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Reduction mechanism of a coordinated superoxide by benzyl alcohol and 2-propanol

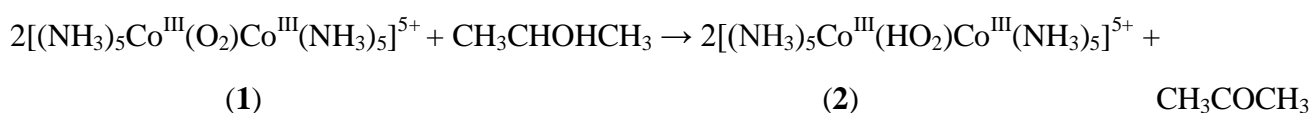
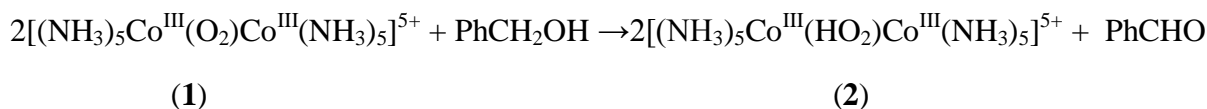
Ritu Mukherjee

Department of Chemistry, Dum Dum Motijheel College, Kolkata 700 074, West Bengal India.

E-mail: ritu069@gmail.com

ABSTRACT

In aqueous acetate buffer media, Benzyl alcohol and 2-propanol reduces the bridging superoxide in $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{O}_2)\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$ (**1**) to corresponding peroxide in the complex, $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{O}_2\text{H})\text{Co}^{\text{III}}(\text{NH}_2)(\text{NH}_3)_4]^{4+}$ (**2**), the reductants being oxidized to benzaldehyde and acetone respectively. The complex **2** thus produced decomposes rapidly to the final products, Co^{II} , NH_3 , etc. instead of reacting with a second molecule of reductants. In the presence of excess reductants over **1**, the reaction obeyed first-order kinetics and exhibited inverse proton dependence. $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{O}_2)\text{Co}^{\text{III}}((\text{NH}_2)(\text{NH}_3)_4)]^{4+}$ (**3**), a conjugate base of **1**, seems to be the kinetically reactive species and the cause for the observed inverse proton dependence. Reaction rate with the reductants significantly decreases with increasing proportion of D_2O replacing water in the solvent and the rate-limiting step seems to be an H-atom transfer.



KEYWORDS: Metal superoxide, Benzyl alcohol, 2-propanol, redox reaction kinetics, H-atom Transfer.

***Corresponding author:**

Ritu Mukherjee

Department of Chemistry,

Dum Dum Motijheel College,

Kolkata 700 074, West Bengal India.

E-mail: ritu069@gmail.com

INTRODUCTION

Free-radical-mediated per oxidation of membrane lipids¹ and oxidative damage of DNA are associated with a variety of chronic health problems, such as cancer, inflammation, atherosclerosis, neurodegenerative processes and aging.² The first step in the oxygen activation mechanisms of metalloenzymes is typically the binding of dioxygen, resulting in electron transfer from metal to O₂ to form a metal-superoxo species.³ The superoxide radical anion, O₂⁻ has thus been implicated as a byproduct of the functioning of aerobic organisms⁴ Consequently, the reactions of superoxide are of special interest. Superoxide is a strong nucleophile, which can form reasonably robust metal complexes in the absence of facile decomposition paths.⁵ Present work deals with the mechanism for base-catalyzed oxidation of benzyl alcohol and 2-propanol to benzaldehyde and 2-propanone respectively by bridging superoxide ligand in the dinuclear complex, [(NH₃)₅Co^{III}(O₂)Co^{III}(NH₃)₅]⁵⁺ (**1**), towards Benzyl alcohol and 2-propanol in the pH interval 4.7–5.45 maintained by acetate buffer.

MATERIALS AND METHODS

Materials

μ-superoxobis[pentaamminecobalt(III)] chloride, [(NH₃)₅Co^{III}(O₂)Co^{III}(NH₃)₅]Cl₅, (**1**) was synthesised by the literature process.⁶ The chloride salt was converted to the corresponding perchlorate salt⁷ and recrystallized from 10% HClO₄. [ε (M⁻¹ cm⁻¹) at 670 nm: found 832, reported⁸ 838]. Benzyl alcohol and 2-propanol (G.R, E. Merck) were used without further purification. Only fresh stocks of Benzyl alcohol and 2-propanol were used for kinetic and stoichiometric studies. Sodium perchlorate solution for maintenance of ionic strength in kinetic measurements was prepared from NaHCO₃ and HClO₄. All other materials used were of reagent grade and used without further purification.

