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Photochemical Oxygenation Reactions of Cobalt(III)-Amine Complexes in Aqueous and Non-Aqueous Solvents: Formation of μ-Peroxo Dinuclear Complexes of Cobalt(II)

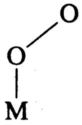
K. SANTHAKUMAR, N. KUMARAGURU, M.N. ARUMUGHAM[†] and
S. ARUNACHALAM[*]
Department of Chemistry, Bharathidasan University, Tiruchirappalli-620 024, India
E-mail: arunasurf@yahoo.com

Steady-state photolysis of a series of cobalt(III)-amine complexes, dissolved in neutral air equilibrated aqueous and non-aqueous solvents, with 254 nm penray lamp, leads to the oxygenation of the photoproduced cobalt(II) amine complexes. The study indicates that the photoproduced cobalt(II)-amine complexes upon reaction with molecular oxygen form a superoxo complex that reacts with the starting complex to give a μ-superoxo dinuclear complex. Subsequently the μ-superoxo complex gives the final product, the μ-peroxo dinuclear complex at room temperature. But in aqueous acidic solution the final photoproduct is cobalt(II) aqua complex.

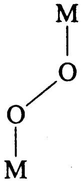
Key Words: Photochemical oxygenation, Cobalt(III)-amine complexes.

INTRODUCTION

The reactions of dioxygen complexes of transition metals have been studied as models for biological processes involving cobalt-dioxygen bonding. The reaction between dioxygen and metal ion is a redox process. One electron reductant reacts with molecular oxygen to form complexes having dioxygen to metal ratios of $1 : 1$[1, 2] or $1 : 2$[3–8] with the binding as shown (1,2 & 3).



(1)



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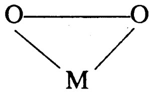

(3)

Complexes of the type 1 are formally considered superoxide complexes of one-electron-oxidized metal ions[9] while those of the type 2 are analogously viewed as μ-peroxo complexes[10]. Two electron donors form complexes of type (3)[10] through an oxidative addition type reaction and it is viewed as a peroxide bound to metal ion which has undergone a two-electron oxidation.

[†] Department of Chemistry, Vellore Institute of Technology, Deemed University, Vellore, Tamil Nadu, India.

Synthetic reversible cobalt-oxygen carriers were made by many scientists[11]. As research on simple iron complexes in solution to mimic the naturally occurring systems of haemoglobin and myoglobin was, for many years, unsuccessful, the reversible oxygenation of cobalt complexes received renewed interest. Basolo and Crumbliss[12, 13] discovered that under the proper conditions in non-aqueous solutions, certain Schiff base cobalt(II) complexes would reversibly bind one molecule of oxygen per molecule of cobalt. In aqueous solution cobalt(II) complexes from μ-peroxo bridged complexes of cobalt(III) with molecular oxygen *via* an intermediate mononuclear superoxo complex[14]. Wilkins *et al.*[15–17] employed a stopper-flow apparatus to investigate the kinetics of the reversible oxygenation of several different cobalt chelates and their results are accounted for by the following mechanism:

$$\mathrm{CoL^{2+} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoLO_2^{2+}} \qquad (1)$$

$$\mathrm{CoLO_2^{2+} + CoL^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} LCo{-}O_2{-}CoL^{4+}} \qquad (2)$$

This mechanism agrees with that proposed by Martell and coworkers[18] in their studies on several cobalt complexes of polyamines, amino acids and polypeptides. Cobalt(II) complexes form 2 : 1 μ-peroxo bridged complexes in aqueous solutions[19, 20]. Whenever the chelating agent has insufficient number of coordinating groups or is present in insufficient concentration or not fully saturate the coordination sites available on the cobalt ion, a second bridge may form[20–23]. The second bridge may be a μ-hydroxo[21, 24], a μ-amido[25] or another μ-type bridge[26, 27]. When only one coordination site is available on each cobalt, formation of second bridge is precluded. Several complexes have been reported in which a monobridged complex is formed at low pH and μ-peroxo-μ-hydroxo dibridged complex is formed at higher pH[28, 29]. This supports the earlier arguments that the formation of a μ-peroxo bridge generally proceeds μ-hydroxo bridge formation[30]. A μ-peroxo bridge may be formed intramolecularly if a ligand capable of binding two metal ions simultaneously[31] with favorable geometry is employed.

