to the scavenging of the DMSO formed so the detected DMSO should be little. It is thus possible that the measurement of DMSO rather than the model prediction is problematic. It has been reported by Gershenzon (2001) that DMS and O_3 can rapidly react in the water with a reaction rate constant of $\sim 10^9$ M^{-1} s^{-1} at room temperature, forming DMSO with a nearly unity yield. In contrast, the liquid phase reaction between DMSO and O_3 was found to be $\sim 10^8$ times slower than that between DMS and O_3, so once DMSO is formed as a product of DMS and O_3 reaction, it will not be rapidly consumed by O_3. It is thus reasonable to assume that the high concentration of DMSO measured in the presence of DMS was an artifact due to the liquid-phase reaction of DMS and O_3 collected in the liquid N_2 trap ($\sim$ -195°C while the melting point of DMS is -98 °C and that of O_3 is -192 °C). Rapid liquid phase reaction of DMS and O_3 is most likely to occur when the cold trap is heated. In order to prove this hypothesis, 600 ppb DMS and 200 ppb O_3 were injected into the chamber, then the chamber air was sampled using the liquid N_2 trap. Since the rate of the reaction of DMS with O_3 in gas phase is known to be in the order of $\sim 10^{-20}$ $cm^3 molecules^{-1}$ s^{-1}, there should be theoretically no or little DMSO detected. Nevertheless, with 10 ppb of DMS decay, 180 ppb of DMSO was detected, which demonstrated that the DMSO sampling method causes a significant amount of artifacts. As a result, measured DMSO concentrations in the experiments containing DMS were not used in this study.

DMSO Reactions	Rate constant [a]	Note
Initial reactions		
1 CH_3-$S(O)CH_3$ + O^3P → SO_2+ $CH_3\cdot$+ $CH_3\cdot$	1.50E+07	(Sander, 2006)
2 CH_3-$S(O)CH_3$ + OH· → CH_3-$S(OH)(O)CH_3$	6.1E-12exp(800/T)	(Sander, 2006)
3 CH_3-$S(O)CH_3$+ NO_3 → NO_2+ $CH_3(O)S(O)CH_3$	2.90E-13	(Sander, 2006)
Primary products		
a. $CH_3\cdot$ Reactions (see CH_4 reactions)		
b. CH_3-$S(OH)(O)CH_3$ reactions		
4 CH_3-$S(OH)(O)CH_3$ → CH_3-$S(O)OH$+ $CH_3\cdot$	1.50E+07	(Veltwisch et al., 1980)
5 CH_3-$S(OH)(O)CH_3$ + O_2 → $CH_3(O)S(O)CH_3$+ HO_2	1.20E-12	(Yin et al., 1990)
c. $CH_3(O)S(O)CH_3$ and its further reactions		
6 $CH_3(O)S(O)CH_3$ + OH → $CH_3(O)S(O)CH_2$+ H_2O	1.00E-14	(Yin et al., 1990)
7 $CH_3(O)S(O)CH_2\cdot$+ O_2 → $CH_3(O)S(O)CH_2OO\cdot$	7.30E-13	(Yin et al., 1990)
Secondary Products		
a. $CH_3S(O)OH$		
8 CH_3-$S(O)OH$ + OH → $CH_3(O)S(O)\cdot$+ H_2O	1.00E-10	(Kukui et al., 2003)
b. $CH_3(O)S(O)CH_2OO.\cdot$ reactions		
9 $CH_3(O)S(O)CH_2OO\cdot$+ NO → $CH_3(O)S(O)CH_2O\cdot$+ NO_2	5.00E-12	(Yin et al., 1990)
10 $CH_3(O)S(O)CH_2OO\cdot$+ CH_3-$S\cdot$ → $CH_3(O)S(O)CH_2O\cdot$+ CH_3-$SO\cdot$	5.00E-11	(Kukui et al., 2003)
11 $CH_3(O)S(O)CH_2OO\cdot$+ CH_3-$SO\cdot$ → $CH_3(O)S(O)CH_2O\cdot$+ $CH_3(O)S(O)\cdot$	4.00E-12	(Yin et al., 1990)
12 $CH_3(O)S(O)CH_2OO\cdot$+ $CH_3(O)S(O)\cdot$ → $CH_3(O)S(O)CH_2O\cdot$+ CH_3-$SO_3\cdot$	2.50E-13	(Yin et al., 1990)
13 $CH_3(O)S(O)CH_2OO\cdot$+ $HO_2\cdot$ → $CH_3(O)S(O)CH_2OOH$+ O_2	1.50E-12	(Yin et al., 1990)
14 $CH_3(O)S(O)CH_2OO\cdot$+ CH_3-$O_2\cdot$ → $CH_3(O)S(O)CH_2O\cdot$+ O_2+ CH_3-O.	1.80E-13	(Yin et al., 1990)
15 $CH_3(O)S(O)CH_2OO\cdot$+ $CH_3(O)S(O)CH_2OO\cdot$ → $2CH_3(O)S(O)CH_2O\cdot$+ O_2	8.60E-14	(Yin et al., 1990)

[a]The unit for first order reactions is s^{-1} and the unit for second order reactions is s^{-1} molecules^{-1} cm^3

Tertiary and further products
a. CH$_3$-S(O)OH reactions

16	CH$_3$-S(O)OH + OH → CH$_3$(O)S(O)·+ H$_2$O	1.60E-11	(Yin et al., 1990)
17	CH$_3$-S(O)OH + CH$_3$-SO$_3$· → CH$_3$(O)S(O)·+ CH$_3$-SO$_3$H	2.00E-13	(Yin et al., 1990)
18	CH$_3$-S(O)OH + CH$_3$-O· → CH$_3$(O)S(O)·+ CH$_3$-OH	1.00E-13	(Yin et al., 1990)
19	CH$_3$-S(O)OH + O^{3}P → CH$_3$(O)S(O)·+ OH·	1.00E-13	(Yin et al., 1990)
20	CH$_3$-S(O)OH + NO$_3$ → CH$_3$(O)S(O)·+ HNO$_3$	1.00E-13	(Yin et al., 1990)
21	CH$_3$-S(O)OH + HO$_2$ → CH$_3$(O)S(O)·+ H$_2$O$_2$	1.00E-15	(Yin et al., 1990)
22	CH$_3$-S(O)OH + CH$_3$-O$_2$· → CH$_3$(O)S(O)·+ CH$_3$-OOH	1.00E-15	(Yin et al., 1990)