Instrumentation

Absorbance and UV-VIS spectra were recorded with a Shimadzu (1601 PC) spectrophotometer using 1.00 cm quartz cell. The kinetics was monitored *in situ* in the electrically controlled thermostated (25.0 ± 0.1 °C) cell housing (CPS – 240 A) at 670 nm, the visible absorption maximum of **1**. The reactions were studied in acetate buffer (pH, 4.7–5.45; total acetate, T_{OAc} = 0.20 M) using a large excess of peroxide over **1**. A pH meter (Toshniwal CL-54, India) with electrodes calibrated with standard buffer solutions was used for pH measurements. Media ionic strength for kinetic studies was adjusted to 0.50 M (NaClO₄). All solutions were prepared in doubly distilled and then freshly boiled water. Reaction media were de-aerated with argon prior to kinetic measurements.

Observed first-order rate constants (k_o) were extracted by non-linear least-squares fitting of the decay of the absorbance (A_t) of **1** versus time (t) data to standard first-order exponential decay equation.

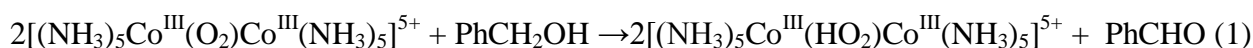
Stoichiometry

The stoichiometry of the reaction was determined by reacting known excess of **1** with known deficient amount of the reductants and calculating the equilibrium absorbance values.

RESULTS AND DISCUSSION

Stoichiometry and the reaction products

With excess [**1**], spectrophotometric determination of the residual [**1**] indicated a 1:2 stoichiometry ($\Delta[\text{PhCH}_2\text{OH}]:\Delta[\text{1}]$). This stoichiometry suggest that the reaction product of PhCH₂OH is benzaldehyde and it was confirmed by Tollens' and Fehling's reagent tests. The final solution after determination of stoichiometry gave a positive Tollens' reagent test but a negative Fehling's test confirming the formation of aromatic aldehyde⁹ Similar determination with 2-propanol also indicated 1:2 stoichiometry ($\Delta[2\text{-prpanol}]:\Delta[\text{1}]$), hence the reaction product of 2-propanol is acetone, confirmed by 2,4-dinitrophenylhydrazine test.⁹ **1** undergoes reduction to its most common reduction product $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{HO}_2)\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$ (**2**).¹⁰ Based on spectral observations, it is established that the reduction of **1** by divalent metal ions like Cr²⁺, V²⁺ and Eu²⁺ in acid media results in a protonated structure for the intermediate peroxo complex (**2**). **2** quickly decomposes to Co(II), NH₃ and O₂^{8,10} and did not affect the overall kinetics. Independent experiments showed that the products benzaldehyde and acetone did not react with **1**. Hence the overall reaction is represented by eqns 1 and 2, which are followed by the rapid decomposition of **2**.



(1)

(2)



(1)

(2)

CH₃COCH₃ (2)

Kinetics and Mechanism

Under the reaction conditions, PhCH₂OH and 2-propanol slowly consumed **1**, reducing the absorbance with time, and the process followed excellent first-order kinetics. A family of time-resolved spectra describing such changes is shown in Fig. 1. The first-order rate constants, k_o increased linearly with [alkanol] (Table 1 and 2, Fig 2 and 3) in the entire pH range studied. k_o and

Scheme 1 leads to eqn. (9).

$$k_{\text{obs}}/[\text{alkanol}] = kKK_a/[\text{H}^+] \quad (9)$$

A plot of $k_{\text{obs}}/[\text{alkanol}]$ versus $1/[\text{H}^+]$ (eqn. 9) yielded excellent straight line with a statistically insignificant intercept (Fig. 3 and 4 for PhCH₂OH and for 2-propanol).

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Table 1. Some representative first-order rate constants (k_o) for the reduction of 1 (0.20 mM) by PhCH₂OH, $I = 0.50$ M (NaClO₄), $T = 25.0$ °C.

