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Kinetics and mechanism of reduction of a coordinated superoxide with hydroxylamine derivatives

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ABSTRACT

Rates for the uncatalyzed reactions of the coordinated superoxide in μ-superoxo bis[pentaminecobalt(III)]$^{5+}$ complex (**1**) with hydroxylamine-N-monosulfonate, $HONH(SO_3)^-$ (HMS) and hydroxylamine-N,N′-disulfonate, $HON(SO_3)_2^{2-}$ (HDS) have been determined. Successive replacement of the $-NH_2$ protons with SO_3H group (electron withdrawing) increased the reaction rate from HMS to HDS but replacement of the O–H hydrogen halted the reaction. HMS and HDS are oxidized to a mixture of N_2O (20%), NO (80%) and SO_4^{2-}. The reactions are first-order in [**1**] and [reductant]. Reaction rate increased with pH though neither HMS nor HDS are involved in protic equilibria within the investigated pH range. We propose **1** is in protic equilibrium with its conjugate acid **1**H which is kinetically a dead-end species. An electroprotic reaction between **1** and the –OH hydrogen in HMS is proposed whereas a simple electron-transfer mechanism has been proposed for the HDS oxidation.

1. Introduction

The superoxide anion, O_2^-, is known to be involved in many biological and catalytic oxidations [1–5] like the superoxide radical anion has been implicated as a by-product of the functioning of aerobic organisms [6]. Free superoxide ions are known to be extremely reactive [7,8]. However, their reactivity can be controlled when bonded to a metal center as in the selected superoxo complex μ-superoxo bis[pentaminecobalt(III)]$^{5+}$ ion (**1**) [9]. Coordination of the superoxo ligand in the μ_2-mode blocks several of its side reactions known in the free state [10] and thus helps in unambiguous mechanistic interpretations on its reactions. We here report the kinetics and mechanism of the redox reactions of **1** with the hydroxylamine-N-monosulfonate (HMS) and hydroxylamine-N,N′-disulfonate (HDS). The kinetics with hydroxylamine itself is too complicated to analyze. Reactivities of O-methyl hydroxylamine, $CH_3–ONH_2$ (O-MeHA), hydroxylamine trisulfonate (HTS) and hydroxylamine-O-sulfonic acid, $HSO_3–ONH_2$ have been also presented for a comparison.

The present work has been carried in the range pH 3.5–5.5 in acetate buffer. In this range, the complex suffers practically no self-decomposition within the reaction period and the $-SO_3H$ group in the reductants, present in the fully deprotonated form, are not involved in any other parallel protic equilibria.

2. Experimental

2.1. Materials and reagents

The pentachloride salt of the superoxo complex **1** was synthesized following a literature process [11]. The chloride salt was converted to the corresponding perchlorate salt [12] and recrystallized from 10% $HClO_4$ (ϵ, M^{-1} cm^{-1} at 670 nm = 834: literature value: 838 [13]). HDS [14,15], HMS [16] and HTS [17] were prepared by reported procedures. Their purity were checked by H, N microanalyses (*Anal.* Calc. in % for $HON(SO_3K)_2 \cdot 2H_2O$: H, 1.63; N, 4.50. Found: H, 1.83; N, 4.37%. *Anal.* Calc. for $HO–NH(SO_3K) \cdot H_2O$: H, 2.36; N, 8.28. Found: H, 2.29; N, 8.37%. *Anal.* Calc. for $K_3[(SO_3)_2NOSO_3] \cdot 2H_2O$: H, 0.95; N, 3.31. Found: H, 0.98; N, 3.40%.). All other reagents including the hydroxylamine-O-sulfonic acid (Aldrich) and the O-methyl hydroxylamine (Alfa-Aesar) were of sufficient purity and used as received. Doubly distilled water was used all through.

2.2. Stoichiometry and reaction products

The reaction stoichiometry with excess reducing agent was determined iodometrically [18] quantifying the unused reducing agent. After completion of the reactions, argon gas was passed through the reaction mixtures to fully purge out any gas that might have generated. NO was qualitatively tested in the ensuing gas by passing it through a fresh $FeSO_4$ solution acidified with sulfuric acid. Presence of sulfate ion in the product mixture was qualitatively detected with the help of $BaCl_2$ solution in the presence of HCl.

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2.3. Kinetic measurements

Kinetics was monitored spectrophotometrically at 670 nm, where only **1** has an absorption maximum. All kinetic runs were carried out in the presence of a large excess of the reducing agent concentration over [**1**] at (25 ± 0.1) °C in an electrically controlled thermostated cell-housing of the instrument (Jasco V-1700). The ionic strength (I) was maintained at 1.0 M (NaCl), unless mentioned otherwise. All kinetics was studied in the range pH 3.5–5.5 maintained with acetate buffer (T_{OAc} = 0.10 M). All pHs were determined with a pH meter (Toshniwal CL-54, India); its electrodes were calibrated using standard buffers as usual. All the reactions were carried out under an inert argon atmosphere. The first-order rate-constants k_o were evaluated from the absorbance-time data by standard non-linear least-squares programs.

