Electron-Transfer Reactions between Aqueous Cobaltous and Cobaltic Ions[1,2]

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Abstract: More detailed data have been obtained for the exchange reaction. The kinetic parameters in $NaClO_4$–$HClO_4$ solution are at $\mu = 0.5\ M$ for the acid-independent path, $\Delta H^* = 10.4$ kcal mole^{-1}, $\Delta S^* = -22$ eu; for the acid-dependent path ($1/[H^+]$), $\Delta H^* = 18.5$ kcal mole^{-1}, $\Delta S^* = +2$ eu. At $\mu = 1.0\ M$ for the acid-dependent path, $\Delta H^* = 11.8$ kcal mole^{-1}, $\Delta S^* = -17$ eu; for the acid-dependent path, $\Delta H^* = 15.3$ kcal mole^{-1}, $\Delta S^* = -6$ eu. In $LiClO_4$–$HClO_4$ solutions at $\mu = 0.5\ M$ for the acid-independent path, $\Delta H^* = 10.3$ kcal mole^{-1}, $\Delta S^* = -21$ eu; for the acid-dependent path, $\Delta H^* = 18.0$ kcal mole^{-1}, $\Delta S^* = -1$ eu. These results suggest that the acid dependence of the rate is not due to a medium effect alone. Effects of $C_2F_3O_2^-$, $C_2H_3O_2^-$, F^-, and SO_4^{-2} on the exchange rate were studied. The latter two ions caused a marked increase in rate. The effect of SO_4^{-2} was studied in some detail.

A considerable amount of work has been done on this system by Bonner and Hunt[4,5] and by Shankar and DeSouza.[6,7] Both sets of authors determined the order of the reaction with respect to the cobaltous and cobaltic ions and found the reaction to be first order in each. Shankar and DeSouza[7] found that the method used for quenching the reaction had no effect on the measured rate of the reaction. The induced exchange, however, appeared to be very large with the quenching mixtures they used. Both Bonner and Hunt and Shankar and DeSouza found a dependence of the rate of reaction on the hydrogen ion concentration, and both proposed a rate law for the reaction

$$\text{rate} = [\text{Co(II)}][\text{Co(III)}]\left[k_1 + \frac{k_2}{[\text{H}^+]}\right]$$

where k_1 is the rate constant for the acid-independent path, and k_2 is the rate constant for the acid-dependent path. Bonner and Hunt,[5] however, cast some doubt upon the acid-dependent path by showing that this result might also be interpreted as a medium effect.

Shankar and DeSouza studied the reaction at 0° under conditions of varying ionic strength.[7] Using the equation

$$\log k = \log k_0 + \frac{2AZ_AZ_B\mu^{1/2}}{1 + B\mu^{1/2}} + C\mu$$

and using the values of C determined by Nasanen for a sodium perchlorate medium,[8] they obtained values of the quantity ($\log k - C\mu$) which were constant at a value of *ca.* 1.65. They found that Z_AZ_B was zero, leading them to the conclusion that at least one of the reacting species, probably the cobaltic species, tends to acquire a charge of zero in solutions of perchlorate ions owing to the appreciable perchlorate complexing. This conclusion appears to be rather doubtful in view of the known very weak complexing ability of perchlorate ion, and also in view of the fact that the quantity ($\log k - C\mu$) was invariant even at low ionic strengths. It is also rather doubtful that an equation of this type should be used at the prevailing ionic strengths and with the highly charged species involved.

Finally, Bonner and Hunt[5] had obtained an activation energy for the reaction in 1 F $HClO_4$ of 13.2 kcal mole^{-1} and an entropy of activation of -13 cal mole^{-1} deg^{-1}. However, even at an acidity of 1 M $HClO_4$, the acid-dependent path contributes significantly to the rate of the reaction. These data, therefore, are not very useful for comparisons with other systems. Shankar and DeSouza determined the activation energies of the acid-independent and the acid-dependent paths at $\mu = 1.0\ M$, with $NaClO_4$ as the supporting electrolyte, to be 12.6 ± 0.5 and 11.6 ± 2.5 kcal mole^{-1}, respectively, and the entropies of activation under the same conditions to be -14 ± 2 and -7 ± 5 cal mole^{-1} deg^{-1}, respectively.

