

Kinetic study of oxidation of nitrite with a metallo superoxide

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Bridging superoxide in $[(\text{en})(\text{dien})\text{Co}^{\text{III}}(\text{O}_2)\text{Co}^{\text{III}}(\text{en})(\text{dien})]^{5+}$ quantitatively oxidizes N(III) to N(V), itself being reduced to hydroperoxo group. Kinetic study and solvent isotope effect indicate two parallel paths: (a) electron transfer and (b) proton coupled electron transfer. The present study also indicates that the ancillary ligands affect the reaction rate substantially. Studies on redox behavior of metal bound superoxide are not many and this study is expected to shed some light on the redox nature of metal bound superoxide.

Keywords: Kinetics, Reaction mechanisms, Oxidation, Metallo superoxides

Superoxide radical drives different biological cycles and shapes lives as we see it¹⁻⁵. The first step in the oxygen activation mechanisms of metalloenzymes is typically the binding of dioxygen and electron transfer from metal to O₂, forming a metal superoxo species⁶⁻¹⁰. In these compounds, nature of the metal ion modulates the reactivity of the superoxide ion. Kinetics and mechanism of reactions of metal-superoxo complexes have therefore attracted attention¹¹. Sykes *et al.*¹² have reported that a given superoxo complex can show important mechanistic variations with apparently similar reducing agents. While several studies concerned with redox behavior of monodentate¹³⁻¹⁵ and bridging superoxide¹⁶⁻¹⁸ have been reported, the effect of ancillary ligands on the redox behavior of superoxide ligands is not known.

As a chemical agent, nitrite has versatile applications and it has recently received much attention as an endogenous source of nitric oxide in hypoxic vasodilatation¹⁹⁻²³. Hence, interaction of N(III) with superoxo species seems interesting. Free superoxide ion has been reported to react reversibly

with N(III) to produce peroxide in fused metal salts^{24, 25}. Herein we present the kinetics of reaction of N(III) with the superoxo complex $[(\text{en})(\text{dien})\text{Co}^{\text{III}}(\text{O}_2)\text{Co}^{\text{III}}(\text{en})(\text{dien})]^{5+}$ (**1**) in aqueous acetate buffer. We took up this study to investigate the mechanism of reaction between N(III) and metallo-superoxide under ambient conditions. The effect of ancillary ligands on the redox behavior of superoxide ligands is also reported.

Experimental

The pure perchlorate salt of the complex ion μ -superoxo[bis(ethylenediamine)bis(diethylenetriamime)cobalt(III)]⁵⁺, viz., $[(\text{en})(\text{dien})\text{Co}^{\text{III}}(\text{O}_2)\text{-Co}^{\text{III}}(\text{en})(\text{dien})](\text{ClO}_4)_5$ (**1**), was synthesized and characterized as reported²⁶. Solid NaClO₄ was prepared by adding NaHCO₃ to HClO₄ and subsequent crystallization. All other materials including sodium nitrite (Merck) were of reagent grade and used as received. All solutions were prepared in freshly boiled doubly distilled water.

After completion of the reaction (absorption at 708 nm ~ 0) between (**1**) and excess N(III), residual N(III) was measured by permanganometry²⁷ and spectrophotometry²⁸. Results from the two methods agreed closely and an average is reported.

Co(II) in the product solution was determined by adding concentrated HCl according to a method elaborated by Sykes *et al.*²⁹.

Absorbances and UV-vis spectra were recorded with a Jasco spectrophotometer (1700) using 1.00 cm quartz cells. A pH meter (Toshniwal CL-54) with electrodes calibrated with standard buffer solutions was used for pH measurements. While reporting pH values in D₂O media, the relation, $pD = pH + 0.4$ was used^{30,31}. EPR spectra were recorded with JES-FA series EPR spectrometer using a field centre 250.000 mT and at a frequency of 9114.872000 MHz.