3. Results and discussion

3.1. Stoichiometry

Each mole of HMS and HDS consumed 2.8 mol of the complex (Table 1). A brown color was seen when the product gas was passed through acidified $FeSO_4$ solution. Also, the reaction products formed a heavy, white precipitate with $BaCl_2$ solution acidified with HCl. The stoichiometric results may therefore be interpreted as part oxidation (20%) to N_2O and part oxidation to (80%) to NO.

$$2HON(SO_3)_2^{2-} + 3H_2O \rightarrow N_2O + 4SO_4^{2-} + H^+ + 4e \quad (20\%) \qquad (1)$$

$$HON(SO_3)_2^{2-} + 2H_2O \rightarrow NO + 2SO_4^{2-} + 5H^+ + 3e \quad (80\%) \qquad (2)$$

The reduced form of **1** has been severally suggested to be **2** [13], the hydroperoxo derivative of **1** and rapidly decomposes [19] to Co^{II}, NH_4^+ ion and O_2.

3.2. Reaction with hydroxylamine disulfonate (HDS)

The reaction obeyed first-order kinetics with respect to [**1**] (Fig. 1), [HDS] (Table 2) and basicity (Fig. 2). None of the added metal ions, Cu^{2+}, Ni^{2+}, Fe^{2+} and Ag^+ exhibited any catalytic effect. Above pH 5.7, the reaction velocity becomes too high to measure with conventional spectrophotometry. On the other side HDS rapidly hydrolyzes [20] to HMS in solution at pH <3. So the kinetic determinations were limited within the range pH 3.5–5.5. The first-order rate-constants (k_o) decreases with increasing ionic strength (Table 3) as expected for reactions between two oppositely charged species.

3.3. Reaction with hydroxylamine monosulfonate (HMS)

Cu^{2+} dramatically catalyzed the reaction such that even impurity level of Cu^{2+} (2.6×10^{-6} M, determined with Atomic Absorption Spectrometry) interferes with the kinetics (Fig. 3a) and addition of 0.10 mM Cu^{2+} completed the reaction instantly.

Table 1
Stoichiometric results for the oxidation HMS and HDS with **1**. T_{OAc} = 0.10 M, I = 1.0 M (NaCl), T = 25.0 (±0.1) °C.

10^5 [Reductant] (M)	10^5 [**1**] (M)	10^5 Δ[Reductant] (M)	[1]/ Δ[Reductant]
[HMS], 23.8	8.0	2.84	2.8[a]
[HMS], 13.3	6.65	2.4	2.8[b]
[HDS], 17.4	5.8	2.1	2.8[a]
[HDS], 13.3	6.65	2.35	2.8[b]

[a] pH 4.5.
[b] pH 4.0.

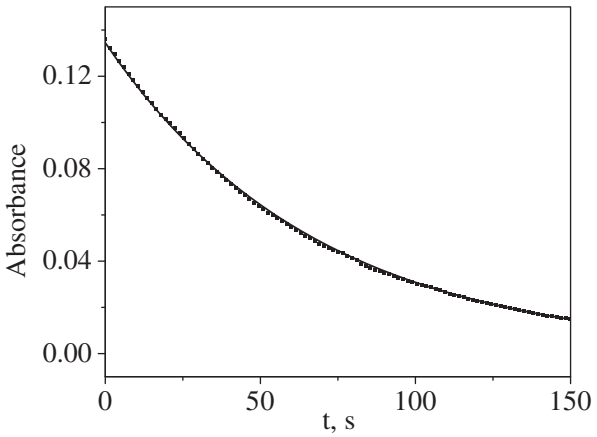

Fig. 1. First-order fit for the oxidation of **1** with HDS. [HDS] = 10 mM, [**1**] = 0.20 mM, pH 4.5, I = 1.0 M (NaCl), T_{OAc} = 0.10 M, T = 25.0 (±0.1) °C.

Table 2
Some representative rate-constants for the reaction of HDS with **1**. [**1**] = 0.2 mM, I = 1.0 M (NaCl), T_{OAc} = 0.10 M, T = 25.0 (±0.1) °C.

10^3 [HDS] (M)	10^3 k_o (s^{-1}) at pH				
	3.4	3.7	4.5	5.0	5.5
2.0	2.8	3.1	7.8	30.0	95.0
5.0	6.6	11.0	15.0	53.0	169.0
10.0	13.9	14.6	28.5	87.6.	[a]
15.0	20.0	21.0	41.0	159.0	[a]
20.0	25.0	27.0	50.0	177.0	[a]

[a] The reactions under the condition are very fast and could not be followed by conventional spectrophotometer.