b. CH$_3$(O)S(O)CH$_2$O· reactions

23	CH$_3$(O)S(O)CH$_2$O· → CH$_3$(O)S(O)·+ H-CO-H	1.00E+01	(Yin et al., 1990)

c. CH$_3$(O)S(O) reactions

24	CH$_3$(O)S(O)·+ NO$_2$ → CH$_3$-SO$_3$·+ NO	5.00E-13	Estimate
25	CH$_3$(O)S(O)·+ O$_3$ → CH$_3$-SO$_3$·+ O$_2$	5.00E-15	(Yin et al., 1990)
26	CH$_3$(O)S(O)·+ HO$_2$ → CH$_3$-SO$_3$ + OH	2.50E-13	(Yin et al., 1990)
27	CH$_3$(O)S(O)· → CH$_3$·+ SO$_2$	1.00E+01	(Mellouki et al., 1988)
28	CH$_3$(O)S(O)·+ O$_2$ → CH$_3$(O)S(O)OO·	2.60E-18	(Yin et al., 1990)
29	CH$_3$(O)S(O)OO· → CH$_3$(O)S(O)·+ O$_2$	3.30	(Yin et al., 1990)
30	CH$_3$(O)S(O)·+ NO$_3$ → CH$_3$-SO·+ NO$_2$	1.00E-14	(Yin et al., 1990)
31	CH$_3$(O)S(O)·+ CH$_3$-O$_2$· → CH$_3$-SO$_3$·+ CH$_3$-O·	2.50E-13	(Yin et al., 1990)
32	CH$_3$(O)S(O)·+ CH$_3$-S· → CH$_3$(O)S(O)S-CH$_3$	4.20E-11	(Yin et al., 1990)
33	CH$_3$(O)S(O)·+ CH$_3$(O)S(O)· → CH$_3$-SO·+ CH$_3$-SO$_3$·	7.50E-12	(Yin et al., 1990)
34	CH$_3$(O)S(O)·+ CH$_3$-S-NO· → CH$_3$(O)S(O)CH$_3$+ NO	6.80E-13	(Yin et al., 1990)
35	CH$_3$(O)S(O)·+ OH· → CH$_3$-SO$_3$H	5.00E-11	(Yin et al., 1990)

d. CH$_3$(O)S(O)OO reactions

36	CH$_3$(O)S(O)OO·+ NO → CH$_3$-SO$_3$·+ NO$_2$	1.00E-11	(Yin et al., 1990)

37	$CH_3(O)S(O)OO\cdot + NO_2 \rightarrow CH_3(O)S(O)OONO_2$	1.00E-12	(Yin et al., 1990)
38	$CH_3(O)S(O)OONO_2 \rightarrow CH_3(O)S(O)OO\cdot + NO_2$	4.20E-03	(Yin et al., 1990)
39	$CH_3(O)S(O)OO\cdot + CH_3\text{-}S\cdot \rightarrow CH_3\text{-}SO_3\cdot + CH_3\text{-}SO\cdot$	6.00E-11	(Yin et al., 1990)
40	$CH_3(O)S(O)OO\cdot + CH_3\text{-}SO\cdot \rightarrow CH_3\text{-}SO_3\cdot + CH_3(O)S(O)\cdot$	8.00E-12	(Yin et al., 1990)
41	$CH_3(O)S(O)OO\cdot + CH_3(O)S(O)\cdot \rightarrow 2\ CH_3\text{-}SO_3\cdot$	3.00E-13	(Yin et al., 1990)
42	$CH_3(O)S(O)OO\cdot + HO_2\cdot \rightarrow CH_3(O)S(O)OOH\cdot + O_2$	2.00E-12	(Yin et al., 1990)
43	$CH_3(O)S(O)OO\cdot + CH_3\text{-}O_2 \rightarrow CH_3\text{-}SO_3 + CH_3\text{-}O\cdot + O_2$	5.50E-12	(Yin et al., 1990)
44	$CH_3(O)S(O)OO\cdot + CH_3(O)S(O)OO\cdot + CH_3\text{-}SO\cdot \rightarrow 2\ CH_3\text{-}SO_3\cdot + O_2$	6.00E-12	(Yin et al., 1990)
45	$CH_3(O)S(O)OO\cdot + CH_3\text{-}S\text{-}OH \rightarrow CH_3(O)S(O)OOH\cdot + CH_3\text{-}SO.$	4.00E-13	(Yin et al., 1990)

e. $CH_3\text{-}SO_3\cdot$ reactions

46	$CH_3\text{-}SO_3\cdot \rightarrow SO_3 + CH_3\cdot$	4.00E-02	Estimate
47	$CH_3\text{-}SO_3\cdot + H\text{-}CO\text{-}H \rightarrow CH_3\text{-}SO_3H + HO_2\cdot + CO$	1.60E-15	(Yin et al., 1990)
48	$CH_3\text{-}SO_3\cdot + HO_2 \rightarrow CH_3\text{-}SO_3H + O_2$	5.00E-11	(Yin et al., 1990)
49	$CH_3\text{-}SO_3\cdot + HONO \rightarrow CH_3\text{-}SO_3H + NO_2$	6.60E-16	(Yin et al., 1990)
50	$CH_3\text{-}SO_3\cdot + H_2O_2 \rightarrow CH_3\text{-}SO_3H + HO_2\cdot$	3.00E-16	(Yin et al., 1990)
51	$CH_3\text{-}SO_3\cdot + CH_3\text{-}OOH \rightarrow CH_3\text{-}SO_3H + CH_3\text{-}O_2\cdot$	3.00E-16	(Yin et al., 1990)
52	$CH_3\text{-}SO_3\cdot + CH_3\text{-}OH \rightarrow CH_3\text{-}SO_3H + H\text{-}CO\text{-}H + HO_2\cdot$	1.00E-16	(Yin et al., 1990)
53	$CH_3\text{-}SO_3\cdot + NO_2 \rightarrow CH_3(O)S(O)ONO_2$	3.00E-15	(Yin et al., 1990)
54	$CH_3(O)S(O)ONO_2 + H_2O \rightarrow CH_3\text{-}SO_3H + HNO_3$	1.00E-15	(Yin et al., 1990)
55	$CH_3\text{-}SO_3 + NO \rightarrow CH_3(O)S(O)ONO$	3.00E-15	(Yin et al., 1990)
56	$CH_3(O)S(O)ONO + H_2O \rightarrow CH_3\text{-}SO_3H + HONO$	1.00E-15	(Yin et al., 1990)

