Reduction of Superoxobridged Dicobalt(III) Cation by Cadmium(I) *via* an Inner-sphere Pathway: Pulse Radiolysis Study

By P. NATARAJAN† and N. V. RAGHAVAN
(*Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana* 46556)

Summary Cadmium(I) has been observed to reduce the μ-amido-μ-superoxo-bis(bisethylenediamine)cobalt(III) cation by an inner-sphere electron transfer process.

MOLECULAR oxygen reactions are known to involve the superoxo and peroxo anions and the chemistry of these species is of both chemical and biological interest.[1] Dioxygen is known to co-ordinate with metal ions and the oxidation state of the co-ordinated dioxygen varies with the type of metal complex involved.[2] Cobalt(II) complexes absorb molecular oxygen and, depending upon the conditions and the types of ligands involved, the dioxygen may be found as the peroxo and superoxo species.[3]

Sykes[4] and his co-workers have investigated the electron transfer reactions involving these complexes extensively. One-electron reduction of the superoxo dicobalt(III) complexes with Cr^{II}, V^{II}, Eu^{II}, Fe^{II}, and $Ru(NH_3)_6^{2+}$ proceeds by an outer-sphere pathway and the redox process involves the dioxygen ligand and not the metal centre.[4] The tris(2,2′-bipyridyl)ruthenium(II) complex ion in the excited state is known to reduce the superoxo complexes of cobalt(III) by an outer-sphere pathway.[5] In this communication we report the reduction of the complex ion (**1**) (en = ethylenediamine) by cadmium(I) generated by pulse radiolysis in an aqueous medium containing methanol. The reduction takes place by an inner-sphere mechanism and a short-lived inner-sphere adduct between the cobalt(III) complex and cadmium(II) has been observed. The formation and redox reactions of cadmium(I) are known.[6,7]

An aqueous solution containing methanol (0·01 M), cadmium sulphate (0·02 M), and complex (5×10^{-5} M) was irradiated with a 10 ns pulse of 10 MeV electrons from the Notre Dame Linear Accelerator. The decay of cadmium(I) was followed optically at 310 nm and the formation of the peroxo complex at 380 nm. Our observations shown in the Figure (A) indicate that cadmium(I) is oxidized by the superoxo complex with a rate constant of $4 \cdot 0 \pm 0 \cdot 4 \times 10^9$ l mol^{-1} s^{-1}. The spectrum of the product monitored in the spectral mode indicated the formation of the corresponding peroxo complex. γ-Radiolysis studies confirmed the formation of the peroxo complex by the oxidation of cadmium(I) by the superoxo complex with no cobalt(II) formation.[8] While the decay of cadmium(I) occurs with a

---

† On leave of absence from the University of Madras, Tiruchirapalli 620020, India.

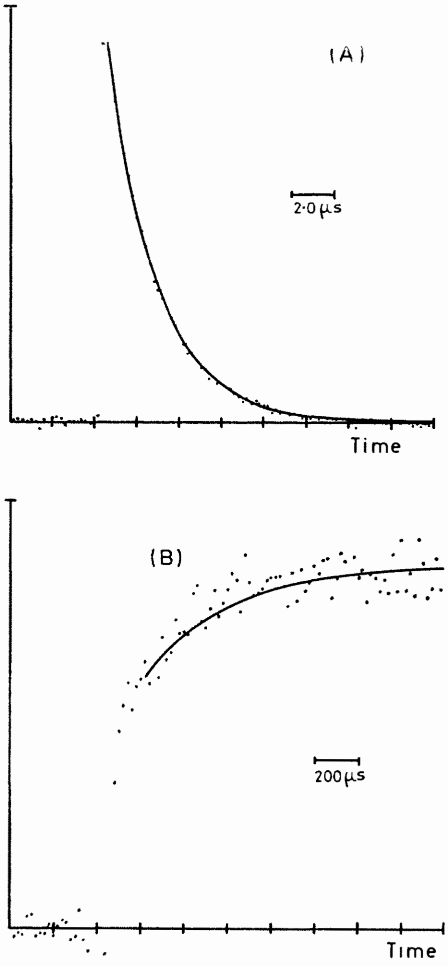
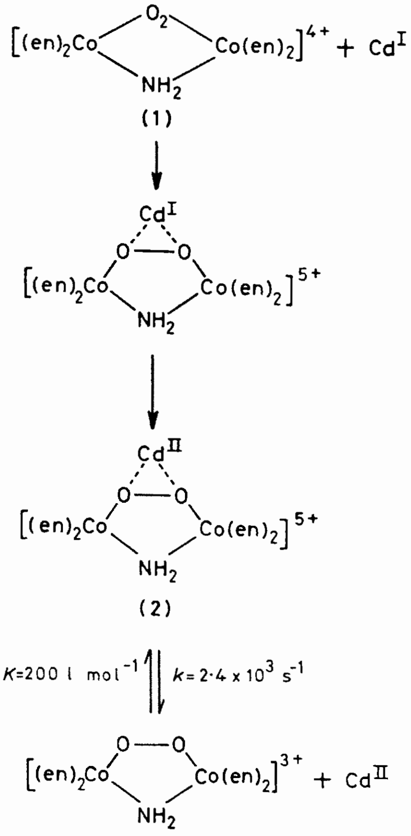