The purpose of this investigation was to study in more detail the effects of hydrogen ion concentration, ionic strength, and various anions on the rate of reaction and to try to obtain more reliable activation parameters for the reaction.

Experimental Section

Radioisotope. The tracer used was 5.2-year Co^{60} obtained from ORNL as $CoCl_2$ in HCl. The tracer solution was fumed repeatedly with $HClO_4$ to convert the sample to $Co(ClO_4)_2$ in $HClO_4$.

Chemicals. $Co(ClO_4)_2$ was prepared by fuming Mallinckrodt AR grade $CoCl_2 \cdot 6H_2O$ with concentrated $HClO_4$. The resulting $Co(ClO_4)_2$ solution showed no test for Cl^-. The $Co(ClO_4)_3$ solutions were usually made by anodic oxidation of acidic $Co(ClO_4)_2$ solutions at 0° using a Pt mesh electrode. On some occasions, the $Co(ClO_4)_3$ was prepared *in situ via* the cobalt(III) carbonate complex following the procedure outlined by Hofmann-Bang and Wulf.[9] The $HClO_4$ used was Mallinckrodt AR grade (70%). The $NaClO_4$ and $LiClO_4$ solutions were prepared by neutralizing the appropriate amount of $HClO_4$ with primary standard Na_2CO_3 or Li_2CO_3, respectively. All other chemicals were reagent grade quality or better.

Quenching–Separation Procedure and Analytical Method. These were essentially identical with the procedures outlined in detail by Bonner and Hunt.[5]

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[2] This paper is based on data in the Ph.D. thesis of H. S. Habib, Washington State University, 1964, available on University Microfilm.

[3] To whom inquiries may be addressed.

[4] N. A. Bonner and J. P. Hunt, *J. Am. Chem. Soc.*, 74, 1866 (1952).

[5] N. A. Bonner and J. P. Hunt, *ibid.*, 82, 3826 (1960).

[6] J. Shankar and B. C. DeSouza, *J. Inorg. Nucl. Chem.*, 24, 187 (1962).

[7] J. Shankar and B. C. DeSouza, *ibid.*, 24, 694 (1962).

[8] R. Nasanen, *Acta Chem. Scand.*, 3, 959 (1949).

[9] N. Hofmann-Bang and I. Wulf, *ibid.*, 9, 1230 (1955).

Exchange Procedure. The exchange mixture, containing the appropriate amounts of Co(II), Co(III), $HClO_4$, supporting electrolyte, and any other ions to be tested, was placed in a tall-form beaker and thermostated to the appropriate temperature. The temperature control was ± 0.05°. The Co(II) concentrations ranged from *ca.* 5×10^{-5} to *ca.* 1×10^{-3} *M*, and the Co(III) concentrations ranged from *ca.* 1×10^{-4} to *ca.* 1×10^{-3} *M*. The tracer, in a separate flask, was likewise thermostated. When temperature equilibrium was attained, the tracer was rapidly pipetted into the stirred reaction mixture. (The pipets used for adding the tracer to the reaction mixture and those used for sampling had the tips cut off to allow rapid flow. Since specific activities of the Co(III) fractions were all that were desired, the size of the samples was immaterial. All pipets used were also thermostated.) At appropriate times, samples were withdrawn from the reaction mixture and rapidly pipetted into the quench mixture with very rapid and efficient stirring.

Specific activities of the Co(III) fractions were determined as (counts/min)/*M* Co(III). The fraction of exchange was obtained by dividing the specific activity of the Co(III) sample at time *t* by the specific activity determined in the same manner for the initial *mixture*.

