S 81. *The Electron Transfer (Exchange) between Cobaltous and Cobaltic Amine Complexes.*

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A study has been made of the electron-transfer processes from the trisethylenediamine complex of bivalent to that of tervalent cobalt, and similarly for the hexammino-complexes. Further, the cross-reactions where one form of cobalt is complexed with ammonia and the other with ethylenediamine have been investigated.

THE process of electron transfer between two ions is a fundamental one. When this process occurs between ions differing only in oxidation number, it can only be studied with the aid of isotope-tracer methods, for the only observable result is isotope exchange. This paper reports, first, the detailed study of the electron-transfer process from the trisethylenediamine complex of bivalent cobalt to that of the same complex of tervalent cobalt, in which the reaction proceeds at an easily measurable rate (half-time, 2—50 hours), and secondly, tests on the same process with the hexammino-complexes, in which the reaction is very much slower. These two reactions proceed without free-energy change. Surveys are also included of the cross-reactions where one form of cobalt is initially present in a hexammino-complex and the other in a trisethylenediamine complex. The reaction with free-energy decrease is quite fast (falling to half the ultimate exchange in 4·4 minutes), and the corresponding one with free-energy increase appears to be exceedingly slow. These studies serve to characterize some interesting kinetic properties of the cobalt complexes involved.

EXPERIMENTAL.

Great care was exercised with the purity of reagents used. Ethylenediamine (en) monohydrate was purified by distillation, the fraction boiling in the range 117·5—118·5° being retained, and new preparations were made frequently.

Trisethylenediaminocobalt(III) chloride, $[Co(en)_3]Cl_3,3H_2O$, was prepared by air-oxidation of cobaltous chloride in the presence of excess of ethylenediamine and recrystallized three times. A new stock was prepared approximately every month. Hexamminocobalt(III) chloride, $[Co(NH_3)_6]Cl_3$, was prepared by oxidation of concentrated cobaltous chloride in concentrated ammonia by diamminosilver chloride, recrystallized twice, and washed with alcohol. The trisethylenediaminocobalt(II) complex or the hexamminocobalt(II) complex was synthesized at the start of a run by adding excess of the amine or ammonia as the last reagent to mixtures of the other components freed from air. Transformation of the cobaltous ion into $[Co(en)_3]^{++}$ by a total ethylenediamine concentration of 0·55M. was more than 99·7% complete, whereas transformation into $[Co(NH_3)_6]^{++}$ by a total ammonia concentration of 5·7M. was approximately 60% complete (Bjerrum, " Metal Ammine Formation in Aqueous Solution," Haas and Son, Copenhagen, 1940). The ionic strength μ was made up to a predetermined value, generally by the addition of C. P. barium chloride.

The radioactive ^{60}Co tracer of 5·3-years half-life was prepared in the M.I.T. cyclotron and carefully purified from possible radioactive contaminants. A correction was made for the inactive cobalt carrier introduced into the system with this preparation. Radiometric assay was carried out by counting the γ-rays from suitable aliquots diluted to 100 ml. in a double-walled cylindrical glass cell placed around a brass Geiger–Müller counter. Appropriate corrections were made for background activity, for loss by coincidence of counts, and for slight differences in geometry among duplicate glass cells. Generally the activity was introduced in the cobaltous complex, and that accumulated in the cobaltic complex computed from the amount observed in the cobaltous complex subtracted from the initial amount. Suitable tests showed complete material balance for activity and no dependence of the reaction rate on the choice of species " labelled."

Early tests showed the necessity of eliminating oxygen as completely as possible to minimize a transitory catalysis of the reaction. This was accomplished fairly well by prolonged de-aeration of the reaction mixture with purified nitrogen just before addition of the complex-former for the cobaltous ion, and carrying out the rate run in a closed system under nitrogen pressure. The nitrogen was bubbled through 1-m. column of 0·2M-chromous chloride continuously regenerated with zinc amalgam, and washed with silver nitrate and water, following H. M. Stone's directions (private communication). Nitrogen was used to drive 10-ml. aliquots into a pipette adjoining the reaction vessel from which they could be withdrawn.

An analysis was made by discharging the samples into a 10—15% excess of hydrochloric acid, which destroys the cobaltous complexes without affecting the cobaltic complexes even during several days. The exchange is thereby brought to a standstill. The cobaltous ion was separated from the cobaltic complex by extraction from 25—30% ammonium thiocyanate with 1 : 1 ether–amyl alcohol. After each phase had been washed once with the other, cross-contamination was found to be less than 0·05%, which is also the upper limit on exchange induced in the separation method.