FIGURE (A) Decay of Cd$^{\mathrm{I}}$ absorbance at 310 nm; (B) formation of peroxo complex; absorbance at 380 nm. Ordinate: Absorbance in arbitary units.

rate constant of $4 \pm 0{\cdot}4 \times 10^{9}$ l mol^{-1} s^{-1}, the formation of the peroxo complex occurs in two steps, the fast process mentioned above followed by a slow process with a first-order rate constant of $2{\cdot}4 \pm 0{\cdot}4 \times 10^{3}$ s^{-1}. The slow process is attributed to the release of cadmium(II) from the complex adduct (**2**). It is known that the peroxo analogue of (**1**) protonates readily at the dioxygen bridge with an equilibrium constant[9] of 7 l mol^{-1} indicating that the peroxo bridge carries a net negative charge. Cadmium(II) forms an adduct with the peroxo complex and we have determined a value of 200 ± 30 l mol^{-1} for the formation constant from the absorbance changes due to the formation of the complex adduct at 380 nm by varying cadmium(II) concentration. The slow process shown in the Figure (B) is due to the release of cadmium(II) from the adduct. Based on the kinetic data, an inner-sphere pathway has been suggested for the reduction of cobalt(III) mononuclear complexes by cadmium(I).[10] For the first time we have observed direct evidence for the inner-sphere adduct formation for the cadmium(I) reduction of a metal complex. Adduct formation between cadmium(I) and the superoxo complex is expected to be favourable since the orbitals of a highly polarizable, soft metal ion such as cadmium(I) should overlap strongly with the π orbitals of the dioxygen entity. The observed growth of absorption at 380 nm is not due to the reaction between CH$_2$OH• and the complex, since the rate constant for this process is of an order of magnitude greater. The mechanism suggested for the reduction of the superoxo complex by cadmium(I) is shown in the Scheme.



SCHEME

This research was supported by the Office of Basic Energy Sciences of the Department of Energy,

(*Received*, 9*th October* 1979; *Com.* 1071.)

---

[1] O. Hayaishi, 'Chemical Models and Mechanisms for Oxygenases in Molecular Mechanisms of Oxygen Activation,' Academic Press New York, 1975.

[2] R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.

[3] A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, 1970, **13**, 1.

[4] (a) A. G. Sykes, *Chem. Br.*, 1974, **10**, 170; (b) A. B. Hoffman and H. Taube, *Inorg. Chem.*, 1968, **7**, 1971.

[5] K. Chandrasekaran and P. Natarajan, *J. Chem Soc., Chem. Commun.*, 1977, 774.

[6] J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. R. Soc. London, Ser. A*, 1965, **286**, 320.

[7] M. Kelm, J. Lilie, and A. Henglein, *J. Chem. Soc., Faraday Trans.*, 1975, **1**, 1132.

[8] P. Natarajan and N. V. Raghavan, to be published.

[9] K. M. Davies and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1418.

[10] D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, 1969, **73**, 1091.