The fractions of exchange thus determined at various times were used in the familiar McKay plots to determine the half-time of the reaction under the prevailing conditions. This quantity was then used in the equation

$$k_{\text{obsd}} = \frac{0.693}{t_{1/2}(\Sigma \text{Co})}$$

to obtain the observed rate constant. The McKay plots obtained were generally very good, with at least five points either on or very close to the line. The induced exchange ranged between 10 and 15%. Many duplicates were run, and the reproducibility was found to be *ca.* ±5%. Reproducibility at higher acid concentrations (*ca.* 0.5 *M* H^+ and higher) was found to be better than ±5%, while at lower acidities (down to 0.2 *M* H^+) the reproducibility was about ±5%. At acid concentrations below *ca.* 0.2 *M*, it was found that the reproducibility was very much poorer. No data obtained at acid concentrations below *ca.* 0.15 *M* were used.

Treatment of Data and Results

For the data in perchlorate solutions, the H^+ effect was treated by using the relation

$$\text{rate} = k_{\text{obsd}}[\text{Co(II)}][\text{Co(III)}] = \left[k_1 + \frac{k_2}{[H^+]}\right] \times [\text{Co(II)}][\text{Co(III)}]$$

The experimentally determined values of k_{obsd} under varying concentrations of hydrogen ion, at constant ionic strength and temperature, were plotted *vs.* $[H^+]^{-1}$. The intercept of such a plot yields a value of k_1, the rate constant for the acid-independent path, and the slope yields a value of k_2, the apparent rate constant of an acid-dependent path. The inverse effect of hydrogen ion concentration is usually taken to signify a prior equilibrium in which the hydrolysis of the Co^{+3} ion takes place. The hydrolyzed Co^{+3} species is then considered to be the reacting species in the acid-dependent path. Hence the rate law

$$\text{rate} = k_{\text{obsd}}[\text{Co(II)}][\text{Co(III)}] = k_1[Co^{+2}][Co^{+3}] + k_2'[Co^{+2}][CoOH^{+2}]$$

From the equilibrium reaction

$$Co(H_2O)_6{}^{+3} + H_2O \rightleftharpoons Co(H_2O)_5OH^{+2} + H_3O^+$$

$$K_h = \frac{[Co(H_2O)_5OH^{+2}][H_3O^+]}{[Co(H_2O)_6{}^{+3}]}$$

One obtains

$$[Co(H_2O)_5OH^{+2}] = \frac{K_h[Co(H_2O)_6{}^{+3}]}{[H_3O^+]}$$

Hence

$$\text{rate} = k_{\text{obsd}}[\text{Co(II)}][\text{Co(III)}] = k_1[Co^{+2}][Co^{+3}] + \frac{k_2'K_h}{[H^+]}[Co^{+2}][Co^{+3}]$$

whence

$$k_2 = k_2'K_h$$

where k_2' is the rate constant for the acid-dependent path.

The values of K_h, necessary for the evaluation of k_2' from values of k_2, are not available at all ionic strengths. Sutcliffe and Weber[10] have determined the values for the enthalpy and entropy of hydrolysis for the Co^{+3} ion to be 10 ± 2 kcal mole^{-1} and 25 ± 7 cal mole^{-1} deg^{-1}, respectively, at an ionic strength of 1.0 *M*. No values could be found in the literature at other ionic strengths. In a later paper, Sutcliffe and Weber[11] cast doubt on the values they had determined because of their discovery of apparent dimeric species in solution. Hence there is an indeterminate amount of error in the activation parameters of k_2 at $\mu = 1.0$ *M*. Since the same values were used to evaluate the activation parameters for the k_2 path at $\mu = 0.5$ *M*, further error can be expected in these.

The values of k_1 and k_2 at various ionic strengths with $NaClO_4$ as the supporting electrolyte are shown in Table I. It may be pointed out that in determining each value of k_1 and k_2, at least ten values of k_{obsd}, obtained at hydrogen ion concentrations between the upper limit of the ionic strength and the lower limit of *ca.* 0.15 *M* [H^+], were used. The slopes (k_2) and intercepts (k_1) of these lines were obtained by a least-squares treatment. The errors represented in Table I were determined by the method outlined by Margenau and Murphy.[12]

Table I. Values of k_1 and k_2 ($NaClO_4$ Supporting Electrolyte)

μM	Temp, °C[a]	k_1, *M* min^{-1}	k_2, min^{-1}
0.5	0.15	25 ± 0.8	4 ± 0.2
0.5	10.60	53 ± 3	15 ± 1
0.5	18.35	92 ± 7	33 ± 3
1.0	0.15	35 ± 3	6.4 ± 0.7
1.0	10.60	86 ± 6	19 ± 2
1.0	18.35	143 ± 11	41 ± 2
3.0	0.15	58 ± 18	15 ± 5
3.0	10.60	183 ± 30	34 ± 15

[a] Temperature controlled to ±0.05°.

