

ELECTRONIC SUPPORTING INFORMATION

Kinetics of oxidation of nitrosodisulfonate anion radical with a metallo-superoxide

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Table S1a. Stoichiometric results in the presence of excess **1** over NDS²⁻.

[**1**] = 1.0 mM, [NDS²⁻] = 0.25 mM, pH = 5.6, T_{OAc} = 0.10 M and $T = 25.0 (\pm 0.1) ^\circ\text{C}$.

$\Delta[\text{NDS}^{2-}] = 0.25 \text{ mM}$.

No. of observation	Initial absorbance at 670 nm	Final absorbance at 670 nm	Amount of 1 reacted (mole lit ⁻¹)	$\Delta[\mathbf{1}]/\Delta[\text{NDS}^{2-}]$
1.	0.830	0.412	0.504	2.016
2.	0.830	0.410	0.506	2.024
3.	0.830	0.414	0.501	2.004

Table S1b. Collection of product gas.

1 = 0.25×10^{-3} mole, $\text{NDS}^{2-} = 2.5 \times 10^{-3}$ mole, $T_{\text{OAc}} = 0.10$ M and $T = 25.0^\circ\text{C}$.

pH	ml. gas produced at 25 °C	Moles of gas produced per mole of 1
5.10	8.3	1.48
5.35	8.3	1.48
5.60	8.2	1.46
5.85	8.3	1.48

Table S1c. BaSO₄ produced on oxidation of NDS²⁻.

1 = 0.25 x 10⁻³ mole, NDS²⁻ = 2.5 x 10⁻³ mole and T_{OAc} = 0.10 M.

pH	Amount of BaSO ₄		Moles of BaSO ₄ produced per mole of 1
	gm	mole	
5.10	0.0601	0.257 x 10 ⁻³	1.03
5.35	0.0595	0.255 x 10 ⁻³	1.02
5.60	0.0599	0.257 x 10 ⁻³	1.03
5.85	0.0590	0.253 x 10 ⁻³	1.01

Table S2. Effect of D₂O on k_{obs} .

[**1**] = 0.20 mM, [NDS²⁻] = 4 mM, pH = 5.85, T_{OAc} = 0.10 M, I = 1.5 (NaCl) M and T = 25.0 (\pm 0.1) °C.

% of D ₂ O (v/v)	$10^3 k_{\text{obs}}$ (s ⁻¹)
0	7.75
20	7.80
40	7.75
60	7.80
80	7.85

Figure S1. Bronsted plot of $\log(k_{\text{obs}})$ vs $I^{1/2}$

$[1] = 0.2 \text{ mM}$, $[\text{NDS}^{2-}] = 4.0 \text{ mM}$, $\text{pH} = 5.35$, $T_{\text{OAc}} = 0.10 \text{ M}$ and $T = 25.0 (\pm 0.1) \text{ }^\circ\text{C}$.

