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### Electron Transfer Rates through the Use of Optical Activity. I. The Electron Transfer Racemization of Ethylenediaminetetraacetatocobaltate(III)—an Example of Electron Transfer without Retention of Configuration

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Systems in which electron transfer between central metal ions of the same element is studied by the use of optical activity may be classed into two categories: (1) those in which absolute configuration is conserved and (2) those in which configuration is not conserved. The former obey the McKay equation  $-\ln \left( \frac{\alpha_t - \alpha_\infty}{\alpha_0 - \alpha_\infty} \right) = R \left[ \frac{(a+b)}{ab} \right]_t$ , while the latter are described by a modified equation  $-\ln(\alpha_t/\alpha_0) = Rt/a$ . The study of the rate of racemization of ethylenediaminetetraacetatocobaltate (III) has been carried out in the presence of the corresponding cobalt(II) complex as a function of concentrations, pH, temperature and nature of the supporting electrolyte. Rates in H<sub>2</sub>O and D<sub>2</sub>O are compared. The over-all rate law is  $-\ln(\alpha_t/\alpha_0) = \left[ 2k' + \left\{ k_1 \left[ \frac{(H^+)}{K + (H^+)} \right] + k_2 \left[ \frac{K}{K + (H^+)} \right] \right\} b \right] t$ . The concentration dependence confirms this system as belonging to category 2 above. No appreciable deuterium isotope effect is observed. While the system was insensitive to general ionic strength effects, a specific cation effect was observed with barium ion. From these results, the most reasonable mechanism for the electron transfer reaction appears to involve direct electron transfer from the reductant to the oxidant, with the original coordination spheres intact in the transition state. The electron transfer rate constants obtained by the use of optical activity in the present investigation are compatible with those obtained by the use of isotopic tracers.

#### Introduction

Isotopic tracers have been used extensively in the study of the electron transfer processes occurring between ions differing only in oxidation state. Such reactions proceed with no net free energy change other than the small effects arising from the redistribution of the originally concentrated isotope. The subject has been reviewed in the recent literature.<sup>1,2</sup>

In 1950, Dwyer and Gyarfás<sup>3</sup> suggested that the use of optical activity should provide a second technique for the study of the rates of electron transfer reactions in suitable systems. The suggestion was offered in conjunction with the observation that the optical rotation vanishes rapidly when equivalent amounts of *d*-tris-(bipyridine)-osmium(III) (specific rotation, +200°) and *l*-tris-(bipyridine)-osmium(II) (specific rotation -2200°) are

mixed. Attempts have been made to apply the measurement of optical activity to the determination of rates of electron transfer for several systems<sup>4,5</sup>; however, the systems previously investigated have either been found to be too rapid<sup>4</sup> or too poorly reproducible<sup>5</sup> to permit detailed study. The results reported here constitute the first detailed study of the rate of electron transfer through the use of optical activity. The system employed involves *d*-ethylenediaminetetraacetatocobaltate(III), *d*-[Co<sup>III</sup>Y]<sup>-</sup>, and ethylenediaminetetraacetatocobaltate(II), [Co<sup>II</sup>Y]<sup>-</sup>. The reaction of interest exhibits no deleterious catalytic effects and proceeds at conveniently measurable rates with satisfactory reproducibility. The results reported here are compared with those obtained from tracer studies<sup>6</sup> on the same system, showing excellent agreement with the limited data from the earlier isotopic experiments. The electron transfer racemization rate has been studied as a function of

(1) H. Taube, "Advances in Inorganic Chemistry and Radiochemistry," Ed. by H. J. Emeleus and A. F. Sharpe, Academic Press, Inc., New York, N. Y., 1959.

(2) B. J. Zwolinski, R. A. Marcus and H. Eyring, *Chem. Revs.*, **55**, 157 (1955).

(3) F. P. Dwyer and E. C. Gyarfás, *Nature*, **166**, 481 (1950).

(4) E. Eichler and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 4145 (1958).

(5) D. H. Busch and W. J. Stratton, unpublished results.

(6) A. W. Adamson and K. S. Vorres, *J. Inorg. Nucl. Chem.*, **3**, 206 (1956).

concentration, pH, temperature and nature of supporting ionic medium. The deuterium isotope effect and specific ion effects have been considered. The rate expressions for electron transfer racemization reactions have been derived.