Wall loss

57	$CH_3\text{-}S(O)CH_3 \rightarrow$	6.00E-05	Experiment
58	$CH_3(O)S(O)CH_3 \rightarrow$	7.00E-05	Experiment

TABLE S2. DMS photooxidation mechanisms

DMS Reaction	Rate constant [a]	Note
Initial reactions		
59 CH_3-S-CH_3 + OH· → CH_3-S-CH_2·+ H_2O	1.13E-11exp(-254/T)	(Atkinson et al., 1997)
60 CH_3-S-CH_3 + OH + M → CH_3-S(OH)CH_3+ M	1.70E-12	(Atkinson et al., 1989)
61 CH_3-S-CH_3 + O^3P → CH_3-SO·+ CH_3·	5E-11exp(0.0409/T)	(Atkinson et al., 1989; Cvetanovic et al., 1981; Nip et al., 1981)
62 CH_3-S-CH_3 + NO_3 →CH_3-S(ONO_2)CH_3	1.4E-13exp(500/T)	(Atkinson et al., 1989; Nip et al., 1981)
63 CH_3-S-CH_3 + NO_2 →CH_3-S(O)CH_3+ NO	9.00E-21	(Balla and Heicklen, 1984)
Primary products		
64 CH_3-S(OH)CH_3+ O_2 → CH_3-S(O)CH_3+ HO_2·	1.30E-12	(Barone et al., 1996)
65 CH_3-S(OH)CH_3 → CH_3-S-OH + CH_3·	5.00E+05	(Yin et al., 1990)
66 CH_3-S(OH)CH_3+ O_2 → CH_3-S(OH)(OO)CH_3	1.00E-12	(Yin et al., 1990)
67 CH_3-S-CH_2·+ O_2 → CH_3-S-CH_2-OO·	7.30E-13	(Schafer et al., 1978)
68 CH_3-S-CH_2·+ NO_3 → CH_3-S-CH_2-OO·+ NO	3.00E-10	(Sander, 2006)
69 CH_3-S(ONO_2)CH_3 → CH_3-S-CH_2·+ HNO_3	1.00E+02	(Yin et al., 1990)
Secondary products		
a. DMSO		
b. Methylthiomethylperoxyl radical $CH_3SCH_2O_2$·		
70 CH_3-S-CH_2-OO·+ NO → CH_3-S-CH_2O·+ NO_2	1.90E-11	(Nielsen et al., 1995)
71 CH_3-S-CH_2-OO·+ CH_3-S-CH_2-OO· → 2CH_3-S-CH_2O·+ O_2	8.60E-14	(Wallington et al., 1986)
72 CH_3-S-CH_2-OO·+ HO_2· → CH_3-S-CH_2-OOH	5.00E-12	(Nielsen et al., 1995)
73 CH_3-S-CH_2-OO·+ CH_3-S· → CH_3-S-CH_2O·+ CH_3-SO·	6.10E-11	(Yin et al., 1990)
74 CH_3-S-CH_2-OO·+ CH_3-SO· → CH_3-S-CH_2O·+ CH_3(O)S(O)·.	4.00E-12	(Yin et al., 1990)
75 CH_3-S-CH_2-OO·+ CH_3(O)S(O)· → CH_3-S-CH_2O·+ CH_3-SO_3·	2.50E-13	(Yin et al., 1990)
76 CH_3-S-CH_2-OO·+ CH_3-O_2· → CH_3-S-CH_2O·+ CH_3-O·+ O_2	1.80E-13	(Yin et al., 1990)

[a]The unit for first order reactions is s^{-1} and the unit for second order reactions is s^{-1} molecules^{-1} cm^3

77	CH_3-S-CH_2-OO·+ NO_2+ M → CH_3-S-CH_2-OONO$_2$·+ M	9.20E-12	(Nielsen et al., 1995)

c. CH_3-S(OH)(OO·)-CH_3

78	CH_3-S(OH)(OO·)CH_3 →CH_3-S(O)CH_3+ HO_2·	1.00E+01	(Yin et al., 1990)
79	CH_3-S(OH)(OO·)CH_3+ NO → CH_3-S(OH)(O)CH_3+ NO_2	5.00E-12	(Yin et al., 1990)

d. CH_3-S-OH

80	CH_3-S-OH + OH → CH_3-SO·+ H_2O	1.10E-10	(Yin et al., 1990)
81	CH_3-S-OH + CH_3-SO$_3$· → CH_3-SO·+ CH_3-SO$_3$H	3.40E-12	(Yin et al., 1990)
82	CH_3-S-OH + CH_3-O· → CH_3-SO·+ CH_3-OH	3.40E-12	(Yin et al., 1990)
83	CH_3-S-OH + O^{3}P → CH_3-SO·+ OH	3.40E-12	(Yin et al., 1990)
84	CH_3-S-OH + NO_3 → CH_3-SO·+ HNO$_3$	3.40E-12	(Yin et al., 1990)
85	CH_3-S-OH + HO_2 → CH_3-SO·+ H_2O_2	8.50E-13	(Yin et al., 1990)
86	CH_3-S-OH + CH_3-O$_2$· → CH_3-SO·+ CH_3-OOH	8.50E-13	(Yin et al., 1990)
87	CH_3-S-OH+CH_3-S-OH → CH_3-S-S(O)CH_3·+ H_2O	3.60E-18	(Yin et al., 1990)

Tertiary products

a. CH_3S(O)OH

(DMSO reactions)

b. CH_3-S-CH_2O·

88	CH_3-S-CH_2O· → CH_3-S·+ H-CO-H	2.00E+01	(Yin et al., 1990)

c. CH_3-S(OH)(O)CH_3 (DMSO reactions)

d. CH_3(O)S(O)CH_3 and its further reactions

(DMSO reactions)