Formation of μ-peroxo-bridged complex of cobalt is preceded by the formation of a 1 : 1 (cobalt : dioxygen), presumably, superoxo complexes[32, 33]. It has been possible to limit the oxygenation reaction to 1 : 1 complex formation by using low dielectric constant solvents[34, 35], dilute solutions or complexes in which steric hindrance prevents bridge formation[36]. There are many evidences for the formation of dinuclear μ-superoxo or μ-peroxo complexes from the mononuclear superoxo precursors. Oxygenation of $\mathrm{Co(CN)_5^{3-}}$ in DMF and that of $\mathrm{Co(s\text{-}Me_2en)_2}$ in EtOH yields stable mononuclear complexes[37, 38]. However, in water, a solvent with high dielectric constant, oxygenation results in the generation of μ-peroxo complexes[39, 40]. *cis*-$\mathrm{[Co(en)_2(NO_2)_2]^+}$ and *cis*-$\mathrm{[Co(pn)_2(NO_2)_2]^+}$ upon charge transfer by photolysis in non-aqueous solvents produce the corresponding cobalt(II) complexes which then react with dissolved oxygen to form μ-peroxo dinuclear complexes[40–43]. In the present paper, we report that the μ-peroxodinuclear complexes are formed not only in non-aqueous solvents but also in aqueous solution. In acidic aqueous solution they do not undergo any oxygenation reactions but form cobalt(II) aqua complex.

EXPERIMENTAL

The complexes *cis*-α-[Co(trien)DACl]$(ClO_4)_2$, *cis*-α-[Co(trien)BACl$(ClO_4)_2$, *cis*-α-[Co(trien)DABr]$(ClO_4)_2$, *cis*-α-[Co(trien)BABr]$(ClO_4)_2$, *cis*-α-[Co(trien)$(DA)_2$]$(NO_3)_3$, *cis*-α-[Co(trien)$(BA)_2$]$(NO_3)_3$, (trien = triethylenetetramine, DA = dodecylamine and BA = butylamine) have been reported in our earlier work[44]. The methanol and acetonitrile solvents used were of spectral grade. Doubly distilled water was used for all the experiments. The amines used as ligands were obtained from Merck. Electronic spectra were recorded using a Hitachi U-3410 UV-Visible spectrophotometer. Steady-state photolysis experiments were carried out by using a 254 nm low pressure mercury pen-ray quartz lamp of Ultraviolet products Inc., California, USA.

RESULTS AND DISCUSSION

Aqueous solutions of complexes were irradiated with 254 nm UV penray lamp. Irradiation for different periods of air-equilibrated solutions results in the gradual increase in the absorbance in the region 355–360 nm and at 500 nm as shown in Fig. 1. The same experiments were done in non-aqueous (pure methanol and acetonitrile) media which produce similar spectral changes as observed in aqueous medium. In methanol and acetonitrile the absorbance changes were observed at 360 nm to 400 nm respectively, as shown in Figs. 2 and 3. In aqueous acidic solution, irradiation produces spectral changes which are not similar to that observed either in neutral water or in non-aqueous medium, thereby indicating the formation of