In Table II are listed values of k_1 and k_2 at $\mu = 0.5$ *M* with $LiClO_4$ as the supporting electrolyte. Arrhenius plots of k_1 and k_2 at the various ionic strengths gave the activation energies and entropies for the acid-independent path and the apparent activation energies and entropies for the acid-dependent paths. The activation energies were converted to enthalpies by means of the relation $\Delta H^* = E_{\text{act}} - RT$.

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(10) L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956).

(11) L. H. Sutcliffe and J. R. Weber, *J. Inorg. Nucl. Chem.*, **12**, 281 (1960).

(12) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., Princeton, N. J., 1956, p 519.

Table II. Values of k_1 and k_2 at $\mu = 0.5\ M$ ($LiClO_4$ as Supporting Electrolyte)

Temp, °C	k_1, M^{-1} min^{-1}	k_2, min^{-1}
0.15	24 ± 0.7	4.4 ± 0.2
10.60	51 ± 3	17 ± 1
18.35	83 ± 6	38 ± 3

Using Sutcliffe and Weber's value for K_h at 18° (1.0×10^{-4}), one obtains at $\mu = 1.0\ M$ the value for k_2' (18°) of *ca.* $4 \times 10^5\ M^{-1}\ \mathrm{min}^{-1}$.

The apparent activation enthalpies and entropies were corrected to the activation parameters for the acid-dependent path by subtracting the enthalpy and entropy of hydrolysis of Co^{+3} at $\mu = 1.0\ M$. The resulting parameters are listed in Table III.

Table III. Enthalpies[a] and Entropies[b] of Activation for the Acid-Independent (ΔH_1^*, ΔS_1^*), Apparent Acid-Dependent (ΔH_2^*, ΔS_2^*), and Acid-Dependent ($\Delta H_2^{*\prime}$, $\Delta S_2^{*\prime}$) Paths

μM	ΔH_1^*	ΔH_2^*	$\Delta H_2^{*\prime}$	ΔS_1^*	ΔS_2^*	$\Delta S_2^{*\prime}$
0.5[c]	10.3	18.0	8.0	−21	−1	−24
0.5[d]	10.4	18.5	8.5	−22	2	−23
1.0[d]	11.8	15.3	5.3	−17	−6	−31

[a] In kcal mole^{-1}. [b] In eu. [c] $LiClO_4$ was used as the supporting electrolyte. [d] $NaClO_4$ was used as the supporting electrolyte.

The effect of various anions on the rate of reaction is illustrated in Table IV. It is readily seen that F^- and SO_4^{-2} accelerate the reaction under the prevailing conditions, whereas acetate and trifluoroacetate have little if any effect.

Table IV. Effect of Various Added Anions on the Rate of Reaction

Salt	[Salt], M	μM	$[H^+]$, M	Temp, °C	k_{obsd}, M^{-1} min^{-1}	k_{obsd}, M^{-1} min^{-1} (ClO_4^-)
NaF	0.1	1.0[a]	0.2	18.55	583	350
Na_2SO_4	4×10^{-3}	0.5[b]	0.2	18.55	553	255
$NaC_2H_3O_2$	0.05	1.0	1.0	10.6	89	103
$NaC_2F_3O_2$	0.1	1.0	1.0	10.6	113	103

[a] $NaClO_4$ supporting electrolyte. [b] $LiClO_4$ supporting electrolyte.