#### Rate Expressions

The results of kinetic studies depending on the use of isotopic tracers usually are analyzed in terms of the McKay equation,<sup>7</sup> in which  $a$  and  $b$

$$-\ln(1 - x/x_\infty) = R[(a + b)/ab]t \quad (1)$$

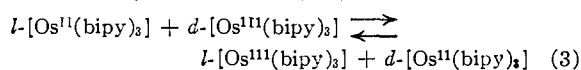
are the initial concentrations of the exchanging species,  $x_\infty$  is the equilibrium concentration of the tagged species,  $x$  is its concentration at any time,  $t$ , and  $R$  is the equilibrium exchange rate, which is assumed to be independent of the presence of the tracer. The equilibrium rate  $R$  is assumed to be a function of the initial concentrations of the exchanging species

$$R = ka^m b^n \quad (2)$$

where  $m$  and  $n$  are the orders with respect to these reactants and  $k$  is the true rate constant.

Two distinct classes of reactions and, consequently, two different equations must be employed in the case of electron transfer processes studied by means of racemization measurements. One class involves the conservation of configuration throughout the course of the reaction. In this case, both exchanging species are configurationally stable. The second kind of reaction proceeds with loss of configuration because one of the exchanging species is configurationally unstable.

Reactions proceeding with the *complete retention of configuration* may be exemplified by the system composed of the 2,2'-bipyridine complexes of osmium(II) and osmium(III).



The configurations of the osmium(II) and osmium(III) complexes are quite stable and the only change in the system is an electron transfer, so that the total concentration of *dextro* and *levo* entities is unaltered, in the course of the reaction. It is merely the distribution of the configurations between the two oxidation states which changes. In such systems, the McKay equation is followed rigorously, for the concentration of the tracer is also conserved. This is not an assumption but has been derived. In terms of rotation ( $\alpha_t$  is total rotation at time  $t$ ;  $\alpha_0$  is the initial rotation; and  $\alpha_\infty$  is the rotation at equilibrium) the rate expression becomes

$$-\ln\left(\frac{\alpha_t - \alpha_\infty}{\alpha_0 - \alpha_\infty}\right) = R[(a + b)/ab]t \quad (4)$$

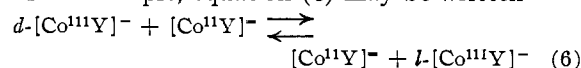
Again  $R$  is a function of the initial concentrations of the reactants (equation 2). If  $m$  and  $n$  are assumed to be unity, the final expression is

$$-\ln\left(\frac{\alpha_t - \alpha_\infty}{\alpha_0 - \alpha_\infty}\right) = k(a + b)t \quad (5)$$

and the rate is dependent upon the initial concentrations of both exchanging species.

The rate expression for the reactions proceeding with *loss of configuration* must be separately de-

rived. Taking the cobalt(II) and cobalt(III) complexes of ethylenediaminetetraacetic acid ( $\text{H}_4\text{Y}$ ) as an example, equation (6) may be written



Since the cobalt(II) complex exhibits no configurational stability, it must be considered to exist as an equimolar mixture of *dextro* and *levo* forms throughout the course of the reaction.

The rate equation may be derived as

$$-dx/dt = R(x/a)^{1/2} - R(1/2)(a - x)/a = R(2x - a)/2a \quad (7)$$

$$\text{Concentration of } d\text{-[Co}^{III}\text{Y}]^- = x$$

$$\text{Concentration of } [\text{Co}^{III}\text{Y}]^- = a$$

$$\text{Concentration of } [\text{Co}^{II}\text{Y}]^- = b$$

Integration of equation 7 gives 8

$$-\ln(2x - a)/a = Rt/a \quad (8)$$

Since it can be shown that  $\alpha_t$  is proportional to  $(2x - a)$  and  $\alpha_0$  is proportional to  $a$ , equation 8 may be rewritten as 9

$$-\ln(\alpha_t/\alpha_0) = Rt/a \quad (9)$$

Recalling equation 2 and assuming  $m$  and  $n$  equal to unity leads to 10

$$-\ln(\alpha_t/\alpha_0) = kbt \quad (10)$$

From equation 10 it may be seen that the rate is parametrically dependent only on the initial concentration of the configurationally unstable species.

Further comment on the process given in equation 6 may be helpful. The relationships existing in such systems come about as a result of the rapid racemization of the optically active cobalt(II) complex, so that equation 6 might be thought of as a series of reactions involving, (a) formation of optically active ( $d$ -)[ $\text{Co}^{III}\text{Y}$ ] from  $d$ -[ $\text{Co}^{III}\text{Y}$ ], followed by (b) racemization of the cobalt(II) complex. If a more detailed description, such as this, is substituted for equation 6, care must be taken to properly introduce the racemization of the cobalt(II) complex, for it is this reaction which removes the parametric dependence of the rate on the total concentration of the cobalt complex.

