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Aqueous Reactions of Sulfate Radical-Anions with Nitrophenols in Atmospheric Context

Supporting Information

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Contents

1. Generation of sulfate radical-anions

Sulfate radical-anions were generation during autoxidation of sulfite anions catalyzed by Fe^{III} cations. The detailed mechanism of autoxidation was presented by Ziajka and Rudzinski [1]and is recalled here, in Table 0.

Table S1. Chain mechanism of S^{IV} autoxidation catalyzed by Fe^{III}.

Nr	Reaction	Rate constant, 25 ^{o}C M^{-1} s^{-1}	References
	Chain initiation		
1	$Fe^{III}OH + HSO_3^- \rightarrow Fe^{II} + SO_3^{\bullet-} + H_2O$	30	[2]
	Chain propagation		
2	$SO_3^{\bullet-} + O_2 \rightarrow SO_5^{\bullet-}$	1.5×10^9	[3]
3	$SO_5^{\bullet-} + HSO_3^- \rightarrow HSO_5^- + SO_3^{\bullet-}$	8.6×10^3, 2.5×10^4	[4,5]
4	$SO_5^{\bullet-} + HSO_3^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} + H^+$	3.6×10^2, 2.5×10^4	[4,5]
5	$SO_4^{\bullet-} + HSO_3^- \rightarrow SO_4^{2-} + SO_3^{\bullet-} + H^+$	3.1×10^8, 3.4×10^8, 2×10^9	[4-6]
6	$SO_5^{\bullet-} + SO_5^{\bullet-} \rightarrow SO_4^{\bullet-} + SO_4^{\bullet-} + O_2$	5.2×10^6, 2.2×10^8	[5,7,8]
	Formation of sulfate		
7	$HSO_5^- + HSO_3^- \rightarrow SO_4^{2-} + SO_4^{2-} + 2\,H^+$	7.14×10^6	[9]
	Regeneration of the initiator		
8	$SO_5^{\bullet-} + Fe^{II} \rightarrow SO_5^{2-} + Fe^{III}$	4.6×10^6, 3.2×10^6	[10,11]
9	$SO_5^{\bullet-} + Fe^{II} \rightarrow SO_4^{2-} + Fe^{III} (+ OH^-)$	3.6×10^4	[11]
10	$SO_4^{\bullet-} + Fe^{II} \rightarrow SO_4^{2-} + Fe^{III}$	3.5×10^7	[2]
11	$HSO_5^- + Fe^{II} \rightarrow SO_4^{\bullet-} + Fe^{III}(OH)$	3.4×10^4	[10]
	Termination		
12	$SO_3^{\bullet-} + SO_3^{\bullet-} \rightarrow S_2O_6^{2-}$	1.6×10^8	[5]
13	$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-}$	1.6×10^8, 4.6×10^8	[7,8,12]
14	$SO_5^{\bullet-} + SO_5^{\bullet-} \rightarrow S_2O_8^{2-} + O_2$	1.3×10^8, 4.8×10^7	[3,6,7]

2. Experimental results for 2-NP, 3-NP, 2,4-DNP and 2,4,6-TNP

Experimental runs with autoxidation of S(IV) in the presence of 2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 2,4-dinitrophenol (2,4-DNP) and 2,4,6-trinitrophenol (2,4,6-TNP). Plots in Figure S1 show consumption of oxygen in reacting solutions.