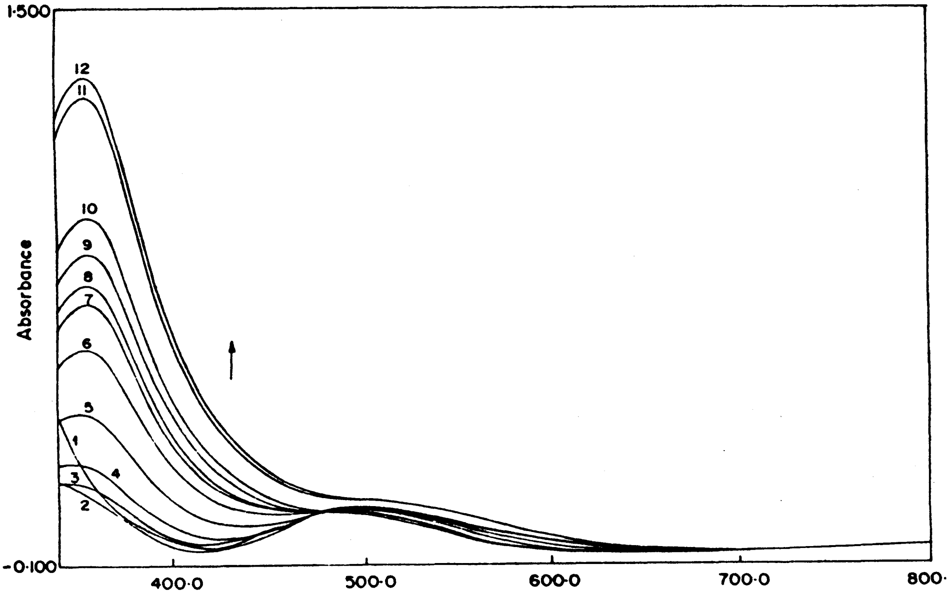

Fig. 1. Steady-state photolysis of *cis*-α-[Co(trien)(BA)Br]$^{2+}$ in neutral aqueous solution at room temperature: 1, unirradiated solution; increase in absorbance is due to successive irradiations

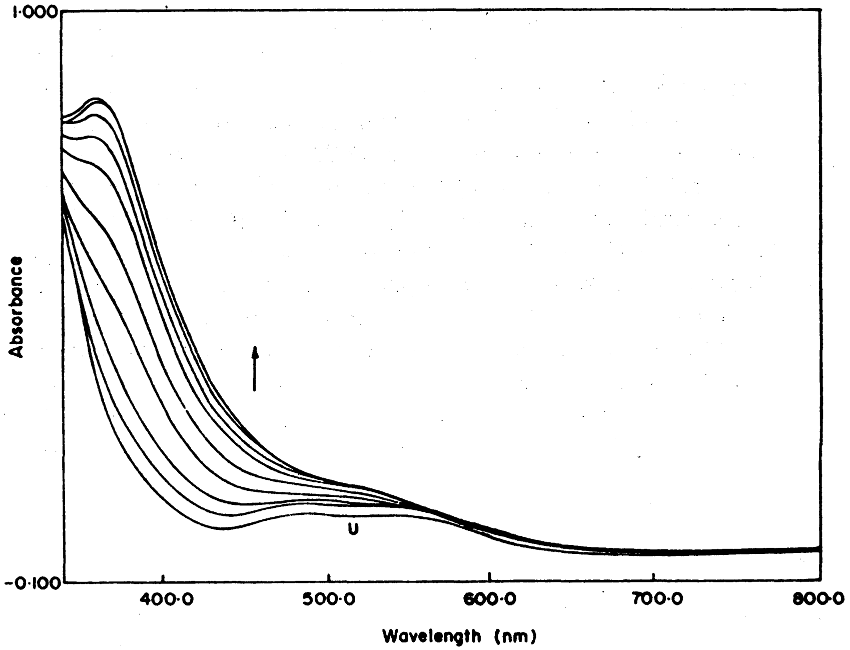

Fig. 2. Steady-state photolysis of *cis*-α-[Co(trien)(BA)Br]$^{2+}$ in nonaqueous solution (CH_3OH) at room temperature: U, unirradiated solution; increase in absorbance is due to different time interval irradiation