[PhCH ₂ OH], M	pH	$10^3 k_o, s^{-1}$
0.02	4.70	1.2
0.02	4.95	1.95
0.02	5.12	3.05
0.02	5.3	4.01
0.02	5.45	5.6
0.02	4.70	1.2
0.04	4.70	2.2
0.06	4.70	3.2
0.08	4.70	4.1
0.1	4.70	5.3

Table 2. Some representative first-order rate constants (k_o) for the reduction of 1 (0.20 mM) by 2-propanol, $I = 0.50$ M (NaClO₄), $T = 25.0$ °C.

[2-propanol], M	pH	$10^3 k_o, s^{-1}$
0.02	4.7	0.15
0.02	4.90	0.25
0.02	5.10	0.40
0.02	5.30	0.53
0.02	5.45	0.73
0.02	4.90	0.25
0.04	4.90	0.29
0.06	4.90	0.41
0.08	4.90	0.53
0.1	4.90	0.68

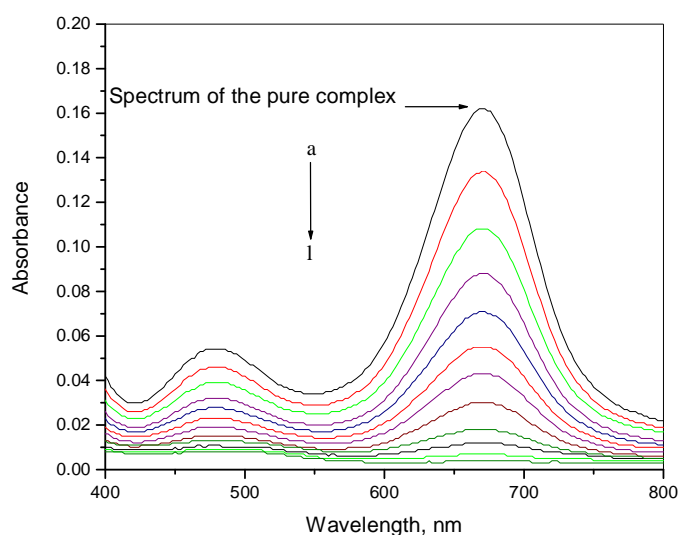


Figure 1. Time-resolved spectra of 0.20 mM of 1 reacting with 0.02M PhCH₂OH. pH = 4.70 in acetate buffer ($T_{OAc} = 0.20$ M), $I = 0.50$ M (NaClO₄), $T = 25.0$ °C.. (a): spectrum of pure complex shown in black; (b) – (l): spectra of reaction mixtures.

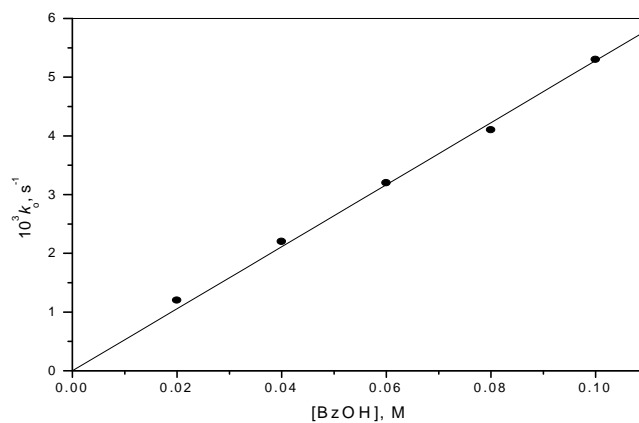


Figure 2. Variation of k_0 with $[PhCH_2OH]$. $[1] = 0.20$ mM, $pH = 4.70$ ($T_{OAc} = 0.20$ M), $I = 1.0$ M ($NaClO_4$), $T = 25.0$ °C.