Ionic strength (*I*) of the media was maintained at 0.5 M by adding NaClO₄. The kinetics was monitored *in situ* in the thermostated (25 ± 0.1 °C) cell housing of the spectrophotometer by measuring the decay in absorbance of (**1**) at 708 nm in acetate buffer. A large excess of N(III) over (**1**) ensured first order conditions. At 708 nm, only (**1**) absorbs³². At least

90 % decay in absorbance (A_t) with time (t) fitted the first order decay routine of ORIGIN 7.0. The first order rate constants (k_o) were evaluated therefrom.

Results and discussion

Results of stoichiometric determination (Supplementary data Table S1) clearly demonstrate that each mole of N(III) consumed two moles of the title oxidant $[(\text{en})(\text{dien})\text{Co}^{\text{III}}(\text{O}_2)\text{Co}^{\text{III}}(\text{en})(\text{dien})]^{5+}$ (**1**), itself being oxidized to N(V). Figure 1 shows a series of time-resolved spectra when (**1**) is reacted with N(III). The visible absorption peak of (**1**) at 708 nm disappeared and the corresponding hydroperoxo complex (**2**), viz., one electron reduced species of (**1**) originated³³⁻³⁶. Thus, (**1**) acts as a one-electron oxidant for N(III) and the latter ultimately is oxidized to N(V) (Scheme 1). The overall reaction thus appears to be,

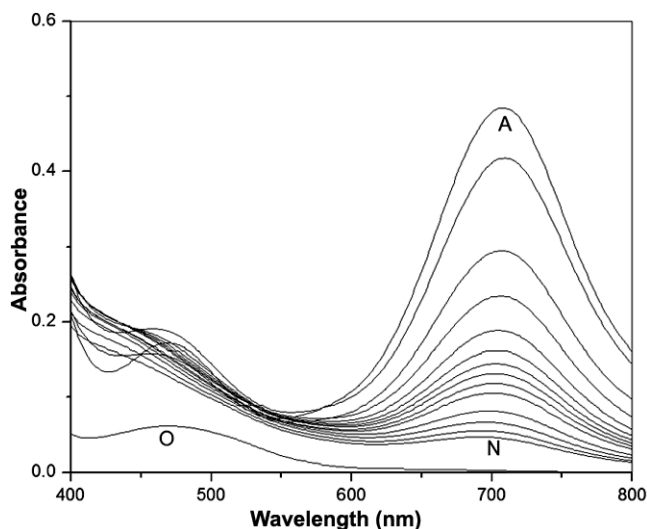
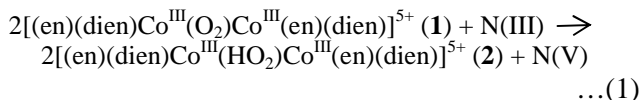
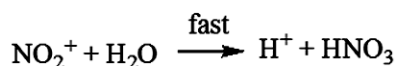
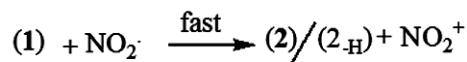
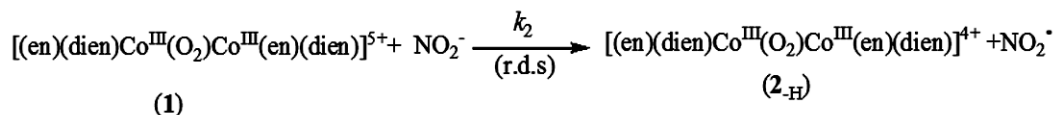
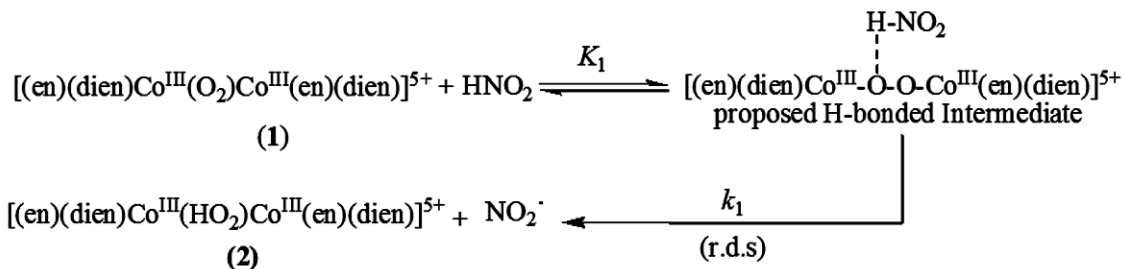
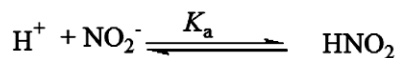