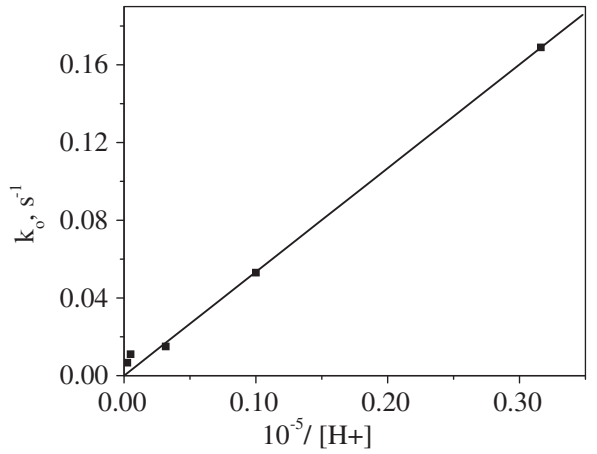

Fig. 2. Inverse acid dependence of k_o for the oxidation of HDS. [HDS] = 5.0 mM, [**1**] = 0.20 mM, I = 1 .0 M (NaCl), T_{OAc} = 0.10 M, T = 25.0 (±0.1) °C.

Table 3
The first-order rate-constants for the oxidation of HDS and HMS with **1** at different media ionic strength. [**1**] = 0.20 mM, pH 4.5, T_{OAc} = 0.10 M, T = 25.0 (±0.1) °C.

Reductant	10^3 k_o (s^{-1}) at I (M)			
	1.0	1.5	2.0	2.5
HDS,10 mM	285.0	250.0	130.0	78.0
HMS, 10 mM[a]	11.0	4.0	2.0	1.2

[a] [dipic] = 0.4 mM.

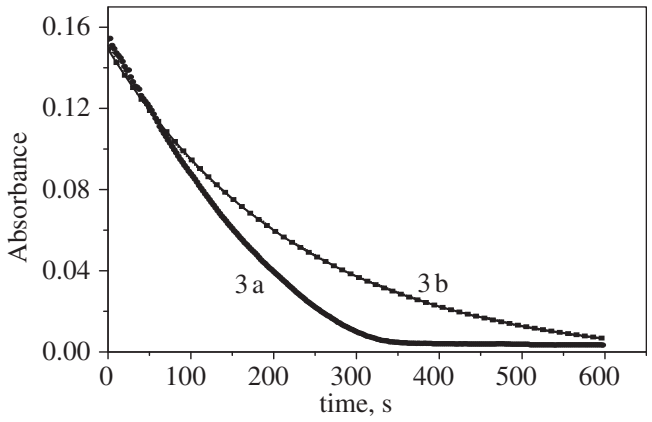

Fig. 3. Effect of a sequestering agent (dipicolinic acid) on the absorbance-time data for the reaction of HMS. [**1**] = 0.20 mM, [HMS] = 10 mM, pH 5.0, I = 1.0 M, T_{OAc} = 0.10 M, T = 25.0 (±0.1) °C (a). Under the same condition, but in presence of 0.4 mM dipicolinic acid (b) resulted.

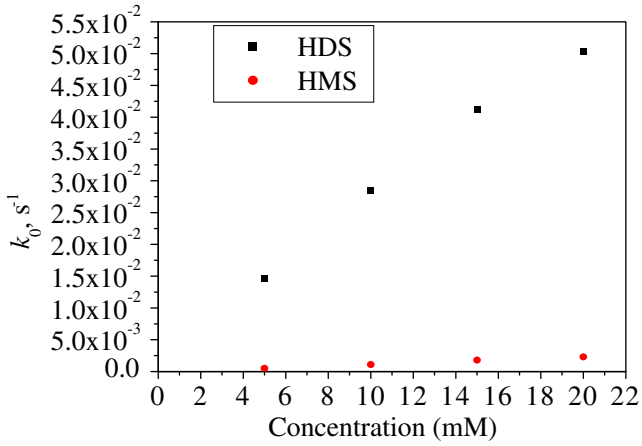

Fig. 4. A comparison of first-order rate constant (k_o, s^{-1}) for the oxidation of HDS and HMS. [**1**] = 0.2 mM, pH 4.5, T_{OAc} = 0.10 M, I = 1.0 M (NaCl), T = 25.0 (±0.1) °C and [dipic] = 0.40 mM for HMS.