#### Experimental

Optically active potassium ethylenediaminetetraacetatocobaltate-(III) 2-hydrate was prepared by the method of Dwyer and Garvan,<sup>8</sup> using optically active *cis*-dinitro-bis(ethylenediamine)-cobalt(III) bromide as a resolving agent. Ethylenediaminetetraacetatocobaltate(II) was prepared by mixing stock solutions of known concentrations of disodium dihydrogen ethylenediaminetetraacetic acid and cobalt(II) nitrate 6-hydrate. The pH of the reacting solution was adjusted with nitric acid, sodium hydroxide or suitable buffer. Ionic strength of the solutions was adjusted with nitrate salts. The stoppered flask containing this solution was then placed in a thermostat and the samples were withdrawn periodically for the measurement of optical rotations.

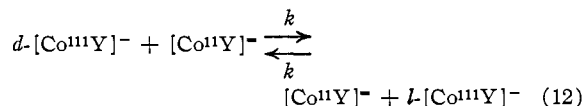
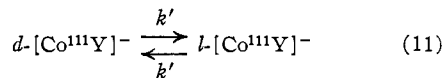
The optical rotations were determined with a precision of  $\pm 0.003^\circ$  using a Rudolph Model 80 photoelectric polarimeter, and the ratio of the rotation at a given time to that of a sample withdrawn immediately after the initiation of the reaction was taken as a measure of the extent of the reaction. Most of the rotations were measured using a Hanovia Xenon high pressure arc at a wave length of 450  $\mu$  and some of the later runs were made using a mercury lamp at a wave length of 436  $\mu$ . The latter is more convenient. The zero of the polarimeter was determined using the racemate at the same concentration as was used in measuring the rotation. A one decimeter tube was used for all the readings.

(8) F. P. Dwyer and F. L. Garvan, *Inorg. Syntheses*, **6**, 192 (1960).

(7) H. A. C. McKay, *Nature*, **142**, 997 (1938).

## Results and Discussion

The hexadentate complex,  $d\text{-[Co}^{\text{III}}\text{Y]}^-$ , undergoes racemization at temperatures of 100, 90, 85 and 74°, and this racemization is catalyzed by the presence of  $[\text{Co}^{\text{II}}\text{Y}]^-$  (Table I). The pseudo first-order rate  $R'$  is determined from the slope of a straight line which is obtained when  $-\log(\alpha_t/\alpha_0)$  is plotted against time  $t$  in accord with equation 10. From the data it is seen that racemization occurs by two paths, both of which are first order in  $d\text{-[Co}^{\text{III}}\text{Y]}^-$  and one of which must depend on  $[\text{Co}^{\text{II}}\text{Y}]^-$ . It is therefore assumed that racemization is occurring simultaneously by a thermal process described by equation 11 and by an electron transfer process described by equation 12.



From the equations 11 and 12, the form of the experimental rate law is obtained (equation 13)

$$-\ln(\alpha_t/\alpha_0) = (kb + 2k')t \quad (13)$$

The experimental pseudo first-order rate constant  $R'$  may be interpreted in terms of the two constants,  $k$  and  $k'$ , and the concentration of  $[\text{Co}^{\text{II}}\text{Y}]^-$ ,  $b$ , using the relationship

$$R' = kb + 2k' \quad (14)$$

where  $k$  is the electron transfer rate constant and  $k'$  is the thermal racemization rate constant. A plot of  $R'$  versus  $b$  (Table I) produces a straight line, with  $k$  and  $k'$  being determined from the slope and the intercept, respectively. The values of the rate constants from such a determination at 100° are  $k' = 0.015 \text{ hr.}^{-1}$ ;  $k = 2.5 \text{ M}^{-1} \text{ hr.}^{-1}$ . The value of  $k'$  also was determined independently as  $0.015 \text{ hr.}^{-1}$ , in complete agreement with the value given above (see first three entries, Table II). The absence of any parametric rate dependence on the initial concentration of  $d\text{-[Co}^{\text{III}}\text{Y]}^-$  is clearly shown by the entries in rows two and four of Table I.