For the F^- catalysis, the concentration of F^- in the solution was obtained by using the known concentration of NaF and the dissociation constants of HF and HF_2^- obtained by Ahrland, *et al.*[13] The sulfate ion catalysis was studied in a little more detail. Sutcliffe and Weber[14] showed that Co^{+3} associates with at least one SO_4^{-2} at temperatures below *ca.* 30°. Assuming then that the catalysis of the reaction is due to the reactivity of the $CoSO_4^+$ species, the rate of the reaction was studied as a function of SO_4^{-2} concentration at various temperatures. The rate law for the reaction would then be, presumably

$$\text{rate} = \left[k_1 + \frac{k_2}{[H^+]}\right][Co(II)][Co(III)] + k_3[Co^{+2}][CoSO_4^+]$$

From the equilibrium reaction

$$Co^{+3} + SO_4^{-2} \rightleftharpoons CoSO_4^+$$

$$K_1 = \frac{[CoSO_4^+]}{[Co^{+3}][SO_4^{-2}]}$$

one can readily see that the rate expression will be

$$\text{rate} = \left[k_1 + \frac{k_2}{[H^+]}\right][Co(II)][Co(III)] + k_3'K_1[Co(II)][Co(III)][SO_4^{-2}]$$

whence $k_3 = k_3'K_1$. From these equations and the expression for the total rate

$$\text{rate} = k_{obsd}[Co(II)][Co(III)]$$

one arrives at the expression

$$k_{obsd} = \frac{k_1 + k_2/[H^+] + k_3[SO_4^{-2}]}{1 + K_h/[H]^+ + K_1[SO_4^{-2}]}$$

Since the quantity ($k_1 + k_2/[H^+]$) is equal to k, the over-all rate constant for the reaction under the same conditions, but in the absence of sulfate ion, and since the quantities in the denominator will all be small compared to 1.0, the expression reduces to

$$k_{obsd} = k + k_3[SO_4^{-2}]$$

The concentration of SO_4^{-2} in the solutions was calculated using the dissociation constants for HSO_4^- given by Willix.[15] These values were used in preference over other values in the literature because they were determined at an ionic strength and at temperatures which were suitable to the present work.

No values of K_1, the formation constant for the $CoSO_4^+$ complex ion, were available in the literature. We therefore assumed that K_1 for $CoSO_4^+$ could be approximated by the value for $FeSO_4^+$ complex ion. Values of $\Delta H°$ for this complex are given by Willix[15] at $\mu = 0.0\ M$. We then assumed that $\Delta H°$ was invariant with ionic strength and used the value $\Delta H° = 6.2 \pm 0.3$ kcal mole^{-1} at $\mu = 0.5\ M$. The value of $\Delta S° = 39 \pm 2$ cal mole^{-1} deg^{-1} at $\mu = 0.0\ M$ given by Willix could not, however, be used at $\mu = 0.5\ M$ because of the stronger dependence of the entropy on ionic strength. We therefore calculated ΔG for the formation of $FeSO_4^+$, using the experimentally observed value of $K_1 = 175$ mole^{-1} l.$^{-1}$ at 18.5° and at $\mu = 0.5\ M$. From the equation

$$\Delta G = \Delta H - T\Delta S \simeq \Delta H° - T\Delta S$$

a value of ΔS at $\mu = 0.5\ M$ was calculated to be 31.5 cal deg^{-1} mole^{-1}.

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(13) S. Ahrland, R. Larsson, and K. Rosengren, *Acta Chem. Scand.*, **10**, 705 (1956).

(14) L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **57**, 91 (1961).

(15) R. L. S. Willix, *ibid.*, **59**, 1315 (1963).

Table V lists the values of k_{obsd} obtained under various conditions. From the slopes of the k_{obsd} *vs.* $[SO_4^{-2}]$ plots, the following values of k_3 ($k_3'K_1$) were obtained: at 0.15°, $k_3 = 3.1 \times 10^4$ M^{-1} min^{-1}; at 10.4°, $k_3 = 1.27 \times 10^5$ M^{-1} min^{-1}; at 18.55°, $k_3 = 3.6 \times 10^5$ M^{-1} min^{-1}. The apparent enthalpy and entropy of activation were found to be 20.5 ± 0.2 kcal mole^{-1} and 28.5 ± 3 cal mole^{-1} deg^{-1}, respectively. The "corrected" values, obtained by subtracting the enthalpy and entropy of formation of $FeSO_4^+$ from these parameters, were found to be 14.2 ± 0.7 kcal mole^{-1} and −3 ± 3 cal mole^{-1} deg^{-1}, respectively.