Further products

a. CH_3-S· reactions

89	CH_3-S·+ O_2 → CH_3-SOO·	5.80E-17	(Sander, 2006)
90	CH_3-SOO· → CH_3-S·+ O_2	6.00E+02	(Yin et al., 1990)
91	CH_3-S·+ O_3 → CH_3-SO·+ O_2	5.70E-12	(Domine et al., 1992)

92	CH_3-S·+ NO_2 → CH_3-S-NO_2·	6.10E-13	(Yin et al., 1990)
93	CH_3-S·+ NO_2 → CH_3-SO·+ NO	6.10E-11	(Yin et al., 1990)
94	CH_3-S·+ NO → CH_3-S-NO·	2.87E-11	(Balla et al., 1986)
95	CH_3-S·+ NO_3· → CH_3-SO·+ NO_2	6.40E-11	(Yin et al., 1990)
96	CH_3-S·+ HO_2· → CH_3-SO·+ OH	3.00E-11	(Yin et al., 1990)
97	CH_3-S·+ CH_3-O_2 → CH_3-SO·+ CH_3-O·	6.10E-11	(Yin et al., 1990)
98	CH_3-S·+ CH_3-S· → CH_3-S-S-CH_3	4.15E-11	(Graham et al., 1964)
99	CH_3-S·+ CH_3-S-NO· → CH_3-S-S-CH_3+ NO	1.40E-12	(Yin et al., 1990)
100	CH_3-S·+ OH· → CH_3-S-OH	5.00E-11	(Yin et al., 1990)
101	CH_3-S-NO·+ hυ → CH_3-S·+ NO	0.5*j[NO_2_to_O^{3}P]	(Yin et al., 1990)
102	CH_3-S+ O_3 → SO_2+ CH_3-O·	5.70E-12	(Domine et al., 1992)
103	CH_3-S+ CH_3-S-CH_3 +(O_2) →CH_3+CH_3-S(O)CH_3+ SO·	8.00E-12	(Barnes, 1986)
b. CH$_3$SOO· reactions			
104	CH_3-SOO·+ NO → CH_3-SO·+ NO_2	1.10E-11	(Turnipseed et al., 1992)
105	CH_3-SOO·+ CH_3-S· → 2CH_3-SO·	8.00E-11	(Yin et al., 1990)
106	CH_3-SOO·+ CH_3-SO· → CH_3-SO·+ CH_3(O)S(O)·	9.00E-12	(Yin et al., 1990)
107	CH_3-SOO·+ CH_3(O)S(O)· → CH_3-SO·+CH_3-SO_3·	3.00E-13	(Yin et al., 1990)
108	CH_3-SOO·+ HO_2· → CH_3-SOOH + O_2	4.00E-12	(Yin et al., 1990)
109	CH_3-SOO·+ CH_3-O_2· → CH_3-SO·+ CH_3-O·+ O_2	5.50E-12	(Yin et al., 1990)
110	CH_3-SOO·+ CH_3-SOO· → 2 CH_3-SO·+O_2	6.00E-12	(Yin et al., 1990)
c. CH$_3$SO· reactions			
111	CH_3-SO·+ O_2 → CH_3-S(O)OO·	7.70E-18	(Yin et al., 1990)
112	CH_3-S(O)OO· →CH_3-SO·+ O_2	1.70E+02	(Yin et al., 1990)
113	CH_3-SO·+ NO_2 → CH_3(O)S(O)·+ NO	3.00E-12	MCM v3.2
114	CH_3-SO·+ NO_2 → CH_3·+ NO + SO_2	3.00E-12	MCM v3.2

115	CH_3-SO· → SO·+ CH_3·	2.66E32exp(-25200/T)	(Yin et al., 1990)
116	CH_3-SO·+ NO_3· → $CH_3(O)S(O)$·+ NO_2	8.00E-12	(Yin et al., 1990)
117	CH_3-SO·+ O_3 → $CH_3(O)S(O)$·+ O_2	1.00E-12	(Tyndall and Ravishankara, 1989)
118	CH_3-SO·+ HO_2 → $CH_3(O)S(O)$·+ OH	1.50E-12	(Yin et al., 1990)
119	CH_3-SO·+ CH_3-SO. → CH_3-S·+$CH_3(O)S(O)$·	7.50E-12	(Yin et al., 1990)
120	CH_3-SO·+ CH_3-O_2 → $CH_3(O)S(O)$·+ CH_3-O·	3.00E-12	(Yin et al., 1990)
121	CH_3-SO·+ CH_3-S-NO· → CH_3-S-S(O)CH_3·+ NO	6.80E-13	(Yin et al., 1990)
122	CH_3-SO·+ OH → CH_3-S(O)OH	5.00E-11	(Yin et al., 1990)
123	CH_3-SO·+ O_3 → SO_2+ CH_3-O_2	3.20E-13	(Borissenko et al., 2003)

d. $CH_3(O)S(O)$ · reactions (DMSO reactions)

e. CH_3-S(O)OO· reactions

124	CH_3-S(O)OO·+ NO → $CH_3(O)S(O)$·+ NO_2	8.00E-12	(Yin et al., 1990)
125	CH_3-S(O)OO·+ CH_3-S· → $CH_3(O)S(O)$·+ CH_3-SO·	7.00E-11	(Yin et al., 1990)
126	CH_3-S(O)OO·+ CH_3-SO· → 2$CH_3(O)S(O)$·	8.10E-12	(Yin et al., 1990)
127	CH_3-S(O)OO·+ $CH_3(O)S(O)$· → $CH_3(O)S(O)$+ CH_3-SO_3	3.00E-13	(Yin et al., 1990)
128	CH_3-S(O)OO·+ CH_3-O_2· → $CH_3(O)S(O)$·+ CH_3-O·+O_2	5.50E-12	(Yin et al., 1990)
129	CH_3-S(O)OO·+CH_3-S(O)OO· → 2$CH_3(O)S(O)$·+ O_2	6.00E-12	(Yin et al., 1990)
130	CH_3-S(O)OO·+ NO_2 → CH_3-S(O)OONO_2	1.00E-12	(Yin et al., 1990)
131	CH_3-S(O)OONO_2 → CH_3-S(O)OO·+ NO_2	4.20E-03	(Yin et al., 1990)

f. $CH_3(O)S(O)OO$· reactions

g. CH_3-SO_3 reactions

132	CH_3-SO_3·+ CH_3-S-CH_3 → CH_3-SO_3H + CH_3-S-CH_2·	6.80E-13	(Yin et al., 1990)

h.CH_3SONO_2 reactions

133	CH_3-S(O)NO_2· → CH_3-SO·+ NO_2	1.00	(Yin et al., 1990)

i.CH_3· reactions

(DMSO reactions)