In an exchange reaction without net molecular transformation of the type

$$[Co^*(en)_3]^{++} + [Co(en)_3]^{+++} \rightarrow [Co^*(en)_3]^{+++} + [Co(en)_3]^{++} \quad . \; . \; . \; . \quad (1)$$

where a is the concentration of $[Co(en)_3]^{++}$ of observed ^{60}Co activity x, and b is the concentration of $[Co(en)_3]^{+++}$ of observed activity y, the rate of increase of activity y is given (McKay, *Nature*, 1938, **142**, 997) as

$$dy/dt = R(x/a - y/b) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where R is the constant frequency of collisions leading to exchange in the given mixture, a function of the concentrations of the constituents of the activated complex :

$$R = (a)^m(b)^n(d)^p(e)^q \ldots. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

whose functional dependence may be determined from runs with different values of the concentrations of possible reactants. The asymptotic activity y_∞ at infinite time is

$$y_\infty = x_0 b/(a + b) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

where x_0 is the initial activity, all as $[Co^*(en)_3]^{++}$.

The integrated exchange equation is

$$-\ln_e(1 - y/y_\infty) = \frac{R(a + b)}{ab} t = \lambda t \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

The data obtained in the rate studies were analyzed by determining the slope λ of plots of $-\ln(1 - y/y_\infty)$ against time t in hours, using only data from linear sections. Equation (5) corresponds to first-order exchange (McKay, *loc. cit.*) and the half-life for exchange, $t_{1/2}$, is equal to $0{\cdot}693/\lambda$.

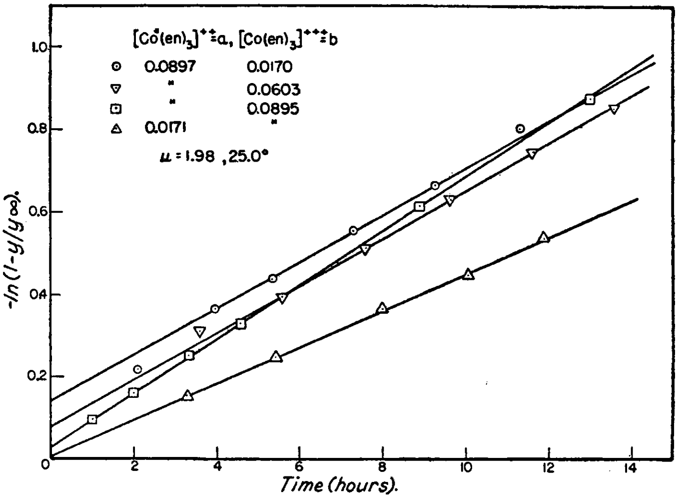
RESULTS.

Over 50 runs were made to study exchange reaction (1) with ethylenediamine complexes. After preliminary testing of conditions for optimum operation and for the possibilities of undesired catalysis, systematic studies were made at ionic strength 0·98 and 1·98 at 25·0° and 45·1° over ranges of $[Co(en)_3]^{++}$ and $[Co(en)_3]^{+++}$ concentrations from 0·0170 to 0·0895M.

It was early observed that the ingress of oxygen in small quantities, enough to oxidize only a few percent. of the cobaltous complex, led to more than 10 times the corresponding accretion of activity in the cobaltic complex in a few hours. Fortunately, this catalytic effect is transitory, and disappears within 2 hours. It leads in the rate studies to an apparent ordinate intercept in the plot for equation (5) of $-\ln(1 - y/y_\infty)$ against time. No run was accepted in which this intercept exceeded 0·2 unit, and generally the values were much lower. After about a day the analytical curve sometimes showed a tendency to turn up slowly. This effect was ascribed to the slow diffusion of oxygen into the reaction vessel from the plastic tubing, and the data from this region were not used. Other tests showed great acceleration of the reaction by powdered silica gel, nickel wire, and powdered glass. Tests showed that the rates in vessels of lusteroid, polystyrene, and glass are indistinguishable, but that paraffin coating gives acceleration of about two-fold. More detailed tests using glass beads of 16 times the surface area of the reactor wall showed 4% heterogeneous catalysis in the ordinary run at the upper limits of $[Co(en)_3]^{++}$ and $[Co(en)_3]^{+++}$ and 8·6% at the lower limits. These figures are probably high because of the greater accessibility of surface to all the solution in the bead tests. Old preparations of the cobaltic complex often gave high rates, presumably owing to the catalytic power of traces of cobaltic hydroxide.