Fig. 1—Kinetic spectra (A-N) of 0.50 mM of (**1**) reacting with 5.0 mM $T_{\text{N(III)}}$ at $\text{pH} = 4.8$, $T = 25.0$ °C till practically all superoxide is consumed. [(A-N): spectra of reaction mixture at time intervals 0, 30, 60, 110, 172, 202, 233, 264, 299, 369, 489, 609, 789, and 14430 s respectively; (O): spectrum after standing overnight].



Scheme 1

With one equivalent reagents like Fe(III)³⁷ or Mn(III)³⁸, N(IV) radicals are formed as intermediate. Similarly, we presume formation of the NO₂· radical, which rapidly consumes the second mole of (1). At a later stage, (2) decomposes to [(en)(dien)CoNO₃]²⁺ (see the last spectra of Fig. 1)²⁹ along with a small amount of Co(II).

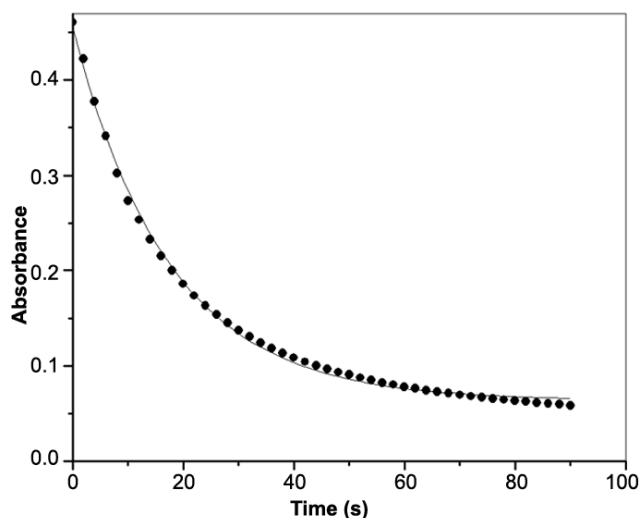
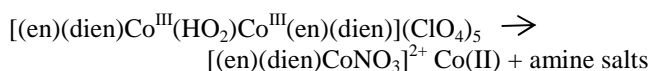


Fig. 2—Decrease in absorbance at 708 nm of (1) with time (experimental points shown in black circles) in its reaction with T_{N(III)}. A good fit (solid line) to the first-order exponential decay equation is seen. {(1) = 0.50 mM; T_{N(III)} = 10.0 mM; pH = 3.60; T = 25.0 °C}.