TABLE I

PSEUDO FIRST-ORDER RATE CONSTANTS FOR RACEMIZATION OF  $[\text{Co}^{\text{III}}\text{Y}]^-$  AT 100°

$[\text{Co}^{\text{III}}\text{Y}]^-, M$	$[\text{Co}^{\text{II}}\text{Y}]^-, M$	$pH$	$R'$ (hr. <sup>-1</sup> )
0.001	0.00	2.0	0.029
.001	.01	2.2	.054
.0194	.00	2.2	.030
.0194	.01	2.1	.054
.0194	.02	2.0	.085
.0194	.03	1.9	.105
.0194	.04	1.8	.139
.0194	.05	1.9	.166

The simple rate constant expressed above is complicated by a dependence on  $pH$  over the range within which the electron transfer rate has been found measurable. The process is impeded at both high and low  $pH$  values and reproducible data have been obtained only within the range of  $pH$  from 2.0 to 4.0. The thermal racemization

TABLE II

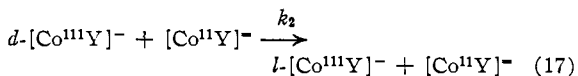
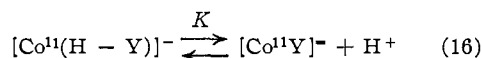
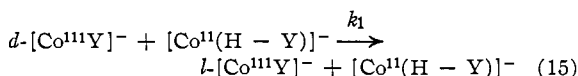
TEMPERATURE AND  $pH$  DEPENDENCE OF THE RATE OF ELECTRON TRANSFER<sup>a</sup>

Temp., °C.	$pH$	$[\text{Co}^{\text{III}}\text{Y}]^-$	$[\text{Co}^{\text{II}}\text{Y}]^-$	$R'$ (hr. <sup>-1</sup> )	$k'$ (hr. <sup>-1</sup> )	$k$ (M <sup>-1</sup> hr. <sup>-1</sup> )
100	2.0	0.001	0.000	0.029	0.015	..
100	3.0	.001	.000	.028	.014	..
100	4.0	.001	.000	.030	.015	..
100	2.0	.0194	.030	.105	.015	2.5
100	2.5	.0194	.030	.096	.015	2.2
100	3.0	.0194	.030	.070	.015	1.4
100	3.5	.0194	.030	.056	.015	0.90
100	4.0	.0194	.030	.053	.015	.77
90	2.0	.0194	.030	.035	.0032	.95
90	3.0	.0194	.030	.023	.0032	.57
90	4.0	.0194	.030	.013	.0032	.23
85	2.0	.0194	.030	.019	.0013	.55
74	2.0	.0194	.030	.0073	....	.24
74	3.0	.0194	.030	.0041	....	.14
74	4.0	.0194	.030	.0027	....	.09

<sup>a</sup> All data are the average of two or more (as many as 10) duplicate experiments.  $k'$  is determined separately with similar care.

rate constant  $k'$  is independent of  $pH$  within this interval at 100° and at 90°; however, this process is accelerated at high  $pH$ .<sup>9</sup> Data on the  $pH$  dependence are reported in Table II. The lower limit of  $pH$  amenable to study is dictated by destruction of the cobalt(II) complex at high  $H^+$ , while the cobalt(III) complex racemizes rapidly at high  $pH$  thus imposing the upper limit.

In a simple model,  $[\text{Co}^{\text{II}}\text{Y}]^-$  is considered to exist in protonated and unprotonated forms which are related by the equilibrium given in equation 16. It is assumed that electron transfer catalyzed racemization takes place simultaneously by two paths as shown in equations 15 and 17.



The rate expression is (equation 18)

$$-dx/dt = \left\{ k_1 \left[ \frac{(\text{H}^+)}{K + (\text{H}^+)} \right] + k_2 \left[ \frac{K}{K + (\text{H}^+)} \right] \right\} ab \quad (18)$$

From this, the second-order rate constant  $k$  is given by equation 19

$$k = k_1 \left[ \frac{(\text{H}^+)}{K + (\text{H}^+)} \right] + k_2 \left[ \frac{K}{K + (\text{H}^+)} \right] \quad (19)$$

From the variation of  $k$  with  $pH$  (Table II),  $K$ ,  $k_1$  and  $k_2$  have been evaluated and are reported in Table III. The cobalt(II) complex,  $[\text{Co}^{\text{II}}\text{Y}]^-$ , has been reported previously to have a  $pK$  of 3.0 at 20°. Formally the process given in equation 15 appears to involve the transfer of a hydrogen atom rather than electron transfer. These alter-

(9) D. W. Cooke and D. H. Busch, Paper Presented before the 136th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

(10) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

natives are considered at greater length below. However, it should be emphasized that the rate law given is an empirical one and that it may also be derived without reference to the nature of the exchange process (*i.e.*, the McKay equation).