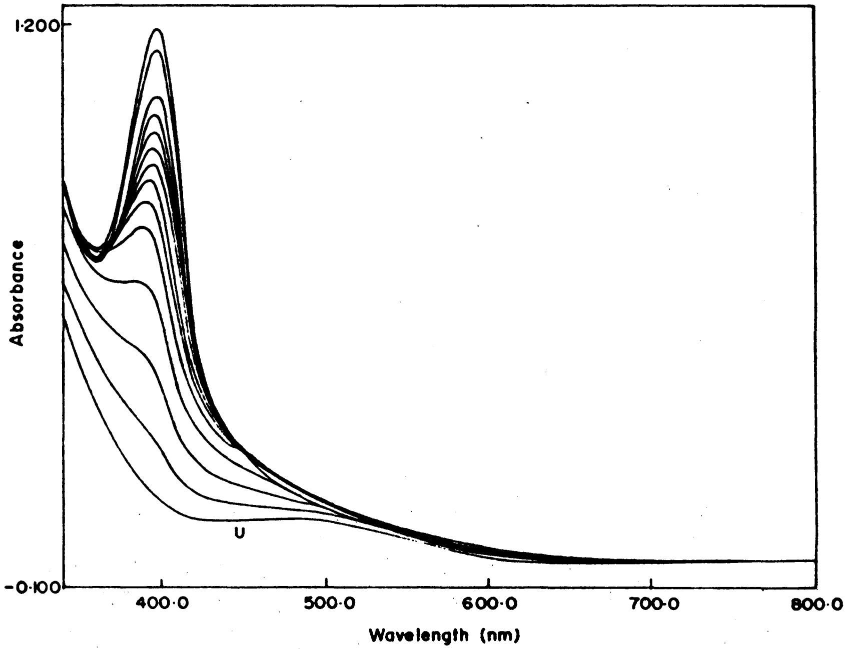

Fig. 3. . Steady-state photolysis of *cis*-α-[Co(trien)(BA)Br]$^{2+}$ in nonaqueous solution (CH_3CN) at room temperature: U, unirradiated solution; increase in absorbance is due to different time interval irradiation

cobalt ions, i.e., starting complex decomposed or Co(II) aqueous complexes produced as shown in Fig. 4. Upon irradiation the wavelength at which changes in absorbance occur for various cobalt(III)-amine complexes are given in Table-1. The spectral data of some peroxo complexes are indicated in Table-2.

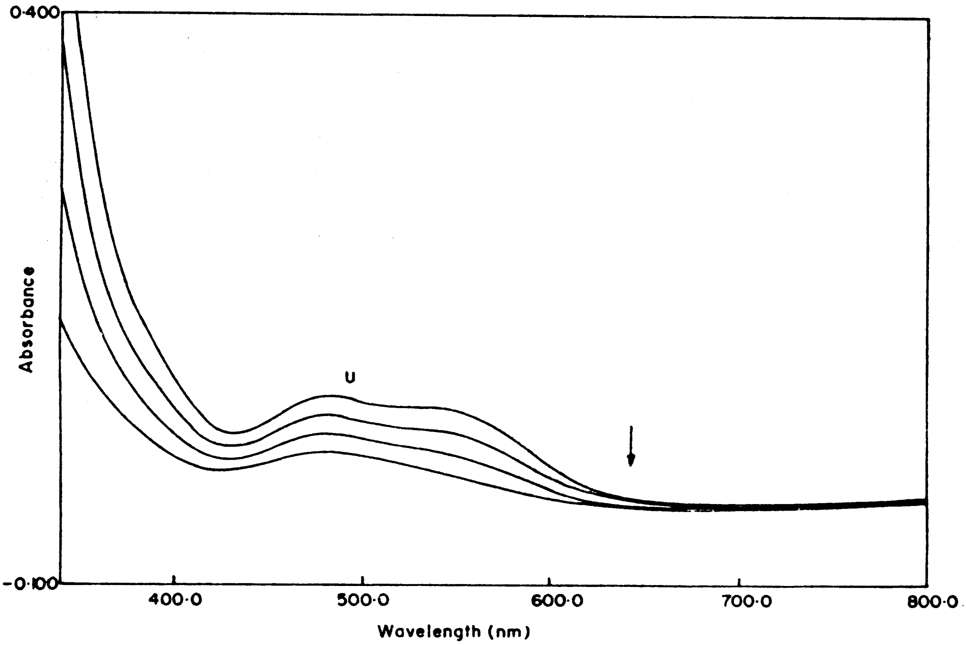

Fig. 4. Steady-state photolysis of *cis*-α-[Co(trien)(BA)Br]$^{2+}$ in acidic aqueous solution (0.1 M $HClO_4$) at room temperature: U, unirradiated solution; decrease in absorbance is due to successive irradiations