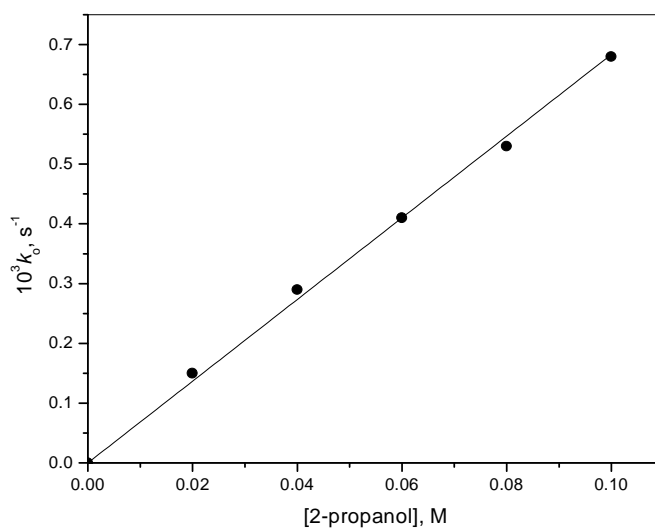


Figure 3. Variation of k_0 with $[2-propanol]$. $[1] = 0.20$ mM, $pH = 4.90$ ($T_{OAc} = 0.20$ M), $I = 1.0$ M ($NaClO_4$), $T = 25.0$ °C.

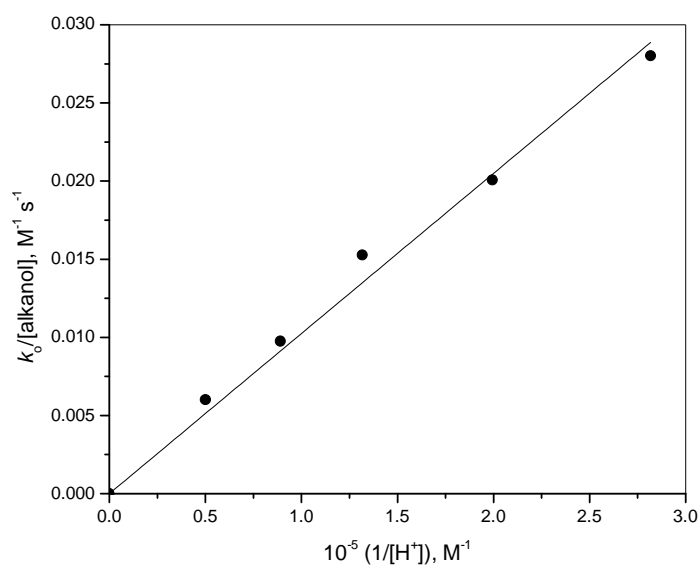


Figure 4. Variation of $k_0/[alkanol]$ with $1/[H^+]$, $[I] = 0.20$ mM, $[PhCH_2OH] = 0.2$ M, $(T_{OAc} = 0.20$ M), $I = 1.0$ M ($NaClO_4$), $T = 25.0$ °C.

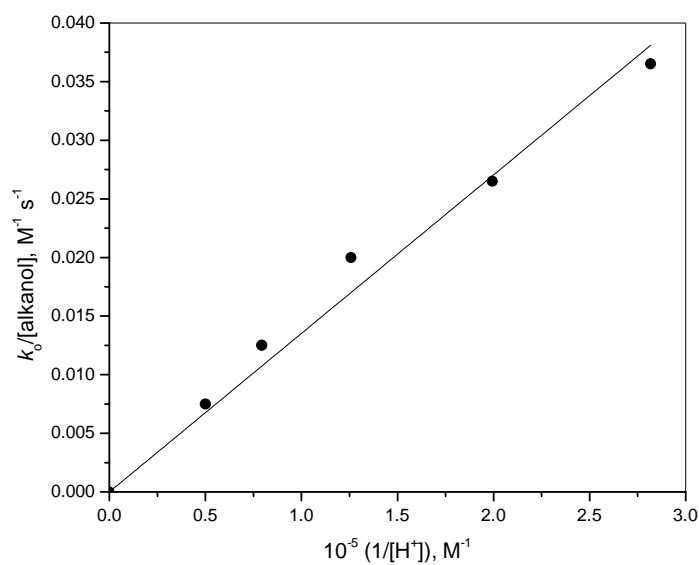


Figure 5. Variation of $k_0/[alkanol]$ with $1/[H^+]$, $[I] = 0.20$ mM, $[2\text{-propanol}] = 0.02$ M, $(T_{OAc} = 0.20$ M), $I = 1.0$ M ($NaClO_4$), $T = 25.0$ °C.