Logarithmic analysis by equation (5) of typical runs is given in Fig. 1, with the best lines drawn through the data, including in several cases a point off the plot. An arbitrary probable error has been assigned to each λ value on the basis of length of the linear portion of the curve and deviation of points from the line in this region.

FIG. 1.



Analysis of typical rate curves for the exchange between labelled trisethylenediaminocobalt (II) *and trisethylenediaminocobalt* (III) *ions;* $\mu = 1·98$, 25·0°.

A series of measurements was made to determine if there was appreciable dependence of the rate on ethylenediamine concentration and on pH. The pH was lowered by substituting ethylenediamine monohydrochloride for much of the barium chloride. The results, presented in Table I, show that neither of these has a significant effect on λ or R, the slight acceleration in runs XV and XIV being a salt effect to be discussed later. The possibility of specific chloride effect (catalysis) was also eliminated in a run in which barium chlorate was substituted for barium chloride, as shown in Table II.

It seems reasonable that the rate function R for the exchange reaction should be of first order with respect to the concentration of both the cobaltous and the cobaltic complex, or that the only exponents in equation (3) differing from zero should be m and n, both unity. This

TABLE I.

Absence of rate dependence on ethylenediamine concentration and on pH.

$[Co(en)_3]^{++}$ = 0·0165M.; $[Co(en)_3]^{+++}$ = 0·0895M.; μ = 0·98; T = 25·0°.

Run.	Ethylenediamine, M.	pH.	Slope λ.	Half-life, hrs.
XVIII, 2	0·55	11·4	0·0244 ± 0·0007	28·4
XIII	1·10	11·6	0·0244 ± 0·0007	28·4
XV	0·55	10·0	0·0265 ± 0·0008	26·2
XIV	0·55	10·2	0·0259 ± 0·0008	26·8

TABLE II.

Absence of specific effect of chloride ion.

$[Co(en)_3]^{++}$ = 0·0170M.; $[Co(en)_3]^{+++}$ = 0·0170M.; μ = 1·98; T = 25·0°.

Run.	Ba^{++}.	Cl^-.	ClO_3^-.	Slope λ.	Half-life, hrs.
XXIX	0·608	1·303	—	0·0196 ± 0·0010	35·3
XLII	0·608	0·085	1·217	0·0190 ± 0·0006	36·4

point, which was very hard to establish except as an idealization, will be reported in detail elsewhere. The concentration of one complex was held at 0·017 or at 0·089M., and the other was varied over this range. Representative data are presented in Table III. The R value was computed for each run, and its logarithm plotted against the logarithm of a or b, the concentration of the complex varied. The data showed essentially linear relationship on this basis, and the slopes m for dependence on $[Co(en)_3]^{++}$ or n for dependence on $[Co(en)_3]^{+++}$ were obtained. The exponent m had the values 1·00, 0·95, and 1·01 for low b, and 0·88, 0·93, and 0·93 for high b under the three sets of conditions μ = 0·98, 25·0°; μ = 1·98, 25·0° and 45·1°. The values for the exponent n were correspondingly 0·68, 0·83, and 0·89 at low a and 0·58, 0·79, and 0·81 at high a.

The dependence of electron transfer on the concentration of cobaltous complex is satisfactorily of first order. That on cobaltic concentration is obviously complicated. It appears to be impossible to explain the low values of n by the assumption of any type of secondary salt effects (polymerization or specific complex formation). The occurrence of polymerization of $[Co(en)_3]^{+++}$ would lead either to constant values of n for different values of b for complete polymerization, or to reaction orders concave downward for partial polymerization. Neither of these conditions is observed. Furthermore, increasing μ should enhance polymerization and increase n. An explanation was found in Bjerrum's concepts of ionic association (*Kgl. Dansk. Vid. Selsk. Medd.*, 1926, No. 9, 7). The abnormal reaction order has its origin in the effect of electrolyte composition upon the activity coefficients of the reactants and the activated complex, since the contribution of the ter-univalent electrolyte to the ionic strength varied from 10 to 55% in typical tests of the b dependence. There is thus less chloride ion for general anion

TABLE III.