TABLE III

CONSTANTS DERIVED FROM pH DEPENDENCE OF RATE			
$T, ^\circ\text{C.}$	$K$	$k_1 (M^{-1} \text{hr.}^{-1})$	$k_2 (M^{-1} \text{hr.}^{-1})$
100	$2.0 \times 10^{-3}$	2.9	0.50
90	$1.1 \times 10^{-3}$	1.0	.29
74	$1.9 \times 10^{-3}$	0.26	.082

From the temperature dependence data (Table II) the *apparent* activation energy (for  $k$  measured at pH of 2) for electron transfer is found to be 21 kcal./mole, in agreement with the value of 22 kcal./mole obtained by Adamson and Vorres<sup>6</sup> by the isotopic method. The entropy of activation is  $-15.4$  cal./deg.-mole, and that obtained by Adamson and Vorres is  $-16.6$  cal./deg.-mole. The activation energy for thermal racemization is 40.6 kcal./mole, and the entropy of activation is 20.6 cal./deg.-mole.

Enthalpies and entropies of activation have been calculated for the reactions given in equation 15 and 17 ( $k_1$  and  $k_2$ ). These are shown in Table IV.

TABLE IV

Constant	$\Delta H^\ddagger$ (kcal./mole)	$\Delta S^\ddagger$ (e.u.)
$k_1$	24.0	-9.0
$k_2$	20.0	-21.0

The data contained in Table III reveal that the protonated cobalt(II) complex  $[\text{Co}^{\text{II}}(\text{H} - \text{Y})]^-$  (equation 15), undergoes more rapid charge transfer with  $[\text{Co}^{\text{III}}\text{Y}]^-$  than does the unprotonated species (equation 17). The expected structure of the protonated cobalt(II) complex involves pentadentate coordination of the EDTA with the sixth position in the coordination sphere of the cobalt atom presumably occupied by a water molecule. This expectation is based on the known structure of a similar nickel(II) complex.<sup>11</sup> The assumption of such a structure presents a difficulty from the standpoint of the symmetry requirements for the actual electron transfer process, since a pentadentate structure is not at all likely for the cobalt(III) complex under the conditions of these experiments.<sup>12</sup>

Although the rate law facilitates the formulations of the cobalt(II) species which are involved in the activated complex, it cannot specify the precise role of the hydrogen ion in the electron transfer process. Questions remain to be considered as to whether the hydrogen atom is transferred, acts as a bridge to facilitate electron transfer or merely serves to reduce electrostatic interactions between reactants; whether direct electron transfer occurs in solution; and what part the coordinated water and the ligand play in the electron transfer process.

When bond forming, or breaking, is important in transition state, direct determination of the

(11) G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 556 (1959).

(12) I. A. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958); R. Dyke and W. C. E. Higginson, *ibid.*, 1998 (1960).

actual point of bond fission within the complex is not possible though it may sometimes be inferred. Recently the difference in the rates at which isotopically substituted molecules react has been used to provide finer details concerning the activated state in examples of reactions of metal complexes.<sup>13-17</sup> The results of the present investigation show that the rate constant is not appreciably affected by the change from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$  as solvent (Table V). From the maximum uncertainties of these data, it is clear that there is virtually no isotope effect which may be associated with hydrogen atom transfer.

TABLE V

RELATIVE RATES IN THE SOLVENTS  $\text{D}_2\text{O}$  AND  $\text{H}_2\text{O}$  ( $\mu = 0.2$ ; pH 2)

$T, ^\circ\text{C.}$	$[\text{Co}^{\text{III}}\text{Y}]^-$	$[\text{Co}^{\text{II}}\text{Y}]^-$	$R^{\text{H}_2\text{O}}$ (hr. <sup>-1</sup> )	$R^{\text{D}_2\text{O}}$ (hr. <sup>-1</sup> )
90	0.0194	0.0300	$0.035 \pm 0.002^a$	$0.034 \pm 0.003^b$
74	0.0194	0.0300	$0.0073 \pm 0.0004^c$	$0.0073 \pm 0.0010^c$

<sup>a</sup> Average of ten experiments. <sup>b</sup> Average of four experiments. <sup>c</sup> Average of six experiments.