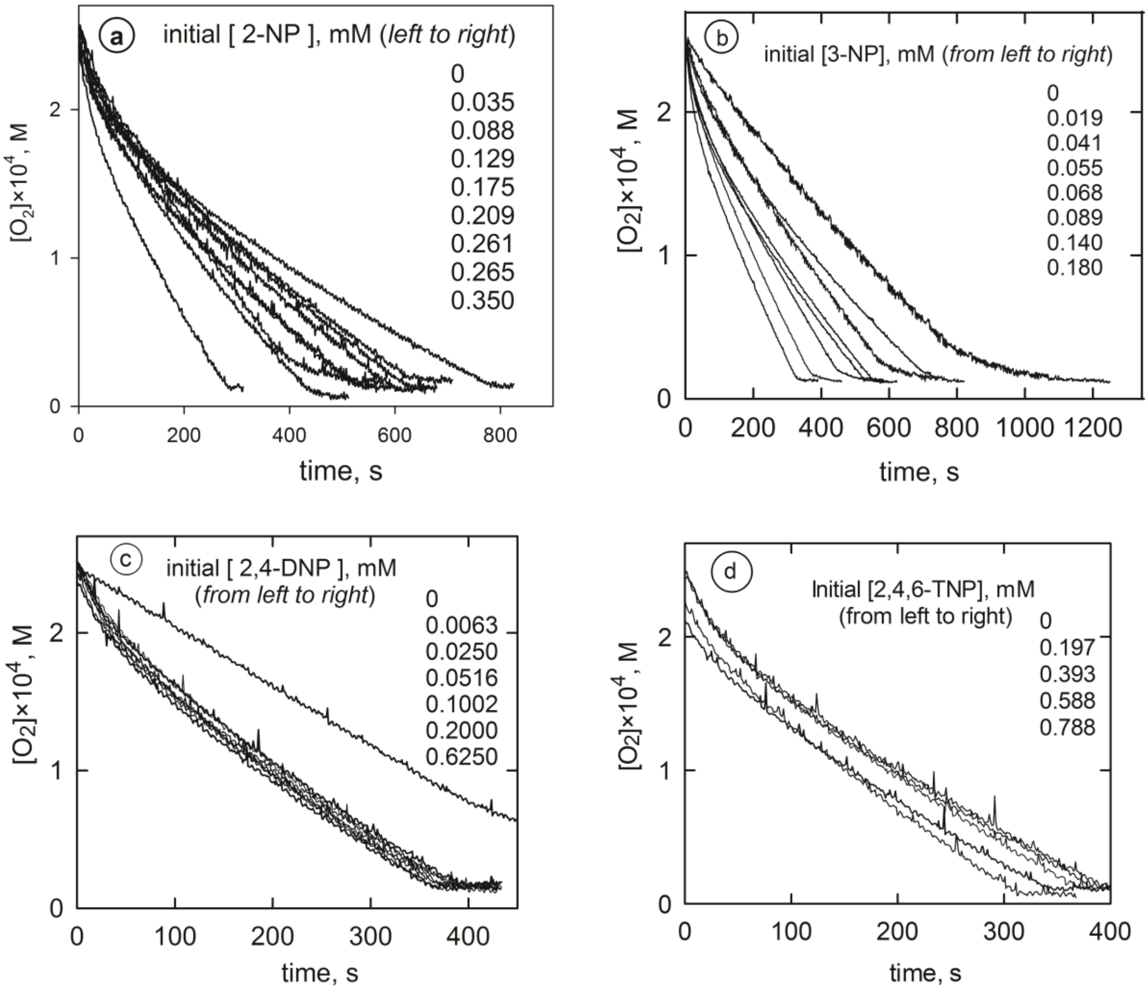

Fig. S1. Concentration of oxygen recorded during autoxidation of $NaHSO_3$ solution in the presence of: (a) 2-NP; (b) 3-NP; (c) 2,4-DNP and (d) 2,4,6-TNP at various initial concentrations.

Figure S2 shows the dependence of reciprocal rates of autoxidation on the initial concentrations of 2-NP, 3-NP, 2,4-DNP and 2,4,6-TNP. All dependencies are linear. The corresponding slopes of linear relations are given on the plots. The quasi-stationary rates of autoxidation were obtained from plots in Fig. S1.