Table V. Values of k_{obsd} for the SO_4^{-2}-Catalyzed Path under Various Conditions[a]

Temp, °C	$[Na_2SO_4]$, M	$[Co]_{total}$, M	k_{obsd}, M^{-1} min^{-1}
0.15	0.01	1.12×10^{-3}	144
0.15	0.06	6.17×10^{-4}	321
0.15	0.1	2.87×10^{-4}	423
0.15	0.017	6.20×10^{-4}	215
0.15	0.025	6.19×10^{-4}	267
10.40	0.004	5.50×10^{-4}	284
10.40	0.02	5.40×10^{-4}	748
10.40	0.008	5.50×10^{-4}	384
10.40	0.012	2.97×10^{-4}	550
10.40	0.017	2.98×10^{-4}	637
18.55	0.0024	3.14×10^{-4}	500
18.55	0.005	2.95×10^{-4}	635
18.55	0.0015	3.20×10^{-4}	395
18.55	0.004	2.95×10^{-4}	553
18.55	0.003	3.12×10^{-4}	493

[a] $[H^+] = 0.2$ M, $\mu = 0.5$ M with $LiClO_4$ as supporting electrolyte.

Discussion

The treatment of the data obtained still suffers from a lack of unambiguous information concerning equilibrium constants for Co^{+3}. The data presented here are in reasonably good agreement with those reported by Bonner and Hunt.[5] The k_1 values ($\mu = 1.0$ M) obtained by Shankar and DeSouza[7] are lower by *ca.* 20%, while their k_2 values range from a factor of 2 to 4 times greater. The ΔH_1^* values agree quite well, but their ΔH_2^* value is *ca.* 25% lower than the value we find. Our data are more extensive, cover a larger range of $[H^+]$, and involve lower induced exchange values so that we believe our results to be the more reliable ones if still not as precise as one would hope.

The effects of ionic strength found earlier[5] are also confirmed, the exchange rate being increased as ionic strength increases. The apparent decrease in ΔH_2^* (Table III) is probably outside the experimental error (estimated at ±0.5 to 1.0 kcal mole^{-1}). The effect may well involve an effect on the presumed hydrolysis equilibrium. The interpretation of the acid dependence of the exchange rate in terms of a $1/[H^+]$ term in the rate law receives support in the good agreement found for the $NaClO_4$ and $LiClO_4$ media (Table III) as activity coefficients for H^+ and Li^+ are similar. It is interesting, however, that Harned's rule plots (log k *vs.* $[HClO_4]/[\Sigma ClO_4^-]$) still give fair straight lines as observed before.[5] We feel that the usual $1/[H^+]$ term interpretation is probably the correct one.

A comparison with the Fe^{+2}–Fe^{+3} system is of some interest even though the uncertainties caused by the lack of confidence in the hydrolysis constant for Co^{+3} are present. Some data are given in Table VI.

Table VI. Comparison of Fe and Co Systems at $\mu \simeq 0.5$

Rate law term	ΔH^*, kcal mole^{-1}	ΔS^*, cal mole^{-1} deg^{-1}
Co^{+2}–Co^{+3}	10.4	−21
Fe^{+2}–Fe^{+3} [a]	9.9	−25
Co^{+2}–$CoOH^{+2}$	8.0	−24
Fe^{+2}–$FeOH^{+2}$ [a]	10.0	−28

[a] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

The resemblance between the two systems is striking and somewhat surprising in view of the rather different electronic structures involved (Co^{+3}(aq) is essentially diamagnetic). Dulz and Sutin[16] have applied the ideas of Marcus to the Fe and Co systems and find that the predicted rate for the reaction

$$Fe^{+2} + Co^{+3} \longrightarrow Fe^{+3} + Co^{+2}$$

is some 10^5 times the experimental rate. Their conclusions are not significantly changed by using the more detailed data reported here.

The rate acceleration due to F^- and SO_4^{-2} ions has also been found in the Fe systems. A detailed understanding of these effects must await more results on the nature of the equilibria involved.

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(16) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).