I. The very weak band at 12,100 cm^{-1} is unaccounted for and is possibly related to a similar weak band found in the spectrum of Bi^+ in chloride melts under special conditions.[2] The ligand-field parameters used for this fit were $F_2 = 976\ \text{cm}^{-1}$, $\lambda = 5020\ \text{cm}^{-1}$, $B_0^2 = 8700\ \text{cm}^{-1}$, and $B_2^2 = 0$. We cannot find an alternative set of parameters, decidedly different from these, that will fit the spectrum in a satisfactory way.

The electron-repulsion parameter, F_2, shows the expected downward shift over the series free ion, chloride ligands, and bromide ligands; namely, 1175, 1056, and 976 cm^{-1}, respectively.

Correspondence

Study of Some Cyano-Metal Complexes by Nuclear Magnetic Resonance. IV. The Activation Energy of Electron Transfer between Ferri- and Ferrocyanide Ions[1]

Sir:

We have previously reported[2] the study of the kinetics of electron transfer between the ferri- and ferrocyanide ions in aqueous solution by the N^{14} nuclear magnetic resonance (nmr) technique. The Arrhenius plot for the reaction rate (Figure 2 of ref 2) was found to be nonlinear and was tentatively interpreted as being due to a change in the reaction mechanism with the temperature. We felt that this is a rather puzzling effect and thus have remeasured the rate constants as a function of the temperature with higher precision and over a considerably larger range of concentrations.

The experimental procedure and the interpretation of the spectra were identical with those described previously.[2] We found that the main sources of error in our previous work were (a) line broadening due to slight overmodulation and (b) exchange broadening (denoted as $\Delta(1/T)$), which was in several cases within experimental error. In the present work we tried to avoid any overmodulation and rejected those measurements in which $\Delta(1/T) < 0.3$ gauss.

The Arrhenius plot for a variety of $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ concentrations is given in Figure 1. The dependence of log K on $1/T$ is linear in the temperature range 25–65°. The result is $E = 4.2 \pm 0.6$ kcal/mole[3] and a preexponential factor equal to $1.2 \times 10^8\ \text{sec}^{-1}$. The activation parameters are $\Delta H^{\ddagger} = 3.6$ kcal/mole and $\Delta S^{\ddagger} = -23.7$ eu/mole at 39°.

It should be noted that the value of E given above is not necessarily the true activation energy of the reaction. Catiyn resonance measurements[1] have shown that their catalytic action is due to ion-pair formation which is a temperature-dependent process. The ΔH for complexation has been estimated[4] for $K^+Fe(CN)_6^{3-}$, the value being -8 kcal/mole, but it is unknown for $K^+Fe(CN)_6^{4-}$. Taking into account this factor might alter the value of E by as much as a factor of 2.

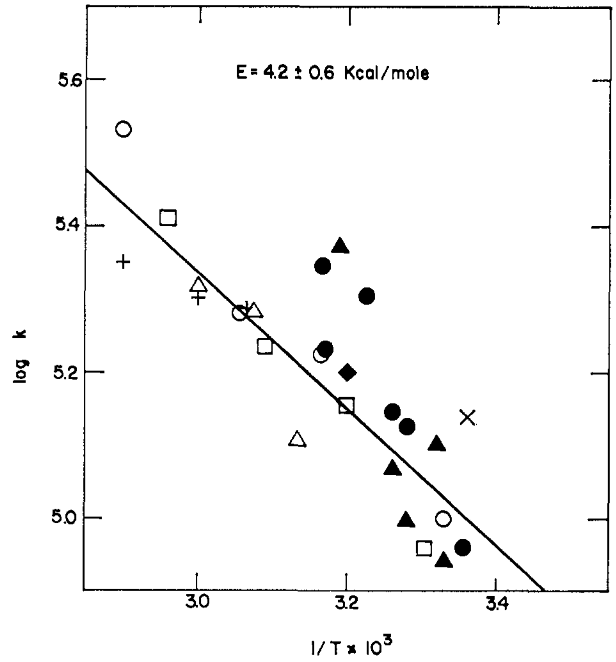

Figure 1.—An arrhenius plot of the rate of electron transfer between $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. $K_3Fe(CN)_6$–$K_4Fe(CN)_6$: +, 0.15 *M*–0.15 *M*; △, 0.20 *M*–0.20 *M*; ○, 0.25 *M*–0.25 *M*; ●, 0.30 *M*–0.30 *M*; ×, 0.35 *M*–0.35 *M*; ◆, 0.30 *M*–0.20 *M*; ▲, 0.40 *M*–0.20 *M*; □, 0.20 *M*–0.40 *M*.