Table S2 (cont'd)

j.CH_3-S(O)CH_2· and its futher reactions

134	CH_3-S(O)CH_2· → CH_3-S·+ H-CO-H	1.00E+03	(Yin et al., 1990)
135	CH_3-S(O)CH_2·+ O_2 → CH_3-S(O)CH_2OO·	1.00E-12	(Yin et al., 1990)
136	CH_3-S(O)CH_2OO·+ NO → CH_3-S(O)CH_2O·+ NO_2	6.00E-12	(Yin et al., 1990)
137	CH_3-S(O)CH_2OO·+ CH_3-S· → CH_3-SO·+ CH_3-S(O)CH_2O·	5.00E-11	(Yin et al., 1990)
138	CH_3-S(O)CH_2OO·+ CH_3-SO· → CH_3(O)S(O)·+ CH_3-S(O)CH_2O·	4.00E-12	(Yin et al., 1990)
139	CH_3-S(O)CH_2OO·+ CH_3(O)S(O)· → CH_3-SO_3·+ CH_3-S(O)CH_2O·	2.50E-13	(Yin et al., 1990)
140	CH_3-S(O)CH_2OO·+ HO_2 → O_2+ CH_3-S(O)CH_2OOH	1.50E-12	(Yin et al., 1990)
141	CH_3-S(O)CH_2OO·+ CH_3-O_2· → O_2+ CH_3-O·+ CH_3-S(O)CH_2O·	1.80E-13	(Yin et al., 1990)
142	CH_3-S(O)CH_2OO·+ CH_3-S(O)CH_2OO· → O_2+ 2CH_3-S(O)CH_2O·	8.60E-14	(Yin et al., 1990)
143	CH_3-S(O)CH_2O· → CH_3-SO·+ H-CO-H	1.00E+02	(Yin et al., 1990)

l.CH_3S-OH and CH_3S(O)OH reactions (DMSO reactions)

m.CH_3-S-S-CH_3 reactions

144	CH_3-S-S-CH_3+ OH· → CH_3-S-OH + CH_3-S·	5.59E-11exp(380/T)	(Atkinson et al., 1989)
145	CH_3-S-S-CH_3+ O^3P → CH_3-SO·+ CH_3-S·	5.62E-11exp(250/T)	(Atkinson et al., 1989; Cvetanovic et al., 1981; Nip et al., 1981)
146	CH_3-S-S-CH_3+ NO_3 → CH_3-S(ONO_2)S-CH_3	7.00E-13	(Yin et al., 1990)
147	CH_3-S(ONO_2)S-CH_3 → CH_3-S(O)NO_2·+ CH_3-S·	1.00E+02	(Yin et al., 1990)
148	CH_3-S-S-CH_3+ hυ → 2 CH_3-S·	5.0E-3*j[NO_2_to_O^3P]	(Yin et al., 1990)

wall loss

149	CH_3-S-CH_3 →	9.00E-06	Experiment
150	CH_3-S-S-CH_3 →	9.00E-06	Estimated

TABLE S3. SO$_2$ photooxidation mechanisms

	SO$_2$ Reactions	Rate constant [a]	Note
SO·reactions			
151	O$_2$+ SO· → SO$_2$+ O^{3}P·	1.39E-13exp(-2280/T)	(Atkinson et al., 1989)
152	NO$_2$+ SO· → SO$_2$+ NO	1.40E-11	(Atkinson et al., 1989)
153	O$_3$+ SO· → SO$_2$+ O$_2$	4.51E-12exp(-1170/T)	(Atkinson et al., 1989)
154	O^{3}P + SO· → SO$_2$	2.20E-11	(Graedel, 1977)
155	OH + SO· → SO$_2$+ HO$_2$	1.10E-10	(Graedel, 1977)
156	SO$_3$+ SO· → 2SO$_2$	2.00E-15	(Graedel, 1977)
SO$_2$ reactions			
157	O^{3}P+ SO$_2$ → SO$_3$	9.75E-13exp(-1000/T)	(Baulch et al., 1984; Kerr, 1984)
158	HO$_2$+ SO$_2$ → SO$_3$+ OH·	1.00E-18	(Atkinson et al., 1989; Atkinson and Lloyd, 1984)
159	CH$_3$-O$_2$·+ SO$_2$ → SO$_3$+ CH$_3$-O·	5.00E-17	(Atkinson et al., 1989; Atkinson and Lloyd, 1984)
160	CH$_3$-O·+ SO$_2$ → CH$_3$-O-SO$_2$·	5.50E-13	(Calvert, 1984)
161	CH$_3$·+ SO$_2$ → CH$_3$(O)S(O)·	2.90E-13	(Graedel, 1977)
162	SO$_2$+ hυ → SO$_2^*$	2*j[NO$_2$_to_O^{3}P]	(Graedel, 1977)
163	OH·+ SO$_2$ → HOSO$_2$	9.07E-13exp (231/T)	(Atkinson et al., 1989; Kerr, 1984)
164	NO$_2$+ SO$_2$ → NO + SO$_3$	2.00E-26	(Sander, 2006)
165	NO$_3$+ SO$_2$ → SO$_3$+ NO$_2$	7.00E-21	(Sander, 2006)
SO$_2^*$ reactions			
166	SO$_2^*$→ SO$_2$	3.70E+06	(Graedel, 1977)
167	SO$_2^*$+ SO$_2$ → SO+ SO$_3$	6.30E-13	(Graedel, 1977)
168	SO$_2^*$+ CO → SO+ CO$_2$	1.10E-14	(Graedel, 1977)
169	HOSO$_2$+ O$_2$ → HO$_2$+ SO$_3$	4.00E-13	(Atkinson et al., 1989; Kerr, 1984)
170	HOSO$_2$+ OH·+ M → H$_2$SO$_4$+ M	1.00E-11	(Graedel, 1979)

[a]The unit for first order reactions is s^{-1} and the unit for second order reactions is s^{-1} molecules^{-1} cm^3