The system under consideration may be characterized as an example of specific hydrogen ion catalysis. Among cases of specific hydrogen ion catalysis for acids of widely varying type and strengths, the ratios of equilibrium constants in  $\text{H}_2\text{O}$  to those in  $\text{D}_2\text{O}$ ,  $K_{\text{H}}/K_{\text{D}}$ , are generally in the range from 2 to 4.<sup>15</sup> Consequently, the observed ratio of the second-order rate constant in  $\text{H}_2\text{O}$  to that in  $\text{D}_2\text{O}$ ,  $k_{\text{H}}/k_{\text{D}}$  is unity or less than unity. It is characteristic of reactions of this type that the bonding of the proton is virtually unaltered in the transition state. In this case, the normal isotope effect is not observed.

Since the reaction given by equation 15 proceeds more rapidly than the competing path (equation 17), the rate in  $\text{D}_2\text{O}$  should be enhanced by the probable shift of the pre-equilibrium in favor of the acid  $[\text{Co}^{\text{II}}(\text{D} - \text{Y})]^-$ . Because the ions  $[\text{Co}^{\text{II}}(\text{D} - \text{Y})]^-$  and  $[\text{Co}^{\text{II}}(\text{H} - \text{Y})]^-$  are moderately strong acids, the isotope effect would be minimal. In addition, the subsequent charge transfer reaction might exhibit a small, normal isotope effect, thus providing opposing effects which would ultimately decrease the net isotope effect. The cobalt(II) complex exists largely as the protonated species at low pH, and, under these conditions the system should be most sensitive to an isotope effect of the type arising from the modification of bonds to hydrogen in the transition state.<sup>18</sup> At a pH of two, the predicted isotope effect from the pre-equilibrium is substantially less than the combined errors of the determination of the rate constants in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . Therefore, in all likelihood, a mechanism involving transfer or bridging by hy-

(13) Dr. R. Stranks, "Modern Coordination Chemistry," Ed. by J. Lewis and R. S. Wilkins, Interscience Publishers, Inc., New York, N. Y., 1960.

(14) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(15) F. A. Long and J. Bigeleisen, *Trans. Faraday Soc.*, **65**, 2077 (1959).

(16) J. Hudis and R. W. Dodson, *J. Am. Chem. Soc.*, **78**, 911 (1956).

(17) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, New York, 1959.

(18) J. C. Sullivan, D. Cohen and J. C. Hindman, *J. Am. Chem. Soc.*, **79**, 3672, 4029 (1957).

drogen atoms should give rise to a rate ratio substantially larger than that observed. Within experimental error, the rates in the two solvents are identical (Table V).

The theory of direct electron transfer as developed by Marcus assumes only "weak overlap" between orbitals on the exchanging atoms in the transition state.<sup>19,20</sup> According to this model, the exchanging species are presumed to come together in the transition state and undergo electron transfer with their original coordination spheres intact. Such a process requires close matching of the two exchanging species in the transition state; *i.e.*, their bond lengths, electronic configurations and solvation spheres must be identical at the instant of electron transfer. Even if it is assumed that both the cobalt(III) and cobalt(II) complexes involve hexadentate coordination in the present system, considerable reorganization of the structure of either or both of the cobalt complexes might be required in the formation of the transition state. Such a rearrangement should be associated with a higher activation energy for the path involving the protonated species than for that in which  $[\text{Co}^{\text{II}}\text{Y}]^-$  undergoes exchange. A qualitative agreement with this suggestion is seen in Table IV.

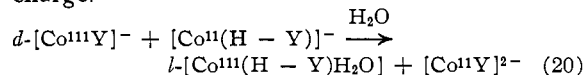
Since, in general, the electrostatic charges of the exchanging species will be different, the role of solvation has received considerable attention. The Franck-Condon principle imposes the restriction that the solvent configuration about the activated complex be a non-equilibrium state. This has been the principal concern of the theory of Marcus.<sup>19,20</sup> The value of the free energy of activation, as given by this theory, is in reasonable agreement with that found experimentally for a number of systems; however, the theory greatly overestimates the rates of electron transfer in cobalt(III)-cobalt(II) systems. The dilatory nature of the charge transfer process in these cases has been discussed in terms of the differing electronic structures and bond lengths of the corresponding cobalt(II) and cobalt(III) complexes.<sup>1,6</sup> Despite the limitations of the Marcus theory, it is interesting to consider the predictions made with regard to entropy of activation. The ratio of the entropies of activation for the two paths for electron transfer in the cobalt(II)-cobalt(III) ethylenediaminetetraacetic acid system is approximately two (Table IV). This is in agreement with the ratio predicted by Marcus' theory. The calculated values of the entropy of activation using the Marcus theory are considerably smaller than the experimental values. This may be due to the fact that the actual entropy of activation consists of a number of terms: the coulombic term, the solvent reorganization term and the ligand field term. However, the Marcus theory does not account for the last term, the ligand field effect. The observed difference in the rates for the two paths may be explained with comparable success by simpler electrostatic theories. In the path involving the protonated species, hydrogen ion may merely serve to reduce electrostatic interactions between the two reactants. Sutin and Gordon<sup>21</sup>