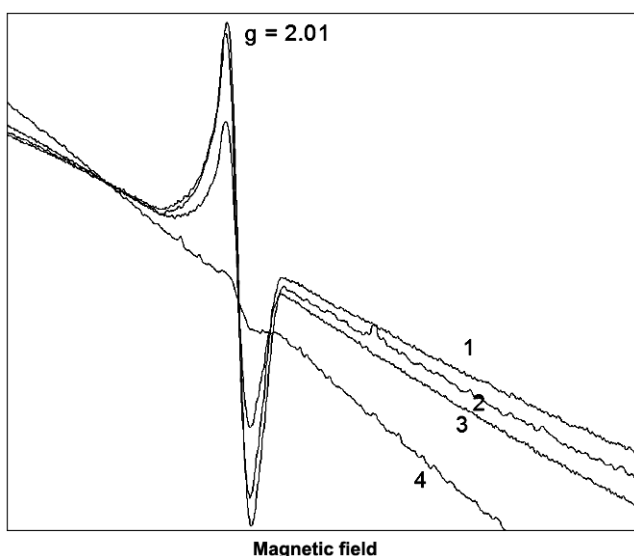


Fig. 3—EPR spectra of (1) (0.5 mM) at liquid nitrogen temperature. Curves 1, 2 and 3 are the epr spectra of the reaction mixture at time intervals of 50 and 110 s respectively. The spectrum of the reaction mixture almost disappears at the end (curve 4). [N(III) = 5.0 mM at pH = 4.6].

Under the experimental conditions, (1) is stable. However in the presence of N(III), absorbance peak of (1) decreases with time (Fig. 1(A-1(N))) by a first order process. (Fig. 2). Simultaneous decrease of the peak height of the epr spectra of (1) (Fig. 3) verifies the attack of N(III) on the bound superoxide and not on Co^{III}. We found no interference from N(IV) in the epr spectra. Presumably, the steady-state concentration of N(IV) is below the epr detection limit.

The first-order rate constant, k_o , increases with T_{N(III)} and a plot of k_o against T_{N(III)} at a fixed pH is a straight line with no significant intercept (Supplementary data Fig. S1, Table S2). k_o increases with [H⁺] and decreases when solvent H₂O is enriched with D₂O ($k_{H_2O}/k_{D_2O} \sim 2$;) (Supplementary data Tables S3 and S4). A plot of $k_o(1+K_a[H^+])$ against [H⁺] (Fig. 4) is linear, where K_a is the protonation constant of nitrite. Apparently, N(III) reduces (1) in two parallel paths: (a) reduction of (1) by electron transfer (ET) from NO₂⁻ (b) reduction of (1) by HNO₂ through a proton coupled electron transfer (PCET) path. The pK_a of HNO₂ is 3.3 (ref. 39); (1) does not protonate¹⁸.

The reaction scheme shown in Scheme 1 is proposed to explain the above observations.

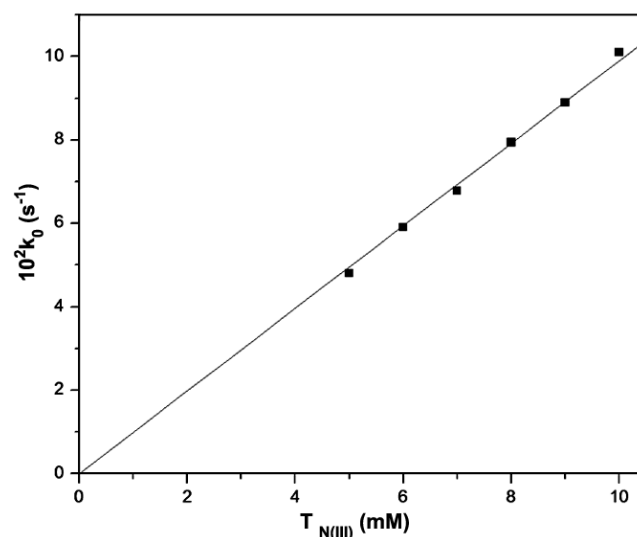


Fig. 4—Plot of $k_o(1+K_a[H^+])$ versus [H⁺]. {(1) = 0.50 mM, T_{N(III)} = 6.0 mM. T = 25.0 °C}.