SO$_3$ reactions

171	SO$_3$+ H$_2$O + M $\rightarrow$ H$_2$SO$_4$+ M	9.10E-13	(Atkinson and Lloyd, 1984; Kerr, 1984)
172	SO$_3$+ O(^{3}P) $\rightarrow$ SO$_2$+ O$_2$	7.00E-13	(Calvert et al., 1978)

wall loss

173	SO$_2$ $\rightarrow$	7.00E-06	Experiment

TABLE S4. Comparison of the wall loss rates of different chemicals in this study and those in literature

chemical	wall loss rate	
	in this study	in literature
DMS	9.0×10^{-6}	1.5×10^{-6} (Yin et al., 1990)
SO_2	2.0×10^{-5}	2.2×10^{-6} (Yin et al., 1990)
O_3	2.5×10^{-5}	4.5×10^{-6} (Yin et al., 1990)
DMSO	6.0×10^{-5}	3.3×10^{-5}(Ballesteros et al., 2002)
$DMSO_2$	7.0×10^{-5}	4.4×10^{-5}(Ballesteros et al., 2002)
H_2O_2	6.7×10^{-4}	2.4×10^{-4}(Qi et al., 2007)

TABLE S5. Integrated reaction rate (IRR) of the initial reactions of DMS decay in different conditions [a]

No.[b]	Reaction	iso-DMS-1	iso-DMS-2	iso-DMS-3
59	CH_3-S-CH_3 + OH·	1.75	1.35	1.71
60	CH_3-S-CH_3 + OH·	0.61	0.48	0.6
61	CH_3-S-CH_3 + O(^{3}P)	1.18	1.62	2.37
62	CH_3-S-CH_3 + NO_3·	0.77	1.13	0.93
63	CH_3-S-CH_3 + NO_2	0.01	0.01	0.01
103	CH_3-S·+ CH_3-S-CH_3	0.96	0.96	1.26
132	CH_3-S-CH_3 + CH_3-SO_3·	0.51	0.49	0.47

[a]Refer to Table 3 for the experimental conditions.
[b]Refer to Table S2 for the reaction number
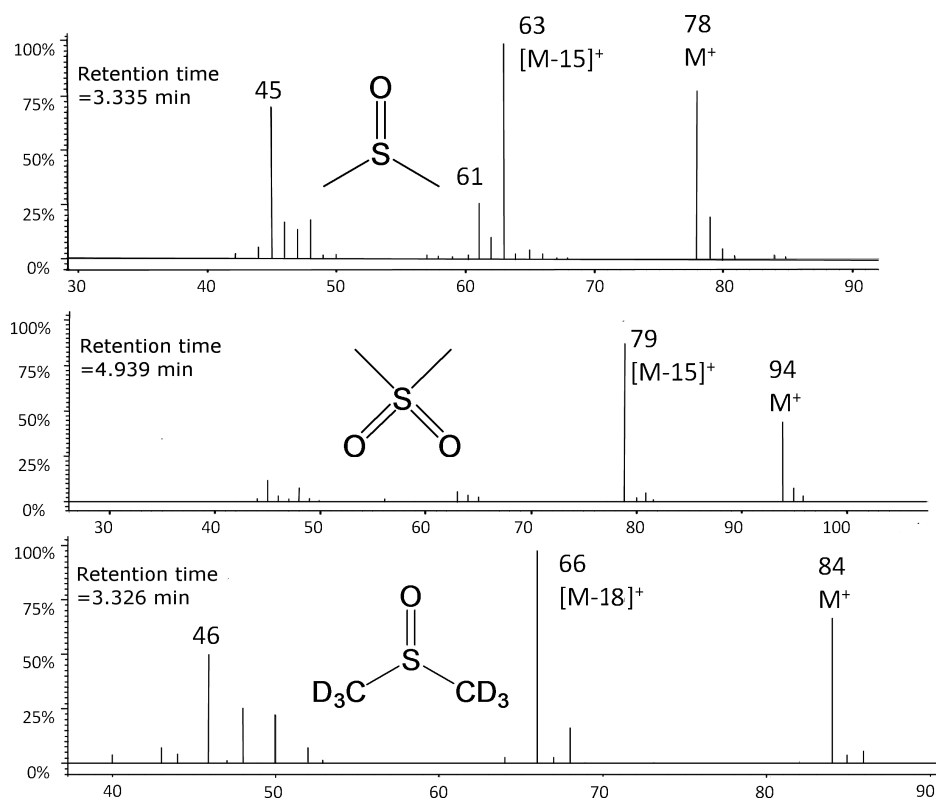
FIGURE S1. Mass fragmentation spectra in the EI mode (with GC retention time) for d_6-DMSO, DMSO and $DMSO_2$

(A) Profiles of DMSO, DMSO$_2$ and SO$_2$ **(B) Profiles of NO, NO$_2$ and O$_3$**
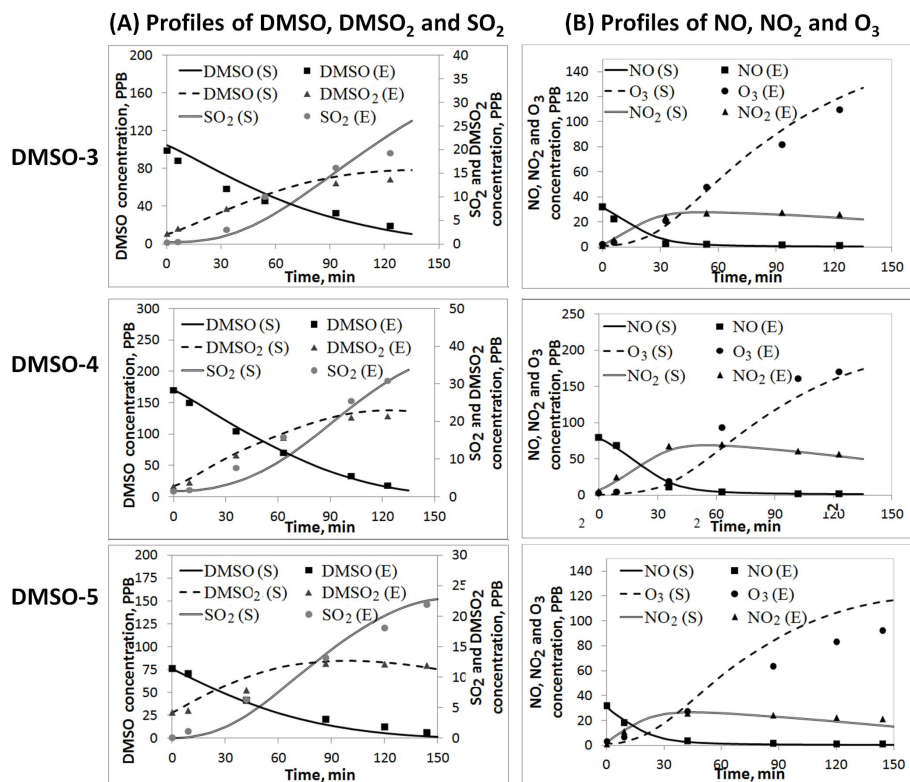
FIGURE S2. The time profiles of DMSO, DMSO$_2$, SO$_2$, NO$_x$ and O$_3$ for the photooxidation of DMSO in the presence of NO$_x$ (Exp DMSO-3, Exp DMSO-4 and Exp DMSO-5 in Table 1). "E" denotes the experimentally observed concentrations of chemical species and "S" for those simulated using the kinetic model.

