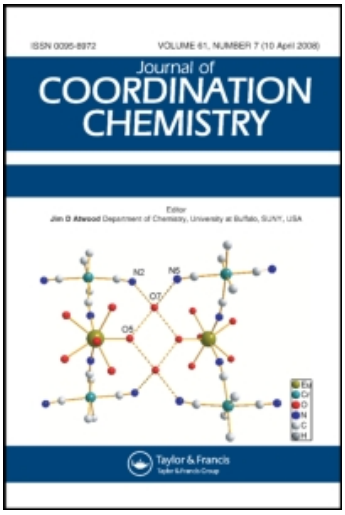

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A review of: "ELECTRON TRANSFER REACTIONS OF COMPLEX IONS IN SOLUTION, by Henry Taube. Academic Press, New York, 1970. v 103 pp. (S5.75)"

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Book Reviews

Publishers are invited to submit, via the editors, books for review in this journal. Any newly published book dealing with a subject relevant to the field of coordination chemistry will be welcome; this includes clear ancillary experimental or theoretical relationships, e.g. from chemistry, biophysics, etc. All books received will be acknowledged in print.

ELECTRON TRANSFER REACTIONS OF COMPLEX IONS IN SOLUTION, by Henry Taube. Academic Press, New York, 1970. v + 103 pp. ($5.75)

This volume is an expanded and updated treatment of the material presented in a series of four lectures by Professor Henry Taube at the Polytechnic Institute of Brooklyn in late 1967. The material, which is referenced, extends into late 1968, with most of the later references coming from Professor Taube's laboratories. This book reflects the author's broad, personal interest in the field of electron transfer chemistry and is a masterpiece in expositional clarity. It is regrettable that such a book was not made available 6 months to a year earlier.

The relaxed, personal style and the inclusion of present and future directions for potentially fruitful investigations in the field were particularly appealing to this reviewer. The use of Roman numerals for both chapter headings and subsections is, at first, confusing. Material in the first three chapters is quite readable, even by the nonspecialist. Specialists in the field will find the fourth chapter most interesting and challenging, although the nonspecialist will certainly want to wade into this fascinating, new area of research.

Approximately one-fourth of the textual material is devoted to a discussion of the hydration of ions and their substitution behavior. The reason for this emphasis is twofold: (1) the author's personal involvement began here, historically speaking; and (2) an understanding of these phenomena is of fundamental importance in the interpretation of mechanisms for electron transfer reactions. The brief descriptions of the methods used in the study of ion hydration and lability should be quite helpful to the nonspecialist, while the specialist is challenged to contemplate new, first-order methods for those ions not amenable to study by present techniques. It is a little surprising that no mention is made of the interchange mechanisms set forth by Langford. It would appear that the substitution data which are discussed on the basis of an S_N1 mechanism are equally well accounted for by Langford's I_d mechanism. Although no changes in the basic conclusions are necessary, the values of k in Table I-1 should be recognized as experimental values so that comparisons (such as those made by the author) between dissimilar species can be corrected for symmetry number factors.

The second chapter deals with activated complexes for electron transfer. There is a brief analysis of the effects and role of cations on the rates of outer-sphere reactions followed by an interesting discussion of relative rate comparisons for various isotopically substituted oxidants. Although certain aspects which appear to be fundamental to the electron transfer process are alluded to in this chapter, the nonspecialist is given little feeling or appreciation for those factors (and their relative magnitudes) which influence the rates of outer-sphere reactions. For the inner-sphere process certain tracer and isotopic fractionation results are nicely exploited for important, detailed information about the inner-sphere activated complex. Consideration is also given to the possibility of seven-coordinate intermediate formation in the inner-sphere mechanism.

In the third chapter, the effects of simple ligands on electron transfer rates for both inner- and outer-sphere reactions are cast in terms of formal equilibrium quotients for the substitution of one halide ion by another in activated complexes. "Both bond formation and permeability to electron flow are, in principle, factors affecting the affinity of activated complexes for ligands . . ." Activation parameters are assessed, albeit unsuccessfully, for mechanistic

information for numerous simple halo ligand systems. For inner-sphere reactions the resonance and chemical mechanisms of electron transfer are discussed in some detail with the conclusion that the latter, in contrast to the former, should be characterized by rates which are relatively insensitive to the identity of the metal ion in the oxidant. A limitation to the distinction between these mechanisms is also noted. Double bridging and halide ion bridging in two-electron transfer reactions are also discussed, though only briefly.

The subject of induced electron transfer is considered in the fourth and final chapter. Various examples of this phenomenon are examined to demonstrate its utility in exploring details of redox mechanisms. For example, it opens the possibility of studying electron transfer from a radical (organic ligand) located at a remote position through an intervening bond system to the acceptor center. Moreover, if the internal oxidant does not influence the action of the external one, the mechanism for oxidation by the external oxidant can be adduced as a one- or two-electron transfer process depending upon whether the internal oxidant is reduced or not. In this chapter the discussion increases considerably in complexity, although through no fault of the author, and the material is best distilled from several careful readings. Additional stimulus for investigation in this area is provided by the possibility that the elusive $Co(NH_3)_5^{2+}$ *may* be an intermediate in the MnO_4^- oxidation of $Co(NH_3)_5O_2CH^{2+}$.

In summary, the author has exceeded the high expectations set forth for him in the foreword, "By showing how the facts of yesterday have given rise to today's concepts, deductions, hopes, fears, and guesses, they should serve as guides to the research and thinking of tomorrow."

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