Impacts of aerosols on the chemistry of atmospheric trace gases: a case study of peroxides and HO_2 radicals

H. Liang[1], Z. M. Chen[1], D. Huang[1], Y. Zhao[1] and Z. Y. Li[1,2]

[1]State Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

[2]School of Earth and Space Sciences, Peking University, Beijing 100871, China

Correspondence to: Z. M. Chen (zmchen@pku.edu.cn)

Supplementary material

Equation S1. Relationship between bulk and surface concentration of HO_2

Table S1. Aerosol aqueous phase reactions extended in the box model calculation

Table S2. Sensitivity of HO_x and H_2O_2 concentration to aerosol optical depth (AOD).

Fig.S1. Dependence of j-values on aerosol optical depth (AOD).

Equation S1. Relationship between bulk and surface concentration of HO_2

The relationship between bulk and surface concentration of HO_2 could be expresses by the following equation (Mao et al., 2013):

$$[\mathrm{HO_2}]_{surf} = \frac{P_{\mathrm{HO_2}}}{k^I} + \left([\mathrm{HO_2}]_{bulk} - \frac{P_{\mathrm{HO_2}}}{k^I}\right) \cdot [3(\frac{\coth q}{q} - \frac{1}{q^2})]^{-1} \quad \text{(S1)}$$

where k^I is the first-order loss constant of HO_2, P_{HO2} is the aqueous-phase production rate of HO_2, and $q = a\ (k^I/D_{aq})^{1/2}$ is the diffuso-reactive parameter, in which a is the radius of the particles, D_{aq} is the HO_2 aqueous phase diffusion constant. According to this correction, the surface concentration is 100% to 180% of the bulk concentration, depending on the radius of the particles and the concentrations of TMI.

Table S1. Aerosol aqueous phase reactions extended in the box model calculation.

NO.[1]	Reactions	k_{298}	Ea/R
R1	$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH + OH^-$	7.0×10^{1}	5050
R2	$H_2O_2 + FeO^{2+} \rightarrow Fe^{3+} + HO_2 + OH^-$	9.5×10^{3}	2800
R3	$H_2O_2 + Fe(OH)^+ \rightarrow Fe(OH)^{2+} + OH + OH^-$	1.9×10^{6}	6200
R4	$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2 + H^+$	2.0×10^{-3}	
R5	$H_2O_2 + Fe(OH)^{2+} \rightarrow Fe^{2+} + HO_2 + H_2O$	2.0×10^{-3}	
R6	$O_2^- + Fe^{2+} + 2H^+ \rightarrow H_2O_2 + Fe^{3+}$	1.0×10^{7}	
R7	$O_2^- + Fe^{3+} \rightarrow Fe^{2+} + O_2$	1.5×10^{8}	
R8	$O_2^- + Fe(OH)^{2+} \rightarrow Fe^{2+} + O_2 + OH^-$	1.5×10^{8}	
R9	$O_2^- + Fe(OH)_2^+ \rightarrow Fe^{2+} + O_2 + 2OH^-$	1.5×10^{8}	
R10	$HO_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2O_2$	1.2×10^{6}	5050
R11	$HO_2 + FeO^{2+} \rightarrow Fe^{3+} + O_2 + OH^-$	2.0×10^{6}	
R12	$HO_2 + Fe(OH)^{2+} \rightarrow Fe^{2+} + O_2 + H_2O$	1.3×10^{5}	
R13	$OH + Fe^{2+} \rightarrow Fe(OH)^{2+}$	4.6×10^{8}	1100
R14	$OH + FeO^{2+} + H^+ \rightarrow Fe^{3+} + H_2O_2$	1.0×10^{7}	
R15	$O_3 + Fe^{2+} \rightarrow FeO^{2+} + O_2$	8.2×10^{5}	
R16	$FeO^{2+} + H_2O \rightarrow Fe^{3+} + OH + OH^-$	1.3×10^{-2}	4100
R17	$FeO^{2+} + Fe^{2+} + H_2O \rightarrow 2Fe^{3+} + 2OH^-$	7.2×10^{4}	842
R18	$Cl_2^- + Fe^{2+} \rightarrow Fe^{3+} + 2Cl^-$	1.0×10^{7}	3060
R19	$O_2^- + Fe(SO_4)^+ \rightarrow Fe^{2+} + SO_4^{2-} + O_2$	1.5×10^{8}	
R20	$HO_2 + Fe(SO_4)^+ \rightarrow Fe^{2+} + SO_4^{2-} + O_2 + H^+$	1.0×10^{3}	
R21	$Fe^{3+} + SO_4^{2-} \rightarrow Fe(SO_4)^+$	3.2×10^{3}	
R22	$Fe(SO_4)^+ \rightarrow Fe^{3+} + SO_4^{2-}$	2.7×10^{1}	
R23	$OH + Cu^+ \rightarrow Cu^{2+} + OH^-$	3.0×10^{9}	
R24	$O_2 + Cu^+ \rightarrow Cu^{2+} + O_2^-$	4.6×10^{5}	
R25	$H_2O_2 + Cu^+ \rightarrow Cu^{2+} + OH + OH^-$	7.0×10^{3}	
R26	$HO_2 + Cu^+ + H^+ \rightarrow Cu^{2+} + H_2O_2$	3.5×10^{9}	
R27	$O_2^- + Cu^+ + H^+ \rightarrow Cu^{2+} + H_2O_2$	9.4×10^{9}	
R28	$HO_2 + Cu^{2+} \rightarrow Cu^+ + O_2 + H^+$	1.0×10^{8}	
R29	$O_2^- + Cu^{2+} \rightarrow Cu^+ + O_2$	8.0×10^{9}	