Dependence of rate on concentration of the two complexes, ionic strength, and temperature.

Run.	$[Co(en)_3]^{++}$.	$[Co(en)_3]^{+++}$.	Ba^{++}.	Slope λ, hr.$^{-1}$.	Half-life, hrs.
		μ = 0·98; T = 25·0°.			
XVI, 1, 2, 3, 4	0·0170	0·0170	0·275	0·0137 ± 0·0005	50·6
XIX, 1, 3, 4	0·0894	0·0895	0·058	0·0336 ± 0·0012	20·6
XLV	0·0895	0·0895	— *	0·0415 ± 0·0012	16·7
		μ = 0·98; T = 45·1°.			
XLI	0·0170	0·0170	0·275	0·0533 ± 0·0016	13·0
		μ = 1·98; T = 25·0°.			
XXIX	0·0171	0·0170	0·608	0·0196 ± 0·0010	35·4
XXVII	0·0897	0·0895	0·391	0·0656 ± 0·0020	10·6
		μ = 1·98; T = 45·1°.			
XXXIX	0·0170	0·0170	0·608	0·090 ± 0·003	7·7
XXXVII	0·0895	0·0895	0·391	0·350 ± 0·010	1·98

* 0·174M-NaCl substituted for 0·058M-$BaCl_2$.

catalysis at high b. The prediction that an increase in rate should occur by substituting sodium chloride for barium chloride is confirmed in Table III, as is the prediction that the reaction order should approach unity as the ionic strength is increased. This competitive action between multivalent cations for anions may be considered as a primary salt effect of second order (cations decreasing cation–cation reactivity) as distinguished from the normal Brønsted primary salt effect (anions increasing cation–cation reactivity) commonly observed. The lack of change in rate on substitution of chlorate for chloride is ascribed to the probable agreement of the radius sums for cobalt complexes and chlorate or chloride ion.

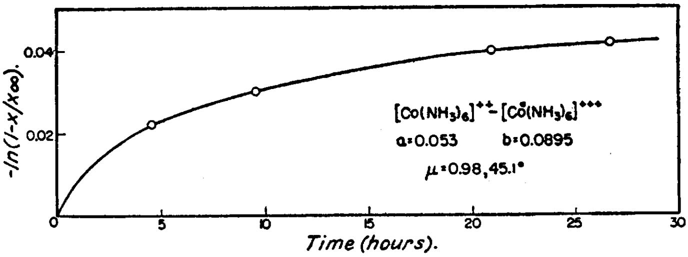
Because of the ionic complexities of the system, it is not surprising that the Arrhenius heat of activation rises for low a and b from 12,750 cals./mole at $\mu = 0{\cdot}98$ to 14,300 at $\mu = 1{\cdot}98$ and for high a and b has the value 15,750 at $\mu = 1{\cdot}98$.

The corresponding exchange reaction between hexammine complexes

$$[Co(NH_3)_6]^{++} + [Co^*(NH_3)_6]^{+++} = [Co(NH_3)_6]^{+++} + [Co^*(NH_3)_6]^{++} \quad . \quad . \quad . \quad (6)$$

was found to be much slower. Following the appearance of the paper of McCallum and Hoshowsky (*J. Chem. Physics*, 1948, **16**, 254) reporting virtual absence of exchange, the problem was re-examined under more favourable conditions. The reaction mixture was 0·089M. in cobaltous complexes, 60% in the form of $Co(NH_3)_6^{++}$, 0·0895M. in $[Co(NH_3)_6]^{+++}$, 5·7M. in ammonia, 0·174M. in ammonium chloride (to lower the pH to about 10·7 to inhibit decomposition of the cobaltic complex to cobaltic hydroxide which might catalyze the reaction), of ionic strength 0·98, and the rate was studied at 45·1°. The logarithmic analysis is given in Fig. 2, with x substituted for y because the tracer was initially in the cobaltic form. The reaction curve was one of the worst encountered for oxygen catalysis because of the small value of exchange that occurred and the large volume of ammonia reagent used. The minimum slope (between points at 20·9 and 26·7 hours) of $\lambda = 0{\cdot}00033$ corresponds to an upper limit, because of the probable catalysis by oxygen diffusing in by this time. Correspondingly the half-life for exchange is taken to be greater than 80 days under these conditions. A blank run with $[Co^*(NH_3)_6]Cl_3$ for 36 hours without cobaltous complex until the time of analysis produced no activity in the cobaltous extract.

