Cr^{2+} Reduction of μ-Superoxo- and μ-Peroxo-complexes

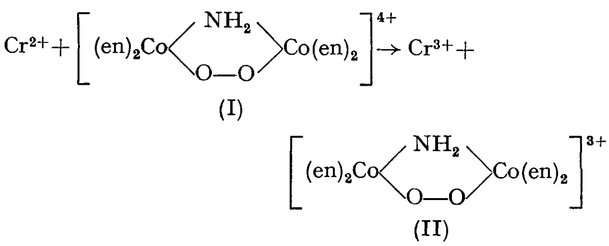
By M. R. HYDE and A. G. SYKES,*
(*Department of Inorganic and Structural Chemistry, The University, Leeds* LS2 9JT)

Summary μ-Superoxo- and μ-peroxo-dicobalt complexes react with Cr^{2+} by outer-sphere and inner-sphere mechanisms respectively; a μ-peroxo-complex with two different metal ions has been identified for the first time; rationalisation of activation parameters for an outer-sphere reaction has been made by considering corrections based upon ion-pair formations.

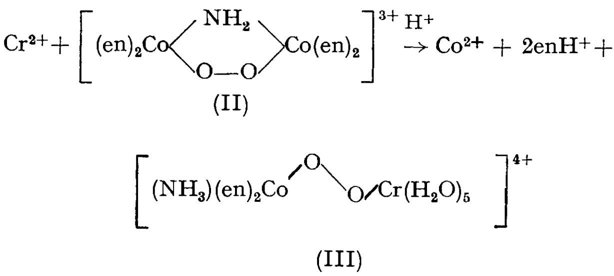
THE five-equivalent Cr^{2+} reduction[1] of the superoxo-complex, $(en)_2Co.\mu(NH_2,O_2){\cdot}Co(en)_2{}^{4+}$ has been investigated and the sequence of reactions determined. The first stage is the one-electron reduction of the superoxo-bridge, resulting in the corresponding μ-peroxo-complex.[2] A cobalt(III) centre is then reduced, but the remaining cobalt(III) is only attacked after the peroxo-bridge has been reduced. Spectroscopic measurements clearly indicate the retention of a dominant cobalt(III) chromophore until the final stage. We comment here on the first two stages of reduction.

The structures of the μ-amido-μ-superoxo- and μ-amido-μ-peroxo-bis[bis(ethylenediamine)cobalt(III)] complexes [(I) and (II) respectively] have been determined.[3] The Cr^{2+} reduction of (I) is too fast to follow by the stopped-flow method, and between 4 and 35°, $I = 2{\cdot}0$M ($LiClO_4$), $[H^+] = 0{\cdot}1$M, the rate constant $k_I > 1{\cdot}4 \times 10^5$ l mol^{-1}s^{-1}. Ion-exchange separation of the products after a 1:1 reaction (using Dowex 50W-X 12 resin),[4] gave one equivalent of hexa-aquochromium(III) as primary product, indicating an outer-sphere mechanism. The reduction of (II) (here designated B) by Cr^{2+} is fast, but can be studied using the stopped-flow method. At 25°, $I = 2{\cdot}0$M ($LiClO_4$), the reaction is first-order in Cr^{2+} and complex, and the rate constant $k_B = 2100$ l mol^{-1} s^{-1}. Activation parameters for k_B are $\Delta H_B^{\ddagger} = 7{\cdot}75 \pm 0{\cdot}25$ kcal mol^{-1} and $\Delta S_B^{\ddagger} = -17{\cdot}5 \pm 0{\cdot}9$ cal mol^{-1} K^{-1}. The protonated form, BH, with a similar structure to (II) does not contribute significantly to the reaction, and at 25°, $I = 2{\cdot}0$M ($LiClO_4$), $k_{BH} \approx 16$ l mol^{-1} s^{-1}. Ion-exchange separation after a 1:1 reaction of (II) gave no mononuclear chromium(III) species. Furthermore, when two equivalents of Cr^{2+} are reacted with (I) only one-equivalent of hexa-aquochromium(III) is produced.

It is concluded that the first stage of reaction [reduction of (I)] is outer-sphere, and the second stage inner-sphere. All the complex (II) is consumed in the second stage, and the spectrum of a species (III) is obtained [equations (1) and (2)].



(1)



(2)

Complexes containing a μ-peroxo-bridge with two different metal ions have not previously been identified. Details of the Cr^{2+} reduction of (III) will be reported in full elsewhere.[5]

Possible reasons why the μ-superoxo-complex (I) should react by an outer-sphere mechanism are, (a) the reaction is too fast for substitution into the Cr^{2+} co-ordination sphere to occur, and/or (b) the μ-superoxo-group has poor donor properties. With regard to (b) we note that whereas protonation of B to BH is extensive (protonation constant $K_P = 7{\cdot}14$ l mol^{-1} at 25°, $I = 0{\cdot}245$M),[6] protonation of (I) or any other superoxo-complex has not yet been detected. We therefore feel that (b) is relevant. However it is possible that (a), if effective, might over-ride (b). It is not immediately clear whether (a) is effective since an allowance for outer-sphere complex formation between Cr^{2+} and (I) is necessary. Thus $k_I = kK_0$, where k is the rate constant for the electron-transfer process, once the outer-sphere complex has formed, and K_0 is the outer-sphere association constant. If (a) is valid k should exceed the rate constant for the loss of water from $Cr(H_2O)_6^{2+}$ ($k = 10^8$—10^9 s^{-1} at 25°).[7]