Table 4
Effect of pH on the oxidation of HDS and HMS with **1**. [**1**] = 0.20 mM, T_{OAc} = 0.10 M, I = 1.0 M (NaCl), T = 25.0 (±0.1) °C. Additionally, for the oxidation of HMS dipicolinic acid (0.40 mM) was added.

pH	[Reductant] (mM)	10^4 k_o (s^{-1})
3.4	5.0[a]	66
3.7	5.0[a]	110
4.0	5.0[a]	130
4.5	5.0[a]	147
5.0	5.0[a]	530
5.5	5.0[a]	1690
3.5	10.0[b]	1
4.0	10.0[b]	3
4.5	10.0[b]	11
5.0	10.0[b]	47
5.5	10.0[b]	149

[a] HDS.
[b] HMS.

Dipicolinic acid (⩾0.40 mM) (Table S1) completely halted the catalyzed path and only the direct redox reaction with HMS could be seen (Fig. 3b). Kinetics of the direct reaction grossly followed kinetic pattern similar to those followed between **1** and HDS. Thus, the direct reaction obeyed first-order kinetics with respect to [**1**], [HMS] and basicity (Table 4). Increase in ionic strength decreased the rate. Under comparable conditions, HDS reacts faster than HMS (Fig. 4).

3.4. Reaction with O-substituted derivatives

Substitution at the O-end of hydroxylamine halted the reactions with [**1**], for example, the O-methyl hydroxylamine (O-MeHA), hydroxylamine O-sulfonic acid (HSO_3–ONH_2) and hydroxylamine trisulfonate (HTS) did not consume [**1**].

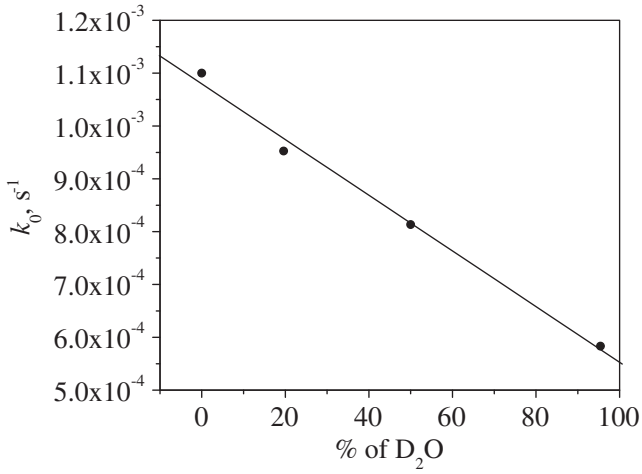

Fig. 5. Effect of mol% of D_2O on the observed first-order rate-constants of the oxidation of HMS. [**1**] = 0.2 mM, [HMS] = 10 mM, [dipic] = 0.40 mM, pH 4.5, T_{OAc} = 0.10 M, I = 1.0 M (NaCl), T = 25.0 (±0.1) °C.

Thus we conclude that the reactions of hydroxylamine utilize its –OH end but not the NH_2 end.

4. Mechanism

The reactions show inverse proton dependence but none of the reducing agents suffer any kind of deprotonation under the reaction condition. Further, presence of the –O–H proton seems essential and electron withdrawing groups on the N of the –NH_2 moiety accelerate the rate. Based on these kinetic observations, it appears

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{5+} + H^+ \underset{}{\overset{K}{\rightleftharpoons}} [(NH_3)_5CoO_2HCo(NH_3)_5]^{6+}$$
$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{1H}$$

$$\mathbf{1} + R \xrightarrow{k} R_{Ox} + [(NH_3)_5CoO_2HCo(NH_3)_5]^{5+}$$
$$\mathbf{2}$$

$$R_{Ox} \xrightarrow{\text{fast}} \text{Products, } N_2O \text{ and NO}$$

$$\mathbf{2} \xrightarrow{\text{fast}} \text{Products, } Co^{II}, NH_4^+ \text{ and } O_2$$

Scheme 1. R = HMS and R_{ox} = one electron oxidized HMS.

1 to be the active oxidant to which the reductants transfer their O–H proton, and an electron (either simultaneously, viz. for HMS redox or separately, viz. for HDS redox, *vide infra*), thus converting **1** to its hydroperoxo derivative **2**, which undergoes rapid decomposition to Co^{2+}. Increased proton concentration partly scavenges **1** at a protic equilibrium (K) forming **1**H and hence decreases the reaction rate. Scheme 1 matches with the kinetic observations as stated, for example, for HMS oxidation.

The HMS reaction showed prominent solvent kinetic isotope effect. A linear relation (Fig. 5) was observed when k_o was plotted against the mol% D_2O in the H_2O–D_2O mixed media suggesting transfer of a single proton at the rate step [21]. However, HDS did not show any solvent kinetic isotope effect. On this basis, an electroprotic mechanism for HMS oxidation but electron-transfer separated from proton transfer for HDS oxidation is proposed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.07.006.

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