R30	$HO_2 + CuSO_4 \rightarrow Cu^+ + O_2 + HSO_4^-$	1.0×10^7	
R31	$O_2^- + CuSO_4 \rightarrow Cu^+ + O_2 + SO_4^{2-}$	1.0×10^8	
R32	$Fe^{3+} + Cu^+ \rightarrow Cu^{2+} + Fe^{2+}$	1.3×10^7	
R33	$Fe(OH)^{2+} + Cu^+ \rightarrow Cu^{2+} + Fe^{2+} + OH^-$	3.0×10^7	
R34	$Fe(OH)^{2+} + Cu^+ \rightarrow Cu^{2+} + Fe^{2+} + 2OH^-$	1.3×10^7	
R35	$Fe(SO_4)^+ + Cu^+ \rightarrow Cu^{2+} + Fe^{2+} + SO_4^{2-}$	1.8×10^6	
R36	$OH + HO_2 \rightarrow H_2O + O_2$	7.0×10^9	
R37	$OH + O_2^- \rightarrow OH^- + O_2$	1.0×10^{10}	
R38	$OH + H_2O_2 \rightarrow H_2O + HO_2$	2.7×10^7	
R39	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	8.6×10^5	
R40	$HO_2 + O_2^- \rightarrow H_2O_2 + O_2 + OH^-$	1.0×10^8	
R41	$O_3 + O_2^- + H_2O \rightarrow OH + 2O_2 + OH^-$	1.5×10^9	
R42	$SO_2 + O_3 + H_2O \rightarrow HSO_4^- + O_2 + H^+$	2.4×10^4	
R43	$HSO_3^- + H_2O_2 + H^+ \rightarrow SO_4^{2-} + H_2O + 2H^+$	6.9×10^7	4000
R44	$HSO_3- + O_3 \rightarrow HSO_4^- + O_2$	3.7×10^5	5530
R45	$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$	1.5×10^9	5280
P1	$O_3 + H_2O \rightarrow H_2O_2 + O_2$	2.98×10^{-4}	
P2	$H_2O_2 \rightarrow 2OH$	4.81×10^{-6}	
P3	$Fe^{3+} + H_2O \rightarrow Fe^{2+} + OH + H^+$	6.41×10^{-6}	
P4	$Fe(OH)^{2+} \rightarrow Fe^{2+} + OH$	5.63×10^{-3}	
E1	$Fe^{2+} + H_2O \leftrightarrows Fe(OH)^+ + H^+$	3.22×10^{-10}	
E2	$Fe^{3+} + H_2O \leftrightarrows Fe(OH)^{2+} + H^+$	6.0×10^{-3}	
E3	$HO_2 \leftrightarrows O_2^- + H^+$	2.05×10^{-5}	
E4	$H_2O_2 \leftrightarrows HO_2^- + H^+$	1.6×10^{-12}	-3700
E5	$Cu^{2+} + SO_4^{2-} \leftrightarrows Cu(SO_4)$	2.3×10^2	
E6	$HSO_4^- \leftrightarrows SO_4^{2-} + H^+$	1.02×10^{-2}	-2700
E7	$HSO_3^- \leftrightarrows SO_3^{2-} + H^+$	6.22×10^{-8}	-1960