(19) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).

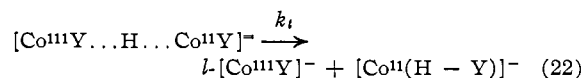
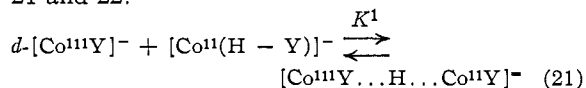
(20) R. A. Marcus, *ibid.*, **26**, 867 (1957).

suggest that the effects of protonation on the rate of oxidation of ferrous ion by tris-(1,10-phenanthroline)-iron(III) may also be understood in terms of a simple electrostatic model.

An additional complication arises with regard to the process described by equation 15. It is to be expected that direct electron transfer would produce a new chemical species,  $[\text{Co}^{\text{III}}(\text{H} - \text{Y})]$ , and the reaction would therefore not involve zero free energy charge. In view of the known rapid and extensive conversion<sup>22</sup> of the pentadentate complex  $[\text{Co}^{\text{III}}(\text{H} - \text{Y})\text{H}_2\text{O}]$  into the hexadentate  $[\text{Co}^{\text{III}}\text{Y}]^-$ , one expects the process given in equation 20 to proceed with a positive free energy charge.



A two step mechanism for the acid-catalyzed path appears to accord with the assembled observations. The first step is presumed to be the rapid formation of a very weak "complex" (equilibrium) in which the proton is symmetrically arranged between the cobalt(II) and cobalt(III) complexes. The second step may then involve the rate-determining electron transfer event, followed by rapid collapse of the complex to give the products shown in equation 15. This is shown in equations 21 and 22.



The rate (for this path alone) is given by equation 23

$$-dx/dt = k_t K^1 (d\text{-}[\text{Co}^{\text{III}}\text{Y}]^-)([\text{Co}^{\text{II}}(\text{H} - \text{Y})]^-) \quad (23)$$

This scheme has the following advantages: (a) neither the formation of a hydrogen bridge, nor the transfer of the hydrogen atom is assumed to occur in the rate-determining step. (b) The reaction may proceed with zero free energy change by direct electron transfer. (c) The apparent electrostatic role of the proton in accelerating the reaction is easily understood.

The simple Debye-Hückel theory predicts that the rates of reaction between ions of charges  $Z_A$  and  $Z_B$  should vary with ionic strength. However, broadly speaking, these predictions have been confirmed for  $\mu \leq 0.01$ . At high ionic strengths, serious deviations from the predicted behavior are observed, since not only does the theory fail to predict the activity coefficients of the ions, but most complex ions, being highly charged, are substantially associated under these conditions.<sup>13</sup> Ion association can cause anomalous ionic strength effects in that the associated complex ion may subsequently react at a rate characteristic of its reduced charge. This is a general ion effect. In addition, there is some evidence<sup>23</sup> that ion pair formation may promote the rate of electron transfer

(21) N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, **83**, 70 (1961).

(22) I. A. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958); R. Dyke and W. C. E. Higginson, *ibid.*, 1998 (1960).

(23) L. Gjertsen and A. C. Wahl, *J. Am. Chem. Soc.*, **81**, 1572 (1959); J. C. Sheppard and A. C. Wahl, *ibid.*, **79**, 1020 (1957).

in other less obvious ways. This implies specific ion effects. For the present system, the reaction is insensitive to changes in ionic strength; however, all measurements have, of necessity, been conducted at higher than ideal ionic strengths. The rates are essentially the same in the absence of added salt ( $\mu = 0.2$ ) and at  $\mu = 0.7$  in the presence of  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{RbNO}_3$  or  $\text{CsCl}$ . The process is accelerated by about 10% at  $\mu = 0.7$

in the presence of  $\text{Ba}(\text{NO}_3)_2$  in agreement with the report by Adamson and Vorres.<sup>6</sup>