This leads to:

$$k_o(1 + K_a[H^+]) = \{k_1K_1K_a[H^+] + k_2\} T_{N(III)}$$

$$\{T_{N(III)} = [NO_2^-] + [HNO_2]$$

$$= [NO_2^-] + K_a[H^+][NO_2^-]; K_a = \frac{[HNO_2]}{[H^+][NO_2^-]}$$

$$= [NO_2^-](1 + K_a[H^+])$$

$$\text{or, } [NO_2^-] = \frac{T_{N(III)}}{1 + K_a[H^+]}$$

Again,

$$T_{N(III)} = [NO_2^-] + [HNO_2]$$

$$K_a = \frac{[HNO_2]}{[H^+][NO_2^-]}$$

$$T_{N(III)} = [HNO_2] + \frac{[HNO_2]}{K_a[H^+]}$$

$$= [HNO_2] \left(1 + \frac{1}{K_a[H^+]}\right)$$

$$= [HNO_2] \left(\frac{K_a[H^+] + 1}{K_a[H^+]}\right)$$

Or,

$$[HNO_2] = \frac{K_a[H^+]T_{N(III)}}{K_a[H^+] + 1}$$

Hence,

$$\text{Rate} = ([1]) (k_1K_1[HNO_2] + k_2[NO_2^-])$$

$$k_o = (k_1K_1K_a[H^+] + k_2) \frac{T_{N(III)}}{1 + K_a[H^+]}$$

Or,

$$k_o(1 + K_a[H^+]) = (k_1K_1K_a[H^+] + k_2)T_{N(III)}$$

A plot of $k_o(1 + K_a[H^+])$ against $[H^+]$ at a fixed $T_{N(III)}$, gives K_1k_1 and k_2 for the HNO_2 and NO_2^- paths as $39 \text{ mol}^{-1}\text{s}^{-1}$ and $4.9 \text{ mol}^{-1}\text{s}^{-1}$ respectively.

The higher rate constant (K_1 is expected to be < 1) for the HNO_2 path as compared to that for NO_2^- in itself is uncommon for a positively charged oxidant and indicates different mechanisms for the two paths. This is another reason for proposing PCET path for HNO_2 , and an ET path for NO_2^- .

Sykes *et al.*^{40,41} showed that rate and mechanism for the oxidation of S^{IV} with the mono-bridged metallo-superoxide complex, $[(NH_3)_5Co^{III}(O_2)Co^{III}(NH_3)_5](ClO_4)_5$

hardly differs from its di-bridged analogue, $[(NH_3)_5Co^{III}(NH_2O_2)Co^{III}(NH_3)_5](ClO_4)_4$. For oxidation of N(III), we found that the ancillary ligands in a metallo-superoxide have important functions. Thus, when ammonia molecules are substituted with the chelating ligands, as in (1), stoichiometry of the reaction and its mechanism differ from those proposed for S^{IV} . Moreover, the rate of reaction for the superoxo complex (1) is slow and the final products are different. The hydroperoxo complex from (1) finally decomposes to $[(en)(dien)CoNO_3]^{2+}$ (3) (Fig. 1(O)) and a small amount of Co(II). Figure 1(O) shows the formation of (3). However, the spectral observation shows that (3) forms in less than quantitative amount and the rest of the amount is presumed to be Co(II). The decomposition is too slow to affect the observed kinetics, whereas the intermediate hydroperoxo complex obtained from the reaction between $[(NH_3)_5Co^{III}(O_2)Co^{III}(NH_3)_5](ClO_4)_5$ and N(III), quickly decomposes to Co^{2+} and other products. Greater stability is expected for $[(en)(dien)Co^{III}(O_2)Co^{III}(en)(dien)](ClO_4)_5$ and may explain the present observations.

Deprotonation of the complex, $[(NH_3)_5Co^{III}(NH_2O_2)Co^{III}(NH_3)_5]^{4+}$ was found to be the source for $[H^+]^{-1}$ -dependence for some very weak acids⁴², but the deprotonation constant for (1) is too small as compared to that of HNO_2 and here plays no kinetic role.

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Supplementary data

Supplementary data associated with this article, viz., Fig. S1 and Tables S1 - S4, are available in electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA51A\(07\)949-953_Suppl Data.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA51A(07)949-953_Suppl Data.pdf).

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