TABLE-1

SPECTRAL CHANGES AFTER STEADY-STATE PHOTOLYSIS OF COBALT(III) AMINES IN H_2O, CH_3OH AND CH_3CN

Complexes	λ_{max}, nm		
	H_2O	CH_3OH	CH_3CN
cis-α-[Co(trien)BABr]$(ClO_4)_2$	355 500 (sh)	360 500 (sh)	395 500 (sh)
cis-α-[Co(trien)DABr]$(ClO_4)_2$	356 500 (sh)	358 500 (sh)	400 500 (sh)
cis-α-[Co(trien)BACl]$(ClO_4)_2$	356 500 (sh)	360 500 (sh)	398 500 (sh)
cis-α-[Co(trien)DACl]$(ClO_4)_2$	356 500 (sh)	360 500 (sh)	398 500 (sh)
cis-α-[Co(trien)$(BA)_2$]$(NO_3)_3$	340 500 (sh)	358 500 (sh)	—
cis-α-[Co(trien)$(DA)_2$]$(NO_3)_3$	342 500 (sh)	358 500 (sh)	—

sh = shoulder

TABLE-2
SPECTRAL DATA[50] FOR PEROXO COMPLEXES

	Complexes	λ_{max} nm (log ε)	
1.	$[(en)_2Co(\mu\text{-}O_2^{2-}, NH_2)Co(en)_2]^{3+}$	500 (2.66)	355 (3.59)
2.	$[(1\text{-}pn)_2Co(\mu\text{-}O_2^{2-}, OH)Co(1\text{-}pn)_2]^{3+}$	510 (2.58)	350 (3.76)
3.	$[(en)_2Co(\mu\text{-}O_2^{2-}, OH)Co(en)_2]^{3+}$	526 (2.50) (sh)	357 (3.69)

sh = shoulder

Cobalt(III) complexes in aqueous acidic solutions undergo three principal types of photoreactions depending on the wavelength of irradiation[45]: (1) Photoredox reactions[46, 47] involving changes in oxidation number of metal and ligands or counterions; (2) Photosubstitution reactions[48], involving changes in the composition of the coordination shell; (3) Photoisomerisation reactions[49], involving changes in the coordination arrangement of the ligands.

Steady-state photolysis of cobalt(III) amine complexes indicates that the irradiation of air equilibrated non-aqueous and aqueous solutions of the cobalt(III) amine complexes produces the cobalt(II) complexes which then react with dissolved oxygen present in the solvent to form μ-peroxo complexes. The spectral details of dinuclear-μ-peroxo dimers with the ligands used in these studies are known[50] and summarized in Table-2. The similarity of the spectra of the photoproducts of the present study with the spectra of the complexes given in Table-2 indicates that the photoproducts of the present study are indeed the μ-peroxo dinuclear cobalt(III) complexes.

From the present study we conclude that the μ-peroxo dinuclear cobalt(III) complexes are formed not only in non-aqueous media but also in neutral aqueous medium at room temperature. We propose that the reaction follows the **Scheme-1**.

$$\begin{array}{c}
\text{cis-}\alpha\text{-}[Co(trien)(BA)Br]^{2+} \\
\Big\downarrow h\nu \\
[Co(trien)(BA)]^{2+} + Br \\
\Big\downarrow O_2 \\
[Co(trien)(BA)(O_2)]^{2+} \\
\Big\downarrow \textit{cis}\text{-}\alpha\text{-}[Co(trien)(BA)Br]^{2+} \\
[(BA)(trien)Co{-}O_2{-}Co(trien)(BA)Br]^{4+} \\
\Big\downarrow \\
[(BA)(trien)Co{-}O_2{-}Co(trien)(BA)]^{4+} + Br^{\bullet}
\end{array}$$

Scheme-1

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