The Cr^{2+} reduction of $(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5^{5+}$ proceeds by an outer-sphere mechanism.[8] At 25·2°, $I = 1{\cdot}0$M, the experimentally determined rate constant $k_S = 2{\cdot}2 \times 10^3$ l mol^{-1} s^{-1}, $\Delta H^\ddagger = 0{\cdot}5$ kcal mol^{-1}, and $\Delta S^\ddagger = -41{\cdot}0$ cal mol^{-1} K^{-1}, and in this and other studies† the enthalpy of activation clearly suggests a significant contribution from ion-pair formation. It is possible to calculate approximate values of K_0 using a modified form of the Fuoss equation,[9] where the calculations are necessarily very approximate for binuclear complexes. For interactions between 2+ and 5+ charges K_0 is $10^{-5.1}$ (5 Å separation) at $I = 0{\cdot}5$M, and since $k_S = kK_0$, this gives k for electron-transfer which borders on the substitution-controlled limit. From the temperature dependence introduced by the Fuoss equation‡ we estimate $\Delta H_0 = ca.\ -4{\cdot}7$ kcal mol^{-1} and $\Delta S_0 = ca.\ -38{\cdot}8$ cal mol^{-1} K^{-1}, and the activation parameters for k are thus $\Delta H^\ddagger = ca.\ 5{\cdot}2$ kcal mol^{-1} and $\Delta S^\ddagger = ca.\ -2{\cdot}2$ cal mol^{-1} K^{-1}. An outer-sphere process is presumably favourable because the superoxo-group is able to accept an electron without significant geometric reorganization. The rate constant for electron-transfer in the Cr^{2+} reduction of (I), after allowing for K_0 (*ca.* $10^{-4.1}$) may well exceed the Cr^{2+} substitution-controlled limit and is probably outer-sphere for this reason alone.

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† The V^{2+} reduction of $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{5+}$ is also outer-sphere and gives activation parameters $\Delta H^\ddagger = -1{\cdot}4 \pm 0{\cdot}6$ kcal mol^{-1}, and $\Delta S^\ddagger = -45 \pm 1{\cdot}5$ cal mol^{-1} K^{-1} (ref. 8). The one-equivalent oxidation of B with $Fe(phen)_3^{3+}$ also gives a negative enthalpy of activation, $\Delta H^\ddagger = -1{\cdot}1 \pm 0{\cdot}08$ kcal mol^{-1}, and $\Delta S^\ddagger = -35{\cdot}1 \pm 0{\cdot}08$ cal mol^{-1} K^{-1}, D. P. Keeton and A. G. Sykes, *J.C.S. Dalton*, 1972, 2530.

‡ We are grateful to Dr. D. Hague for suggesting this approach to us, and for discussions with Dr. G. Davies. Calculations similar to those used here were first reported by M. S. Zetter, Ph.D. Thesis, 1970, University of Kent. A further refinement which we have introduced is to allow for the variations of dielectric constant of an electrolytic solution upon the nature and concentration of the electrolyte. This gives for a 5 Å separation $\Delta H_0 = -(0{\cdot}47 \pm 0{\cdot}11)\, z_1z_2$ kcal mol^{-1} and $\Delta S_0 = -2{\cdot}3 - (3{\cdot}65 \pm 0{\cdot}35)\, z_1z_2$ cal mol^{-1} K^{-1} at 25°, $I = 0$—$0{\cdot}5$M, where z_1 and z_2 are the charges on the ions (with appropriate signs). At $I > 0{\cdot}5$M values of ΔH_0 and ΔS_0 are less satisfactory due to extensive association with ions constituting the ionic background. At higher separations up to 10 Å, ΔH_0 and ΔS_0 are both numerically smaller.

[1] Details of the preparation of this complex are to be found in M. B. Stevenson and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 2293.

[2] For a recent review of binuclear cobalt(III) complexes see A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, 1970, **13**, pp. 1—106.

[3] For details of the structures see U. Thewalt and R. E. Marsh, *Inorg. Chem.*, 1972, **11**, 351, and U. Thewalt, *Z. Naturforsch. B.* 1970, **25**, 596, also Table 1 (p. 6) of ref. 1.

[4] Procedure as in M. R. Hyde, R. Davies, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1838.

[5] M. R. Hyde and A. G. Sykes, to be published.

[6] M. Mori and J. A. Weil, *J. Amer. Chem. Soc.*, 1967, **89**, 3732.

[7] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307, A. McAuley and J. Hill, *Quart. Rev.*, 1969, **23**, pp. 18—36, and H. Diebler, *Ber. Bunsenges, Phys. Chem.*, 1970, **74**, 268.

[8] A. B. Hoffman and H. Taube, *Inorg. Chem.*, 1968, **7**, 1971.

[9] R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059.