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## Electron Transfer Rates through the Use of Optical Activity. II. The Electron Transfer Racemization of Propylenediaminetetraacetatocobaltate(III)—an Example of Electron Transfer with Retention of Configuration

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The rate of electron transfer has been studied in the system composed of the hexadentate propylenediaminetetraacetate complexes of cobalt(II) and cobalt(III) by the use of optical activity. The extreme stereospecificity of the optically active ligand is established, and it has been demonstrated that the less stable isomer of the cobalt(III) complex must exist in relative concentrations of less than 1% at equilibrium, if it exists at all. The form of the rate law clearly delineates this system as involving electron transfer with complete retention of configuration for both exchanging species. It is most reasonably concluded that the labile cobalt(II) complex exists predominantly as a single enantiomer, the configuration of the octahedron being determined by that of the ligand. The cause of this stereospecificity is discernable in terms of the structures of the compounds. A novel statistical resolution of optical isomers is presented.

### Introduction

The system composed of propylenediaminetetraacetatocobaltate(III) and propylenediaminetetraacetatocobaltate(II) (the ligand shall be abbreviated as PDTA hereafter) has been chosen for the purpose of extending investigations<sup>1</sup> of electron transfer processes which catalyze racemization.

The cobalt(III) complex has been resolved into optical antipodes by Dwyer and Garvan<sup>2</sup> who employed active *cis*-dinitrobis-(ethylenediamine)-cobalt(III) bromide. The cobalt(II) complex, which ordinarily is expected to be labile and configurationally unstable, exhibits a characteristic optical rotation in solution.<sup>3</sup> It has been concluded by Bosnick, Dwyer and Sargeson<sup>3</sup> that the cobalt(II) complex exhibits configurational stability as a result of the fact that propylenediaminetetraacetic acid exists in a preferred enantiomeric form when combined with divalent and trivalent metal ions.

The fact that both the oxidant and the reductant conserve configuration determines that the system  $[\text{Co}(\text{PDTA})]^- - [\text{Co}(\text{PDTA})]^-$  be an example of electron transfer catalyzed racemization proceeding with conservation of configuration through the course of the reaction. In this respect, it is comparable to the system composed of  $[\text{Os}(\text{dipy})_3]^{+3} - [\text{Os}(\text{dipy})_3]^{+2}$ . It previously has been shown that such systems should obey the same rate law as those involving isotopic tracers.<sup>1</sup>

The study of the rate of electron transfer in the PDTA system also was expected to provide funda-

mental information on the nature of certain stereospecific relationships, since both the ligand and the cobalt complex are optically active. Comprehensive accounts of stereospecificity have been given by Bailar and Corey<sup>4,5</sup> and Basolo and Pearson.<sup>6</sup>

Theoretically, the hexadentate complex  $[\text{Co}(\text{PDTA})]^-$  can exist in four different isomeric forms, *D-l*, *D-d*, *L-d* and *L-l* (the capital letters refer to the sign of rotation of the whole complex and the small letters, to that of the ligand, usually at the *D*-line of sodium). Dwyer and Garvan<sup>2</sup> attempted to isolate all the possible isomers but were only able to obtain *D-l* and *L-d*. The highly stereospecific nature of the complexing agent was demonstrated by experiments in which they found that the configuration of the ligand obtained from the separately resolved metal complex was optically pure and identical in rotation with the ligand which was prepared from optically active propylenediamine. The fact that only *l*-PDTA is obtained from *D*- $[\text{Co}(\text{PDTA})]^-$  and only *d*-PDTA from *L*- $[\text{Co}(\text{PDTA})]^-$  provides strong, though not conclusive, evidence for the non-existence of the isomers *L-l* and *D-d*. This experimental result may be a consequence of the difference in physical properties (solubility, etc.) and/or thermodynamic stability of the diastereoisomers. Small amounts of some isomers may not be detectable by a preparative technique. If the thermodynamically less stable *D-d* and *L-l* isomers of  $[\text{Co}(\text{PDTA})]^-$  exist in such small amounts as to escape detection

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(5) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(1) Y. A. Im and D. H. Busch, *J. Am. Chem. Soc.*, **83**, 3357 (1961).

(2) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 2955 (1959).

(3) B. Bosnick, F. P. Dwyer and A. M. Sargeson, *Nature*, **186**, 966 (1960).

(6) F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.