FIG. 2.



Analysis of the rate of exchange between hexamminocobalt (II) *and labelled hexamminocobalt* (III) *ions in* 5M-*ammonia*, μ=0·98, 45·1°.

It seemed useful to use the same techniques to study the cross-reactions between ethylenediamine and ammino-complexes. According to Bjerrum (*loc. cit.*) the molar electrode potentials of the hexammino-system and the trisethylenediamine system at 30° and $\mu = 1$ are $-0{\cdot}057$ volt and $+0{\cdot}259$ volt (the latter more reducing).

The reaction

$$[Co^*(en)_3]^{++} + [Co(NH_3)_6]^{+++} = [Co^*(en)_3]^{+++} + [Co(NH_3)_6]^{++} \quad . \quad . \quad . \quad (7)$$

should therefore go with a free-energy decrease of 7300 cals./mole. The decrease of activity x in the cobaltous fraction was followed as a function of time in a solution with both complexes initially at 0·0895M. (a), with ethylenediamine excess at 0·27M., ionic strength 0·98 at 25·0°. It is expected that reaction (7) will be followed rapidly by transformation of the hexamminocobalt(II) complex into the ethylenediamine complex :

$$[Co(NH_3)_6]^{++} + 3en = [Co(en)_3]^{++} + 6NH_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In fact, analysis of the cobaltous product after completion of the reaction by both gravimetric and spectrophotometric procedures showed that it was $[Co(en)_3]Cl_3$.

The reaction proceeded rapidly, following a rate equation based on the assumption of equation (7) as rate determining, followed rapidly by equation (8). This equation predicts that the

$[Co(NH_3)_6]^{+++}$ concentration r should decrease exponentially with time from an initial value of r_0 with a decay constant of k_2a. The rate of disappearance of activity x in the cobaltous fraction is thus

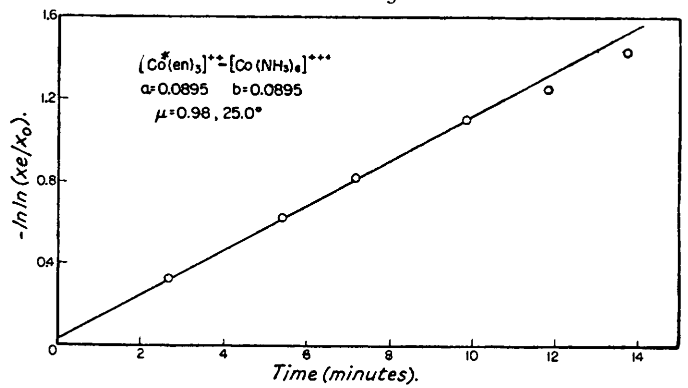
$$-dx/dt = k_2xr_0e^{-k_2at} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Taking into account the facts that at zero time $r_0 = a$ in the given reaction and $x = x_0$, it is found that at $t = \infty$, $x_\infty = x_0/e$, and the predicted rate equation can be expressed as

$$-\ln_e\ln_e xe/x_0 = k_2at \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The log–log analysis of the run is given in Fig. 3. The slope of the line corresponds to a value of k_2a equal to 0·109 ± 0·003 min.$^{-1}$. At 3·5 minutes, the rate of exchange had fallen to half its initial value, at 4·4 minutes the value of x had fallen halfway to its asymptotic value $0{\cdot}386x_0$, and at 13·8 minutes (the last point) the value of $0{\cdot}47x_0$ was observed. After several hours, activity was found distributed equally between the two oxidation states, probably owing to participation of reaction (6) at enhanced rate from oxygen catalysis. Unfortunately, time did not permit the determination of the reaction constants at another temperature.

FIG. 3.



Analysis of the rate of exchange between labelled trisethylenediaminocobalt (II) *and hexamminocobalt* (III) *ions with excess of ethylenediamine,* $\mu = 0{\cdot}98$, 25·0°.

