

## Direct Determination of the Rate Constant for the Reaction of Molecular Oxygen with a Cobalt(II) Ammine Complex

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Kinetics and mechanisms of the absorption of oxygen by transition metal complexes have been investigated primarily in aqueous medium [1]. The important factors responsible for the uptake of oxygen and its release by metal complexes are not well understood [2]. Formation of dioxygen adducts and their structure have been of interest in non-aqueous solvents [3]. However, determination of the rate constant for the oxygen uptake by metal complexes to give 1:1 adduct could not be carried out since the reactions are fast even at low temperature in most cases. At ambient temperatures secondary reactions interfere with the rate measurements. We report in this communication the reaction between a cobalt(II) ammine complex, produced photochemically as a transient in acetonitrile solution, and molecular oxygen studied by flash photolysis.

In neat acetonitrile dinitrobis(ethylenediamine)-cobalt(III) perchlorate,  $cis\text{-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$ , is soluble and follows Beer's law. There is no solvation reaction for hours and the complex could be recovered quantitatively on evaporation of the solvent. Irradiation of a solution of  $cis\text{-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$  in spectroquality (Aldrich) acetonitrile with light obtained from a medium pressure mercury lamp using a 330 nm cut off filter produces the spectral changes shown in Fig. 1a. The spectral changes correspond to the features attributed to cobalt(II) complex-oxygen adducts [6, 7]. The final product in the steady photolysis reaction does not show any e.p.r. signal. Irradiation of a solution, deaerated by freeze-thaw procedure (6 cycles) under identical conditions does not produce the spectral changes shown in Fig. 1a; the only spectral change observed is a small decrease in absorbance in all the regions of the absorption spectrum. Oxygenation of the irradiated solution does not produce the spectral changes shown in Fig. 1a.

Flash photolysis of the deaerated solution using a conventional flash set up with acetone as the filter

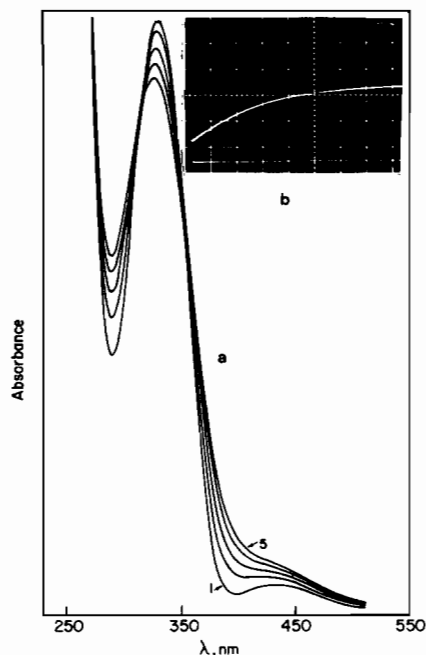


Fig. 1a) Absorption spectra of the unirradiated solution, 1, and successive irradiated solutions, 2–5, of the complex  $cis\text{-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]$  in acetonitrile. 1b) Increasing absorbance of a flash photolysed solution of the complex, time scale: 0.5 ms/division;  $\lambda = 500$  nm. Flash duration: 30  $\mu\text{s}$  from the start.

(flash duration 30  $\mu\text{s}$ ) produces no transient species. On the other hand, air equilibrated solutions produce the transient shown in Fig. 1b. The rate of transient growth is enhanced if oxygenated solutions are used instead of air-equilibrated solutions.

Cobalt(II) ammine complexes absorb light in the intense charge-transfer-to-metal absorption bands leading to the redox decomposition of the complex to give cobalt(II) [4]. Photochemical studies of the ammine complexes of cobalt(III) have been carried out in acidic aqueous solutions and the primary photoproduct cobalt(II) ammine complex breaks down in microsecond time scale producing aqueous cobalt(II) in solution [5]. The quantum yield for the redox decomposition is not sensitive to the oxygen present in the solution.

The spectral changes observed in the steady photolysis of the aerated acetonitrile solution of the complex and the transient formation in the flash experiment corresponds to the reaction of oxygen with the primary photoproduct formed. Photolysis of  $cis\text{-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]$  in water and in water-alcohol solutions produce cobalt(II) and the linkage isomer,  $\text{Co}(\text{en})_2(\text{NO}_2)(\text{ONO})^+$  [8]. There is no observed reaction between the primary product and oxygen in water solution due to the lability of the cobalt(II) complex. In acetonitrile, molecular oxygen reacts

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with the photoproduct to give 1:1 complex with oxygen which slowly undergoes dimerization and other secondary reactions well known for this type of oxygenation reactions. The rate constant measured for the initial rapid reaction in Fig. 1b corresponds to  $5.5 \times 10^2 \text{ s}^{-1}$ . Knowing the concentration of oxygen in air-equilibrated acetonitrile to be  $1.6 \times 10^{-3} \text{ M}^{-1}$  the bimolecular rate constant for the 1:1 oxygen adduct formation is calculated to be  $3.4 \pm 0.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . The observed rate constant for the 1:1 oxygen adduct formation is very similar to the value ( $4.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) reported for the  $\text{Co}(\text{en})_2^{2+}$  complex in water [1].

The primary photoproduct  $(\text{en})_2\text{CoNO}_2^+$  is not stable [5] in aqueous medium to react with the oxygen present in the solution. However it appears that the rate of substitution of solvent to the cobalt(II) complex is slower in acetonitrile at least by three orders of magnitude; dissolved oxygen reacts with the cobalt(II) ammine complex before it breaks down. Oxygenation of the irradiated solution does not lead to the formation of oxygen adducts since the cobalt(II) ammine complex is solvated completely by the time the solution is oxygenated. The method described here makes it possible to produce cobalt(II) complexes, with different ligands, photochemically and to study the oxygen adduct formation.

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