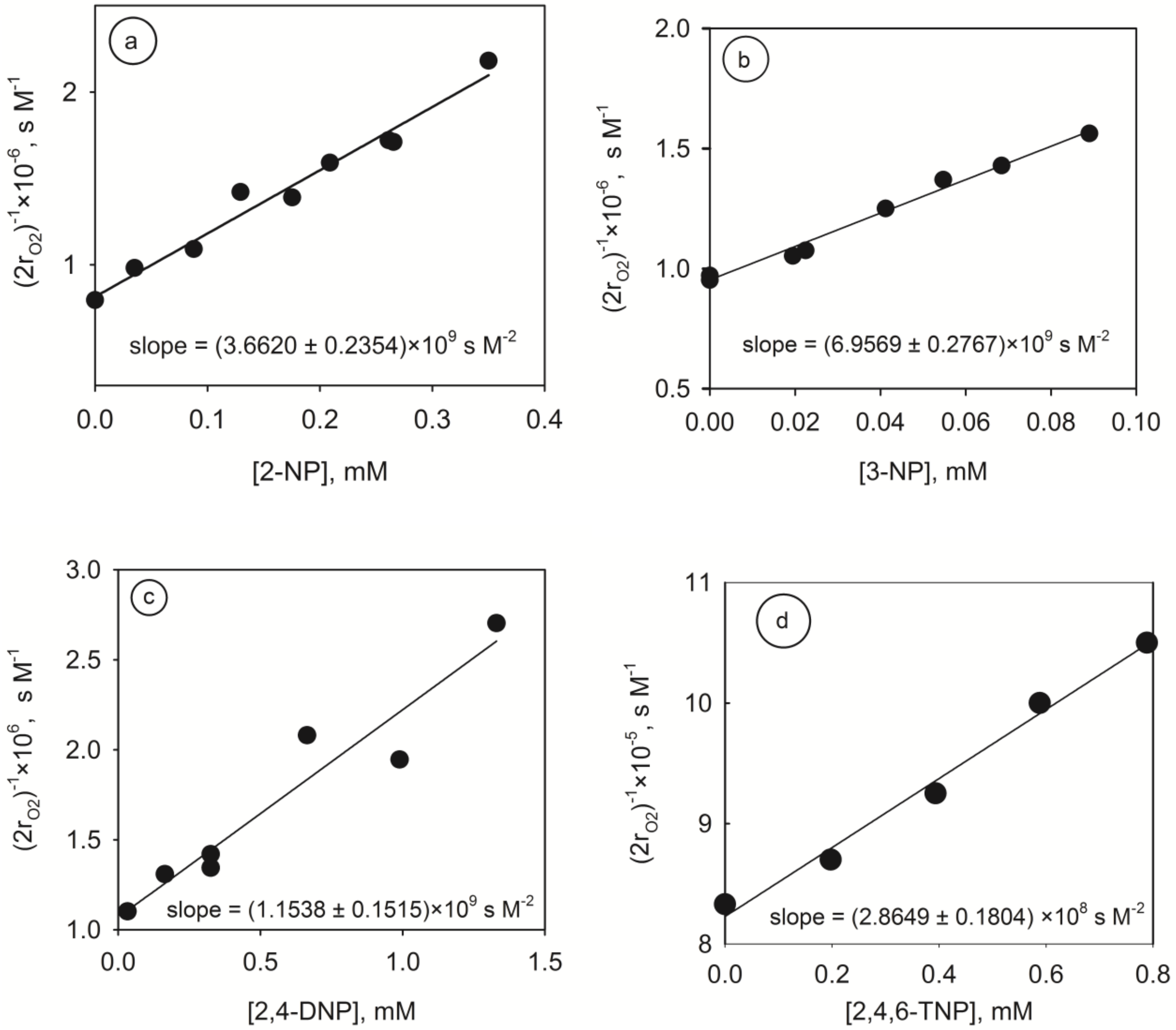

Fig. S2. Linear plots of reciprocal quasi-stationary rates for autoxidation of S(IV) in the presence of: (a) 2-NP; (b) and (d) 2,4,6-TNP at various initial concentrations.

3. Correction of the rate constants for diffusional limitations

The observed second order rate constants were corrected for diffusional limitations using a simple resistance-in-series model:

$$k_{observed}^{-1} = k_{reaction}^{-1} + k_{diffusion}^{-1}$$ (S1 a.k.a 4))

$$k_{diffusion} = 4\pi(D_A + D_B)(r_A + r_B)N \times 10^{3}$$ (S2 a.k.a 5)

where all k are second order rate constants (M^{-1} s^{-1}), D are diffusion coefficients of reactants A and B (m^2 s^{-1}), r are reaction radii of reactant molecules A and B (m), and N is the Avogadro number.

Diffusion coefficients of nitrophenols in aqueous solutions were calculated using the method of Wilke and Chang [13]:

$$D = 7.4 \times 10^{-12} \frac{(\mathrm{XM})^{0.5}\mathrm{T}}{V_m^{0.6}\eta} \quad \mathrm{m^2\ s^{-1}}, \tag{S3}$$

where: X = 2.6 for water; M – molar mass of a diffusing compound, g mol^{-1}; T – temperature, K; V_m – molar volume of a diffusing compound, cm^3 $mole^{-1}$; η – viscosity of the solvent, mPa s or 0.01 g cm^{-1} s^{-1} (0.8891 mPa s for water at 298 K).