The reverse of reaction (7) with a free-energy increase of 7,300 cals./mole would be expected to be slower by the factor 2×10^5 at the same concentrations and temperature. A run was made at ionic strength 0·98 at 45·1° in 5·7M-ammonia plus 0·174M-ammonium chloride, with $[Co(NH_3)_6]^{++} = 0{\cdot}053$M. and $[Co^*(en)_3]^{+++} = 0{\cdot}0895$M. A very small exchange was observed, increasing erratically to 0·15%, in 27 hours, corresponding to a lower limit of the half-life for exchange of about 500 days. This value, on the limits of error, has not been corrected for any oxygen catalysis. Because of the position of the equilibrium in reaction (7), however, this would not necessarily measure the rate of the reaction unless the rate of the reverse of reaction (8) serves to bring the $[Co^*(en)_3]^{++}$ product into the reservoir of the $[Co(NH_3)_6]^{++}$ complex.

TABLE IV.

Summaries of bimolecular rate constants k_2 *for exchange from data for complexes at* 0·0895M., $\mu = 0{\cdot}98$. [Units for k_2 : l./mole-hour.]

Co^{II} complex.	Co^{III} complex.	k_2 (25·0°).	k_2 (45·1°).
$[Co(en)_3]^{++}$	$[Co(en)_3]^{+++}$	0·188	(0·85) *
$[Co(NH_3)_6]^{++}$	$[Co(NH_3)_6]^{+++}$	—	<0·0023
$[Co(en_3)]^{++}$	$[Co(NH_3)_6]^{+++}$	73	—
$[Co(NH_3)_6]^{++}$	$[Co(en)_3]^{+++}$	—	<0·0004 (?)

* Extrapolated.

DISCUSSION.

To facilitate comparison of the rate studies reported here, the data for the bimolecular rate constants k_2 for the four reactions studied are presented in Table IV. This constant is equal to $\lambda/(a + b)$ for the data treated by equation (5). Because of the salt effect, the data have been computed uniformly from observations at $a = b = 0{\cdot}0895$ at ionic strength 0·98, and are presented for the two temperatures.

It is noteworthy that the rate constant and activation energy for the ethylenediamine system is roughly equal to the corresponding values for the thallous–thallic system in nitric acid (Harbottle and Dodson, *J. Amer. Chem. Soc.*, 1948, **70**, 880; Prestwood and Wahl. *ibid.*, p. 880). The rate constant itself at 25° is not much greater than that calculated for the ferrous–ferric system (0·07) in perchloric acid (Van Alten and Rice, *ibid.*, p. 883). The rates of exchange in both these systems of aquo-complexes are, on the other hand, very sensitive to chloride catalysis because of the formation of specific chloride complexes of the oxidized forms.

It is remarkable that such a difference exists between the rate in the ethylenediamine system and that in the hexammino-system. If the entropy of activation is due largely to electrostatic factors as suggested by Moelwyn-Hughes (*Proc. Roy. Soc.*, 1936, **155**, *A*, 308), the entropy values should be nearly the same for the two reactions. It would seem, then, that the slowness of exchange with the second is due to an activation-energy increment of about 4000 cals./mole. This increment may come from the necessity of closer approach of the two complexes for effective electron transfer. This effect may perhaps be related to the smaller covalent character of the hexammine complex, as reflected in the electrode potentials, which indicates that the unpaired electron on the cobaltous atom should have more 3*d* character in 3*d*–4*d* hybridization and consequently less extension in space.

The catalysis by oxygen may be explained by the formation of a metastable cobaltous complex $[CoX_5O_2]^{++}$, where X is an amino-nitrogen atom of ethylenediamine. The O_2 addendum may provide a resonance path to project the unpaired electron from the cobaltous atom further out for transfer purposes. It is probable that the oxygen addendum is ejected from the cobaltic complex formed, and used repeatedly by other cobaltous ions before it is eventually reduced to peroxide and then to water.

The increase in the rate constant noted in the reaction between $[Co(en)_3]^{++}$ and $[Co(NH_3)_6]^{+++}$ over that in the symmetrical $[Co(en)_3]^{++}$–$[Co(en)_3]^{+++}$ system is probably due to the availability of part of the free-energy decrease to lower the heat of activation. Half of the free-energy decrease would account for the observed increase in rate constant.

As suggested in the discussion in the previous section, a clear-cut interpretation cannot yet be given of the apparent infinitesimal exchange in the system $[Co(NH_3)_6]^{++}$–$[Co(en)_3]^{+++}$ in excess of ammonia. From data given by Bjerrum (*loc. cit.*) it is expected that reaction (8) will have an equilibrium constant of about 10^9. The interpretation of the exchange data will depend on the clarification of the relative rates of the reverse of reactions (7) and (8).

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