

Part I

ELECTRON TRANSFER PROCESSES

By
A. McAULEY

Introduction

BY A. McAULEY

The format of this Part closely follows that in Volume 1. Although a 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 as comprehensively as possible all the areas in which studies are currently being undertaken. Compilations of data have also been assembled to allow easier comparison of the rate constants and thermodynamic parameters of reactions of a similar type.

Electron transfer processes between two metal ions continue to be examined, and a recent monograph¹ sets out clearly the various modes of interaction between the reactant species. The effects of non-bridging ligands on these processes have been discussed,² the main influence of such groups, both on oxidant and reductant, being to change the activation free energy by altering the overall free energy of the reaction. Although the donor ligands involving either N- or O-co-ordination have been most utilized, the effects of thioether ligands as non-bridging ligands have also been studied.³ In the reactions of chromium(vi), the three-unit change in oxidation state contrasts with the (usually) single electron transfer step in most metal ion reactions. The reactions of this ion with both aquo-metal ions and complex species have been reviewed.⁴

Several other useful reviews of reactions involving metal ions have also been published. Redox reactions of chromium(III)-amine species have been described⁵ and a survey has been made of the solution chemistry together with reaction paths involved in the redox reactions of various plutonium species.⁶ Oxidation reactions of thallium(III) have also been described.⁷ Developments in the redox chemistry of peroxides have been reviewed,⁸ the nature of the reactions which involve iron(III) in various complexed forms providing a fascinating example of the manner in which geometry and co-ordination to the metal centre greatly affect the reactivity of the system. Redox properties of cobalt chelates, with delocalized

¹ H. Taube, 'Electron Transfer Processes in Solution', Academic Press, New York 1971.

² J. E. Earley in *Progr. Inorg. Chem.*, 1970, **13**, 243.

³ J. H. Worrell and T. A. Jackman, *J. Amer. Chem. Soc.*, 1971, **93**, 1045.

⁴ J. H. Espenson, *Accounts Chem. Res.*, 1970, **3**, 347.

⁵ C. S. Garner and D. A. House, in 'Transition Metal Chemistry', ed. R. L. Carlin, Marcel Dekker, New York, 1970, vol. 6, p. 226.

⁶ J. M. Cleveland, 'The Chemistry of Plutonium', Gordon and Breach, New York, 1970, p. 47.

⁷ A. G. Lee, 'The Chemistry of Thallium', Elsevier, Amsterdam, 1971, p. 295.

⁸ S. B. Brown, P. Jones, and A. Suggett, *Progr. Inorg. Chem.*, 1970, **13**, 159.

electronic structure have been described,⁹ and transfer processes involving metalloporphyrins have been reviewed.¹⁰ In the case of dithiolene complexes of transition metals,¹¹ the mode of reaction is influenced by solvent, the extent of conjugation of the ligands, and substituents on the donor atoms.

The oxidation of organic substrates by metal-ion species continues to be a fruitful source of study. The question of bonded and non-bonded interactions in one-electron transfer processes has been explored,¹² and several papers have been devoted to the nature of possible metal ion-substrate intermediates.¹³⁻¹⁵ The question of covalent bond formation between oxidant and reductant as a pre-requisite to the electron transfer step has also been investigated for a large number of reactions.¹⁶ The mechanisms of reactions of lead(IV) with organic species have been reviewed¹⁷ and the reactions of oxygen-containing radicals and hydrogen atoms with metal ions in various oxidation states have been surveyed.¹⁸ The introduction of such ions into a system where radical polymerization is occurring results in retardation of the chain polymerization, both oxidizing and reducing ions being involved in the termination processes. The role of electrons in radical systems has been examined,¹⁹ and heterolytic oxidation reactions of hydrogen peroxide in acid solutions have also been reviewed.²⁰

⁹ G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc. (A)*, 1970, 2870.

¹⁰ P. Hambright, *Co-ordination Chem. Rev.*, 1971, 6, 249.

¹¹ J. A. McCleverty, in 'Reactions of Molecules at Electrodes', ed. N. S. Hush, J. Wiley and Sons, London, 1971.

¹² J. S. Littler in 'Essays on Free-Radical Chemistry', Chemical Society Special Publication No. 24, p. 383.

¹³ C. F. Wells and C. Barnes, *J. Chem. Soc. (A)*, 1971, 380.

¹⁴ K. B. Wiberg and S. K. Mukherjee, *J. Amer. Chem. Soc.*, 1971, 93, 2543.

¹⁵ C. M. Bell, E. D. McKenzie, and J. Orton, *Inorg. Chim. Acta*, 1971, 5, 109.

¹⁶ E. Chaffee and J. O. Edwards, ref. 2, p. 205.

¹⁷ J. B. Aylward, *Quart. Rev.*, 1971, 25, 407.

¹⁸ E. T. Denisov, *Uspekhi Khim.*, 1971, 40, 43.

¹⁹ T. J. Kemp and T. J. Stone, ref. 12, p. 365.

²⁰ T. A. Turney, *New Zealand J. Sci.*, 1971 14, 299.