Chemical Co., St. Louis, Mo., for a supply of the starting ketone IV.

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THE OUTER SPHERE ACTIVATED COMPLEX IN THE REDUCTION OF Co(III) SPECIES[1]

Sir:

In much of the work done on oxidation-reduction reactions of Cr(II), the role of the bridged activated complex has been emphasized.[2,3,4,5] In particular, when Co(III) or Cr(III) complexes are oxidizing agents, proof has been adduced that the reactions proceed through activated complexes in which there is interpenetration of coördination spheres. We now report the results of experiments using a complex of Cr(II) which reacts by means of activated complexes in which there is no interpenetration in the same sense.

The reaction of Cr^{++}aq. with $Co(NH_3)_6^{+++}$ is slow[2] and the specific rate at 25° at $\mu = 0.41$ (Cl^- as the anion) has now been measured as 0.16 $m.^{-1}$ $min.^{-1}$. However, when Cr^{++}aq. is converted to $Cr(dip)_3^{++}$ (dip = 2,2′ bipyridine), the rate of the reaction is much increased. Thus at $\mu = 0.20$ (NaCl) and 25°, the specific rate of the reaction between $Cr(dip)_3^{++}$ and $Co(NH_3)_6^{+++}$ is 1.5×10^4 $m.^{-1}$ $min.^{-1}$. The rate is independent of the concentration of 2,2′ pyridine as long as a sufficient excess is present, and it is independent of *p*H over a considerable range, 5.5 to 3.5. It has been shown that 3 bipyridine groups are associated with each Cr^{++} under these conditions, and that the chromium product is $Cr(dip)_3^{+++}$. At low *p*H, the rate of the reaction increases, presumably because $Cr(dip)^{++}$ or $Cr(dip)_2^{++}$ reacts with $Co(NH_3)_6^{+++}$ even more rapidly than does $Cr(dip)_3^{++}$.

The interest in the observation we report is not so much that 2,2′-bipyridine so markedly increases the reactivity of Cr^{++} for $Co(NH_3)_6^{+++}$, but rather that it opens up the possibility of studying the reduction of the large class of Co(III) complexes by a reagent which acts retaining an intact coördination sphere. Considerable work with Cr^{++}aq., which with all Co(III) complexes studied except $Co(NH_3)_6^{+++}$ and perhaps $Co(NH_3)_5OH_2^{+++}$ makes use of a bridged activated complex, has already been done. Thus a systematic study can be made of the influence on the rate by each of the distinct mechanisms of changing the composition of the oxidizing agents; furthermore the chemical and isotopic effects characteristic of each type of mechanism can now be assessed. It perhaps needs to be emphasized that Co(III) complexes qualify especially for these studies because they undergo substitution slowly.

It is interesting to note that even when a bridged activated complex is not involved, $Co(NH_3)_5OH_2^{+++}$ reacts with a reducing agent much more rapidly than does $Co(NH_3)_6^{+++}$, and the rate ratio using $Cr(dip)_3^{++}$ is *ca.* 90. On changing the solvent from H_2O to D_2O, the rate at which $Co(NH_3)_6^{+++}$ reacts with $Cr(dip)_3^{++}$ is reduced by less than 10%, but a slight decrease, *ca.* 30%, is noted when $Co(NH_3)_6^{+++}$ is used as oxidant. However, when $Co(NH_3)_5OD_2^{+++}$ reacts in D_2O the rate is decreased by a factor of *ca.* 2.5 from the rate for $Co(NH_3)_5OH_2^{+++}$ in H_2O (this rate ratio can be compared to the decrease of 3.9 observed[6] in making a similar comparison with Cr^{++}aq. as reductant). A striking difference between the two kinds of mechanisms is in the sensitivity to the change from $Co(NH_3)_5OH_2^{+++}$ to $Co(NH_3)_5OH^{++}$. This change occasions an increase in specific rate by a factor of *ca.* 10^7 when Cr^{++}aq. is the reductant,[6] but by less than 100, and perhaps by as little as 10, when $Cr(dip)_3^{++}$ reacts.

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[1] This work is supported by the Atomic Energy Commission under Contract #AT(11-1)-378.

[2] H. Taube and H. Myers, THIS JOURNAL, **76**, 2103 (1954).

[3] H. Taube and E. L. King, *ibid.*, **76**, 4053 (1954).

[4] D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

[5] A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958).

[6] A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959).

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BOOK REVIEWS

Nouveau Traité de Chimie Minerâle. Tome IV. Group II: Glucinium – Magnesium – Calcium – Strontium – Baryum – Radium. PAUL PASCAL, Membre de l'Institut, Professeur honorâire à la Sorbonne. Masson et Cie., 120 Boulevard Saint-Germain, Paris 6, France. 1958. xxxix + 973 pp. 17 × 26 cm. Price: Broché, 7.500 fr., cartonné toilé, 8.500 fr.

The preparation of a systematic and encyclopaedic treatise on inorganic chemistry was no trifling job, seventy-five years ago; every decade that has passed since then has made it a progressively more daunting enterprise. The Arcadian simplicity of Roscoe and Schorlemmer and the earliest editions of Gmelin have given place to multi-volume productions of size and price so formidable as to restrict them almost automatically to the institutional market. The reviewer is inclined to regard the 1908–1937 edition of Abegg-Auerbach as the last comprehensive account of inorganic chemistry that had some claim to readability; those skeptical of the validity of such a claim are reminded of Donnan on copper. Mellor's treatise, staggering as the single-handled labor of a sexagenarian with little more than secretarial assistance, is known to all of us as a mine of information and references on early experimental observations but it is only intermittently readable. The gallant attempt of Yost and Russell to use a portion of the Periodic Table to illustrate how a modern systematic treatise on inorganic chemistry might be written has been much and justly admired; but their effort has, alas, provoked no "envious fever of emulation."

The encyclopaedic treatise is here to stay unless it is doomed to ultimate displacement by the punch-card. Since no such work is likely to complete a cycle of revision in less