Part I

ELECTRON TRANSFER PROCESSES

By

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Introduction

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The format of this Part follows closely that of the previous volumes in this series. Although some degree of selection has had to be imposed owing to the large number of papers involving electron-transfer processes, an attempt has been made to cover comprehensively all the areas in which studies are currently being undertaken. As in the previous volumes, compilations of data have been assembled to allow more direct comparison of rate constants and thermodynamic parameters of reactions of a similar type.

Differing aspects of the subject have been dealt with in several publications. A very readable account of the present 'state of the art' in inorganic mechanisms has been published by Tobe[1] in which there are chapters dealing with redox systems involving both interactions between two metal-ion complexes and also reactions where ligands are oxidized or reduced. A series of review articles on this subject has appeared in a volume edited by Edwards,[2] including an account of chromium(VI) oxidations of inorganic substrates,[3] where both one-electron and two-electron systems are discussed, together with the role of Cr^{V} and the fate of Cr^{IV} in these reactions.

Electron-transfer processes between two metal ions continue to be investigated and in several papers the importance of medium effects has been noted. In a re-examination of the role of co-ordinated water as a bridging ligand in the Cr^{II} reduction of penta-amminecobalt(III) complexes, the use of lithium perchlorate yields data[4] which are consistent with a single-term rate law instead of the two-term law noted previously in solutions where sodium perchlorate was used as the supporting electrolyte. Similar effects have also been observed in the corresponding reaction of the cobalt(III)–malonato-complexes.[5] The metal-ion reduction of cobalt(III) complexes containing co-ordinated sulphur donor atoms has been studied with interesting differences in reactivity when compared with the corresponding N- or O-donor systems.[6,7] Radical intermediates of sufficiently long life for spectrophotometric identification have been observed in the chromium(II) reduction of the corresponding carboxylato-

[1] M. L. Tobe, 'Inorganic Reaction Mechanisms', Nelson, London, 1972.
[2] *Progr. Inorg. Chem.*, ed. J. O. Edwards, Wiley, New York, Vol. 17, Part II, 1972.
[3] J. K. Beattie and G. P. Haight, ref. 2, p. 93.
[4] D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635.
[5] C. Lavalee and E. Deutsch, *Inorg. Chem.*, 1972, **11**, 3133.
[6] M. Gilroy, F. A. Sedor, and L. E. Bennett, *J.C.S. Chem. Comm.*, 1972, 181.
[7] J. H. Worrell, R. A. Goddard, E. M. Gupton, and T. A. Jackman, *Inorg. Chem.*, 1972, **11**, 2734.

penta-ammine complex ions.[8] A review has also been written[9] in which comparison has been made between vanadium(IV) and iron(II) as reductants in aqueous electron-transfer processes.

The plenary lectures at the 14th I.C.C.C. Meeting at Toronto have been published,[10] as have the papers presented at the Bressanone Conference.[11] Several other useful reviews of reactions involving metal ions have been published. The oxidation–reduction of the cobalt centre in vitamin B_{12} has been discussed[12] and recent developments in the bioinorganic chemistry of this complex have also been described.[13,14] Electron-transfer catalysts involving metalloenzyme systems have also been reviewed by Williams.[15] The role of transition metals in homogeneous catalysis has been described[16] and homolytic oxidation and reduction reactions of organic compounds by metallic ions have been reviewed.[17]

[8] E. S. Gould, *J. Amer. Chem. Soc.*, 1972, **94**, 4360.
[9] D. R. Rosseinsky, *Chem. Rev.*, 1972, **72**, 215.
[10] *Pure Appl. Chem.*, 1973, **33**, No. 4.
[11] *Coordination Chem. Rev.*, 1972, **8**, Nos. 1 and 2.
[12] J. M. Pratt, 'The Inorganic Chemistry of Vitamin B_{12}'. Academic Press, London, 1972.
[13] R. H. Prince and D. A. Stotter, *J. Inorg. Nuclear Chem.*, 1973, **35**, 321; J. Lewis, R. H. Prince, and D. A. Stotter, *ibid.*, p. 341.
[14] G. N. Schrauzer, *Pure Appl. Chem.*, 1973, **33**, 545.
[15] R. J. P. Williams, *Inorg. Chim. Acta, Rev.*, 1971, **5**, 137.
[16] R. G. Linck, 'Transition Metals in Homogeneous Catalysis', ed. G. N. Schrauzer, Marcel Dekker, New York, 1971, p. 297.
[17] J. S. Littler, 'M.T.P. International Review of Science', Organic Chemistry, Series 1, Vol. 10, ed. W. A. Waters, Butterworths, London, 1973, p. 237.