Profiles of MSA and H$_2$SO$_4$
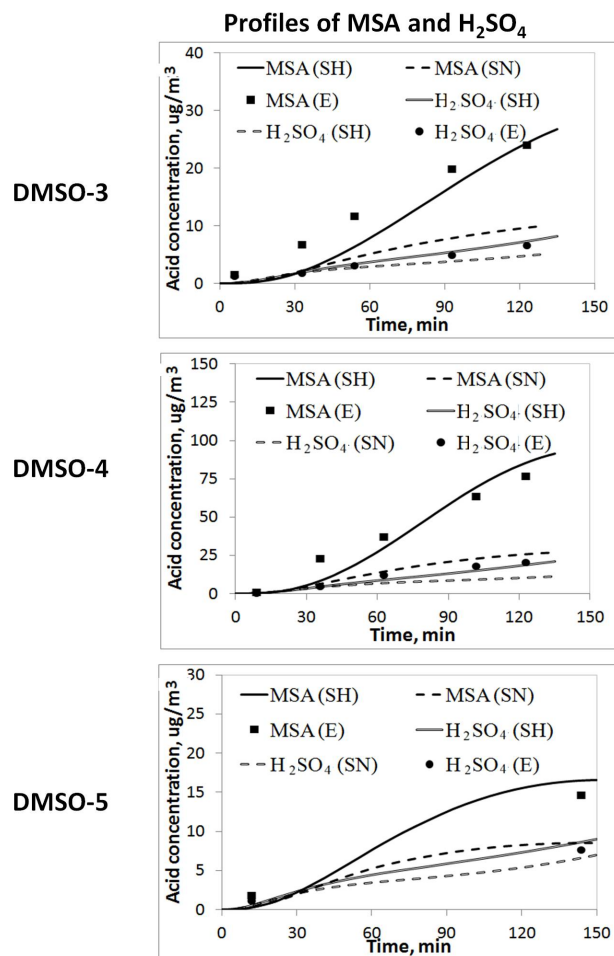
FIGURE S3. Model simulation of MSA and sulfuric acid for the photooxidation of DMSO in the presence of NO$_x$ (Exp DMSO-3, Exp DMSO-4 and Exp DMSO-5 in Table 1) with (SH) and without (SN) including heterogeneous reactionS "E" denotes the experimentally observed concentrations of chemical species and "S" for those simulated using the kinetic model.

(A) Profiles of DMS, DMSO$_2$ and SO$_2$ **(B) Profiles of NO, NO$_2$ and O$_3$**
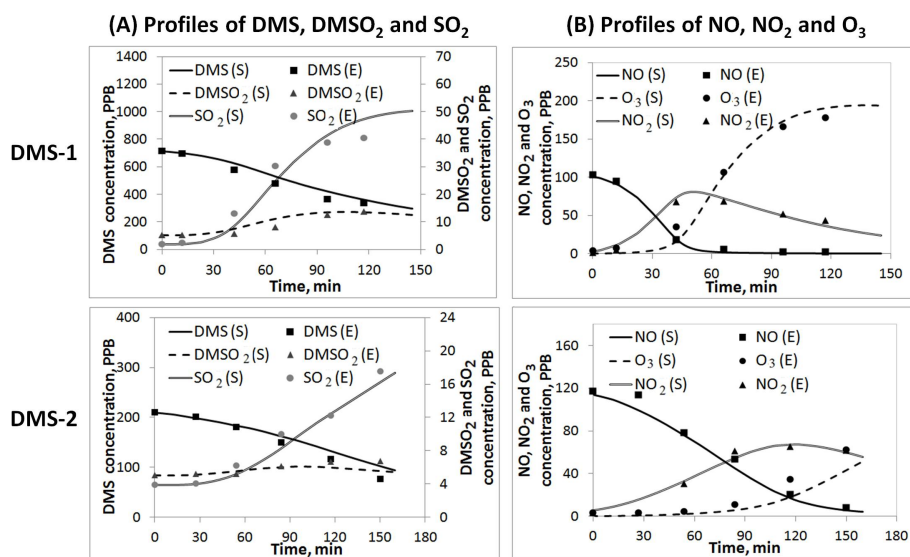
FIGURE S4. The time profiles of DMS, DMSO$_2$, SO$_2$, MSA, sulfuric acid, NO$_x$ and O$_3$ for the photooxidation of DMSO in the presence of NO$_x$ (Exp DMS-1 and Exp DMS-2 in Table 1). "E" denotes the experimentally observed concentrations of chemical species and "S" for those simulated using the kinetic model.
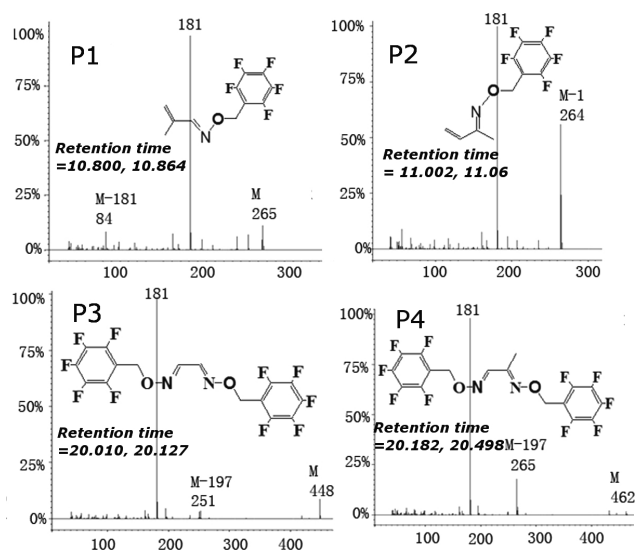
FIGURE S5. Mass fragmentation spectra in the EI mode (with GC retention time) for PFBHA derivatives of major carbonyl products originated from isoprene photooxidation in the presence of NO_x. P1: methacrolein (mono-derivatives), P2: methyl vinyl ketone (mono-derivatives), P3: glyoxal (di-derivatives), P4: methylglyoxal (di-derivatives)