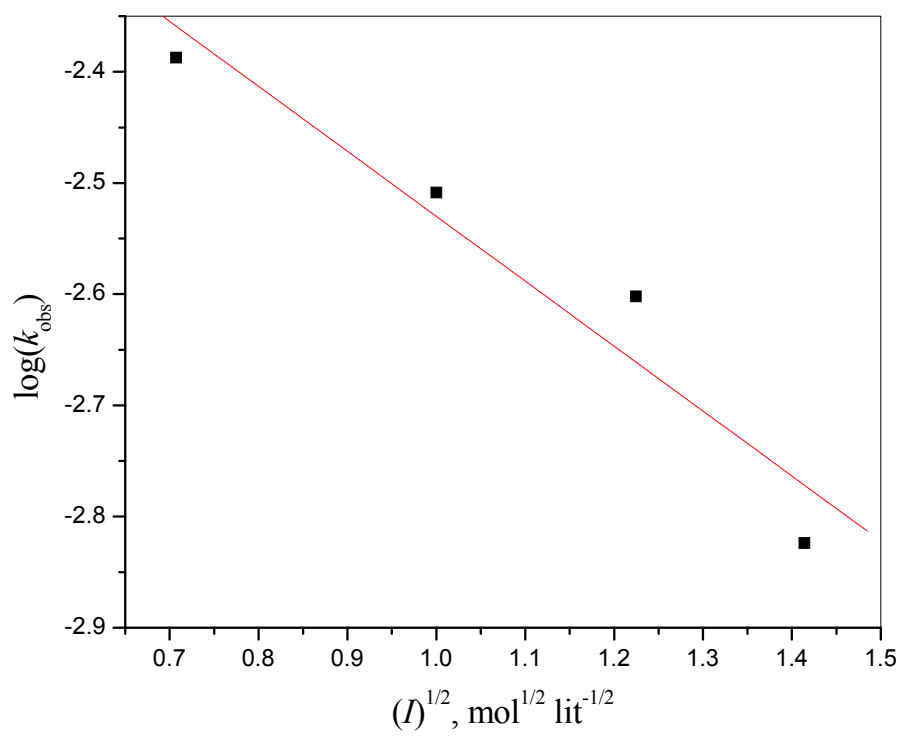


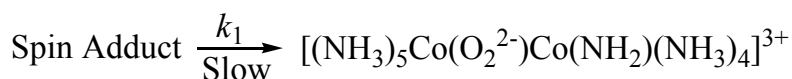
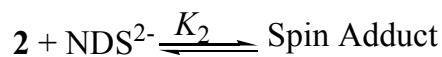
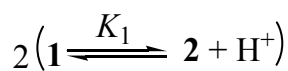
Table S3. Comparison of rate constants[†] of HDS with NDS²⁻.

[**1**] = 0.20 mM, T_{OAc} = 0.10 M, I = 1.5 (NaCl) M and T = 25.0 (\pm 0.1) °C.

Reducing agent	Concentration (mM)	pH	$10^3 k_{\text{obs}}$ (s ⁻¹)
HDS	2.0	5.0	8.1
HDS	2.0	5.5	25.0
HDS	5.0	5.0	14.2
HDS	5.0	5.5	44.3
NDS ²⁻	2.0	5.1	0.7
NDS ²⁻	2.0	5.6	2.1
NDS ²⁻	5.0	5.1	1.7
NDS ²⁻	5.0	5.6	5.5
NDS ²⁻	6.0	4.4	0.6 ^a
HDS	5.0	4.5	5.0 ^a

[†]All the rate constants (k_{obs}) are counting by considering the stoichiometric factors.
^aAt I = 1.0 (NaCl) M.

Derivation of rate law:



$$K_1 = \frac{[\mathbf{2}][\text{H}^+]}{[\mathbf{1}]} \quad \text{OR} \quad [\mathbf{2}] = \frac{K_1[\mathbf{1}]}{[\text{H}^+]}$$

$$K_2 = \frac{[\text{Spin Adduct}]}{[\mathbf{2}][\text{NDS}^{2-}]}$$

OR

$$[\text{Spin Adduct}] = K_2[\mathbf{2}][\text{NDS}^{2-}] = \frac{K_1 K_2 [\mathbf{1}][\text{NDS}^{2-}]}{[\text{H}^+]}$$

$$\text{Rate} = k_1[\text{Spin Adduct}] = \frac{k_1 K_1 K_2 [\mathbf{1}][\text{NDS}^{2-}]}{[\text{H}^+]} \quad \dots\dots(1)$$

Again, considering the stoichiometric factor

$$\text{Rate} = 2 k_{\text{obs}} \cdot [\mathbf{1}] \quad \dots\dots(2)$$

Comparing equation (1) and (2),

$$k_{\text{obs}} = \frac{0.5 k_1 K_1 K_2 [\text{NDS}^{2-}]}{[\text{H}^+]}$$