[1]R refers to reactions, P refers to photolysis, and E refers to equilibria.

Table S2. Sensitivity of HO_x and H_2O_2 concentration to aerosol optical depth (AOD).

AOD	OH (pptv)	HO_2 (pptv)	H_2O_2 (ppbv)
0	0.60	29.7	2.18
1	0.26	17.0	0.38
2	0.08	6.3	0.06
3	0.03	4.5	0.03
4	0.02	4.4	0.02
5	0.01	4.8	0.03

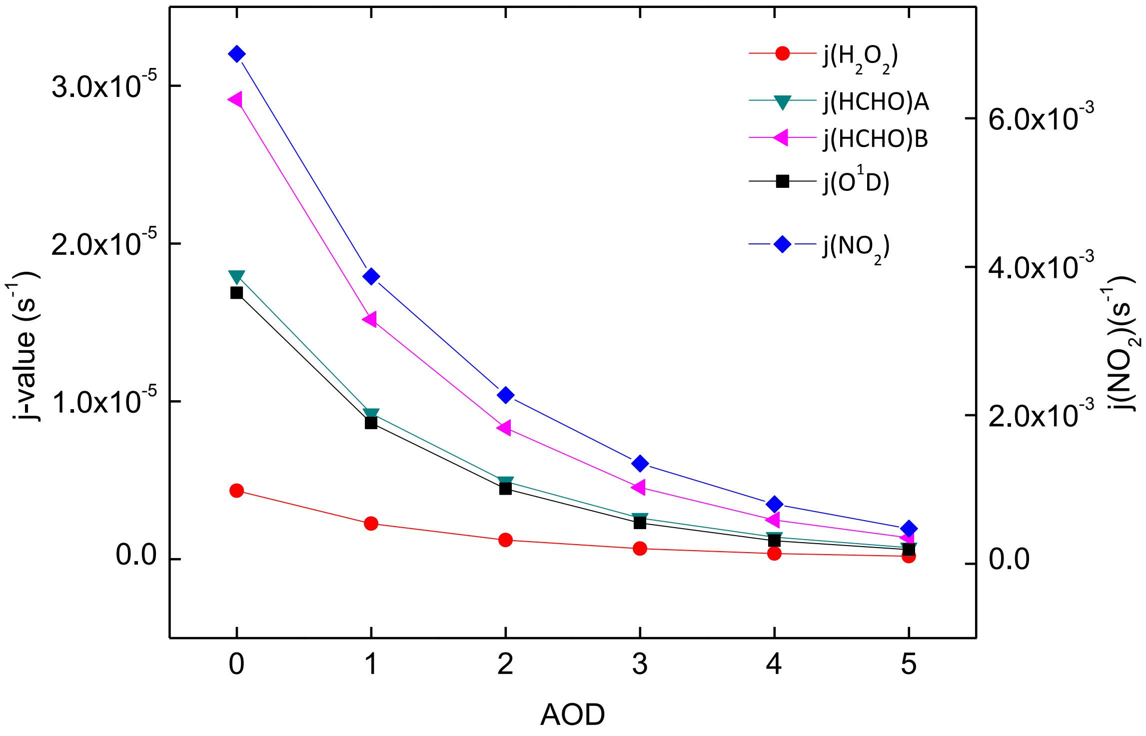

Fig. S1. Dependence of j-values on aerosol optical depth (AOD).

References

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