(A) Profiles of isoprene, P1, P2, P3 and P4   **(B) Profiles of NO, NO$_2$ and O$_3$**
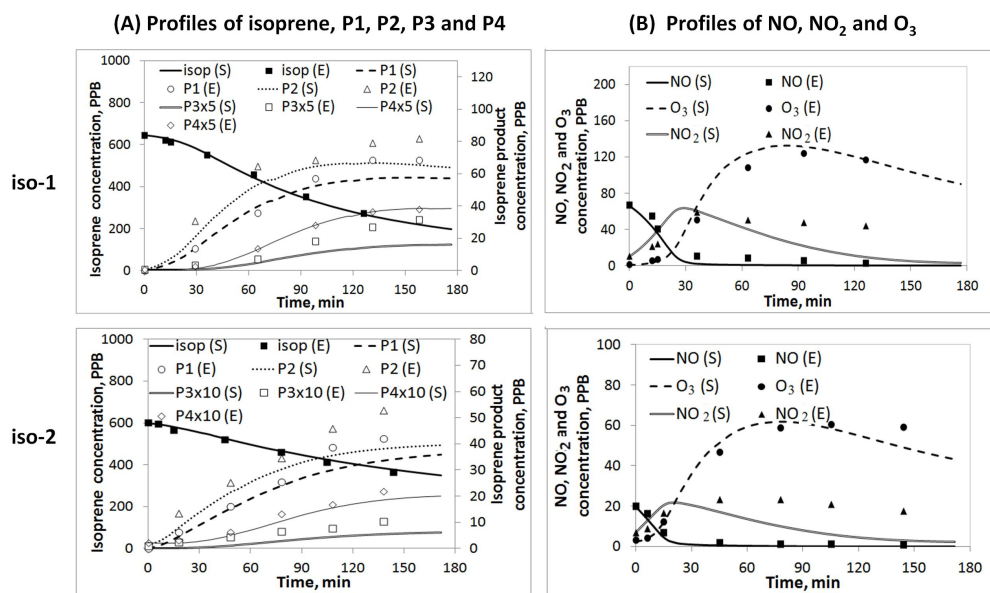
iso-1

iso-2

FIGURE S6. The time profiles of isoprene, P1–P4, NO$_x$ and O$_3$ from the photooxidation of isoprene in the presence of NO$_x$ (Exp iso-1 and Exp iso-2 in Table 2). "E" denotes the experimentally observed concentrations of chemical species and "S" for those simulated using the kinetic model.

FIGURE S7. The time profiles of gaseous products (P1–P4), NO_x and O_3 from the photooxidation of DMS and NO_x in the presence of 560 ppb of isoprene (Exp iso-DMS-1), 1360 ppb of isoprene (Exp iso-DMS-2) and 2248 ppb of isoprene (Exp iso-DMS-3). "E" denotes the experimentally observed concentrations of chemical species and "S" for those simulated using the kinetic model.
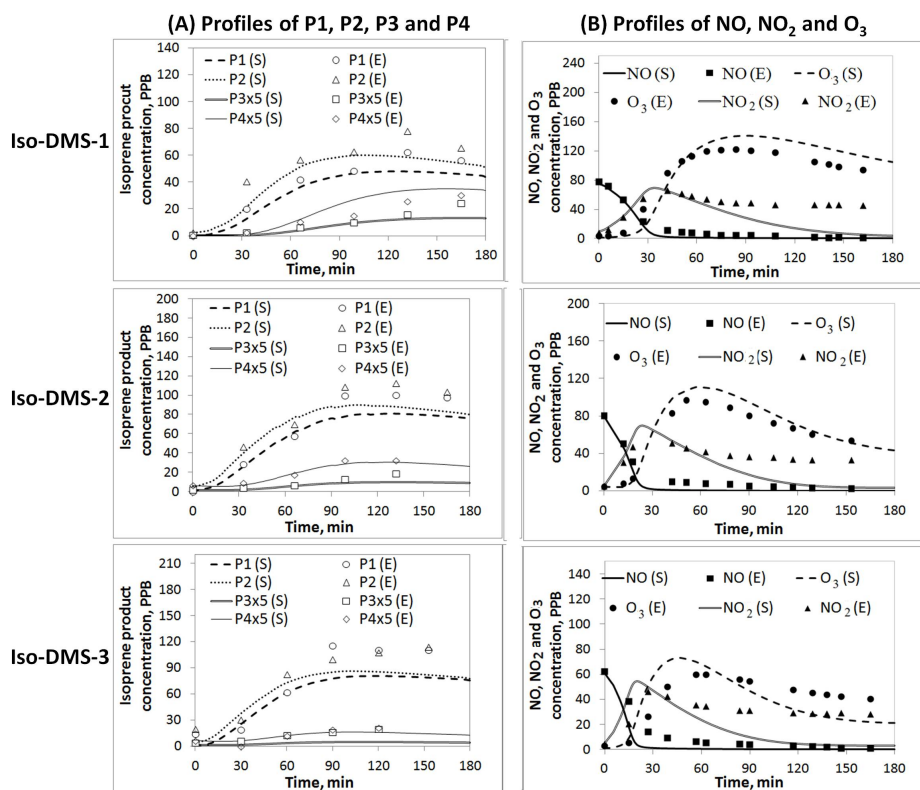
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