Molar volumes of nitrophenols were calculated using the method of Tyn and Calus [14,15]:

$$V_m = 0.285 V_c^{1.048}, \quad \mathrm{cm^3\ mole^{-1}} \tag{S4}$$

where: V_c is a critical volume, cm^3 $mole^{-1}$, which can be estimated using the method of group contributions by Joback and Reid [16].

Molecular radii of nitrophenols were calculated using Equation (S5). The values of V_c, V_m, D and r are collected in Table S1.

$$r = \sqrt[3]{\frac{3V_m}{4\pi N}}, \tag{S5}$$

Table S2. Properties of nitrophenols and sulfate radical anion

		2-NP	**3-NP**	**4-NP**	**2,4-DNP**	**2,4,6-TNP**	**SO_4^-**
V_c	cm^3 mol^{-1}	370.5	370.5	370.5	432.5	534.5	
V_m	cm^3 mol^{-1}	140.3	140.3	140.3	165.0	205.9	
D	m^2 s^{-1}	2.429×10^{-9}	2.429×10^{-9}	2.429×10^{-9}	2.536×10^{-9}	2.476×10^{-9}	1.06×10^{-9} [A]
r	m	3,817×10^{-10}	3,817×10^{-10}	3,817×10^{-10}	4,029×10^{-10}	4,339×10^{-10}	3.8×10^{-10} [B]

[A] – the same as for $S_2O_3^{2-}$ [17]; [B] – the same as for hydrated sulfate ion [18].

4. Atmospheric significance

Rate of conversion of a NP by a reactant X in the gas phase ($r_{X,g}$) was compared to the rate of conversion of this NP by sulfate radical anions in the aqueous phase contained within the gas phase ($r_{SO4,aq}$×ω):

$$\frac{r_{\mathrm{X},g}}{r_{\mathrm{SO_4},aq}\omega} = \frac{k_{\mathrm{X},g}}{k_{\mathrm{SO_4},aq}H_{d,\mathrm{X}}H_{d,\mathrm{NP}}\omega} \cdot \frac{[X]_{aq}}{[\mathrm{SO_4^{\cdot-}}]_{aq}}, \tag{S6 a.k.a 10}$$

where: ω m^3 m^{-3} is the atmospheric liquid water contents; $k_{X,g}$ dm^3 mol^{-1} s^{-1} is the rate constant for the reaction of X with NP in the gas phase; $k_{SO4,aq}$ dm^3 mol^{-1} s^{-1} is the rate constant for the reaction of $SO_4^{\bullet-}$ with NP in the aqueous phase; H_d is the dimensionless Henry's constant for X or for NP defined by Equations (S7); $[X]_{aq}$ and $[SO_4^{\bullet-}]_{aq}$ are the aqueous-phase concentrations of X and $SO_4^{\bullet-}$.

$$H_d = HRT,\ if\ H\ is\ in\ \mathrm{mol\ dm^{-3}atm^{-1}} \tag{S7a}$$

$$H_d = HRT\rho,\ if\ H\ is\ in\ \mathrm{mol\ kg^{-1}atm^{-1}}, \tag{S7b}$$

where R is the gas constant, atm dm^3 mol^{-1} K^{-1}; ρ is the density of the solution, practically equal to the density of solvent.

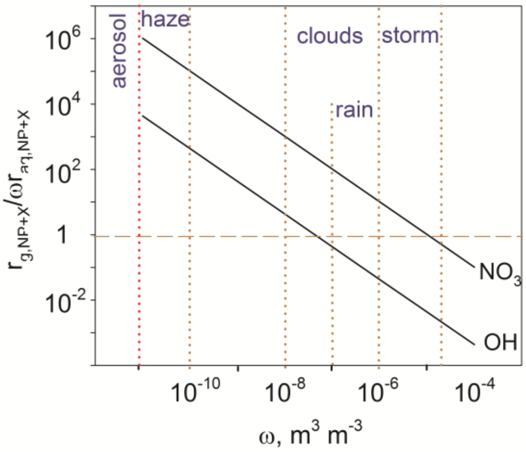

Fig. S3. The ratio of the gas-phase and the aqueous-phase conversions of 2-NP by OH and NO_3 radicals (the gas-phase and aqueous-phase concentrations are bound by Henry's equilibria).

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