TABLE I

KINETIC RESULTS FOR $H_3Fe(CN)_6$–$H_4Fe(CN)_6$ MIXTURES

Concn,[a] *M*	*t*, °C	Line width, gauss	$\Delta(1/T)$, gauss	*k*, $\text{mole}^{-1}\ \text{sec}^{-1}$
0.2	23.5	2.72	0.22	1.8×10^3
0.2	32.5	2.51	0.31	2.6×10^3
0.2	44	2.28	0.43	3.6×10^3
0.2	51.5	2.18	0.54	4.5×10^3
0.3	24	2.74	0.26[b]	1.4×10^3
0.3	38	2.40	0.36[b]	2.0×10^3
0.3	55	2.05	0.53[b]	3.0×10^3

[a] Concentration given for each component [b] The "natural" line width correction is taken from 0.4 *M* solutions because a concentration of 0.6 is not attainable.

We have attempted to measure the effect of substituting the potassium with hydrogen or cesium cations on the activation energy. The results for the $H_3Fe(CN)_6$–$H_4Fe(CN)_6$ system are shown in Table I. The rates were evaluated using the slow-exchange approximation

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[1] Part III: to be published in the proceedings of the XIVth Colloque Ampere, Ljubljana, Yugoslavia, Sept 1966.

[2] M. Shporer, G. Ron, A. Loewenstein, and G. Navon, *Inorg. Chem.*, **4**, 361 (1965).

[3] Mean-square deviation calculated by least squares.

[4] D. W. Larsen and A. C. Wahl, *ibid.*, **4**, 1281 (1965).

formula.[5] The rapid deterioration of the solutions at elevated temperatures and the slowness of the exchange reaction (by a factor of about 60 compared to $K_3Fe(CN)_6$–$K_4Fe(CN)_6$) severely limit the range of these measurements. A rough estimate for E would be 5 ± 1 kcal/mole. Several measurements taken at various temperatures with CsCl added to a $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ solution did not show any significant deviation from the line given in Figure 1.

These results tentatively lead us to the conclusion that the catalytic effect of the cations on the electron-transfer reaction between $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ is not expressed in their E values. This might be expected if the capability of ion-pair formation is the rate-determining factor in the reaction.

[5] C. S. Johnson, Jr., in "Advances in Magnetic Resonance," J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965, p 33.

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RECEIVED DECEMBER 1, 1966

Hydrolysis of Carbonatobis(ethylenediamine)cobalt(III)

Sir:

Previous work on the rates of hydrolysis[1] and carbonate[2] exchange of the carbonatobis(ethylenediamine)cobalt(III) ion have resulted in several inconsistencies. The analysis of the carbonate ion-exchange rate yields a value of 1.1 × 10^{-10} for the acid dissociation constant of $Co(en)_2OH_2CO_3H^{2+}$ whereas the hydrolysis rate data give 3.2 × 10^{-4}. Also the exchange and hydrolysis studies give values for the hydrolysis rate constant of 1 × 10^{-5} and 5 × 10^{-4} sec^{-1}, respectively. We have recently studied the hydrolysis of carbonatopentaamminecobalt(III) and the rate and equilibrium constants obtained from this study have led to a reinterpretation of the data on the bis-ethylenediamine complex.

The rate constant for hydrolysis and the K_a of $(NH_3)_5CoCO_3H^{2+}$ at 25° are[3] 2 × 10^{-2} sec^{-1} and 6 × 10^{-9} M, respectively. It is assumed that these values will be about the same for the bis-ethylenediamine complex. The hydrolysis rate constant should be similar if it is assumed that the bicarbonato complex hydrolyzes with O–C bond breaking as indicated by ^{18}O tracer experiments.[4,5]

In addition we have made use of the equilibrium constants determined by Scheidegger and Schwarzenbach[6] on the $Co(en)_2CO_3^+$ system. However, to be consistent with the pentaammine system we have given a different assignment to the pK values determined by Scheidegger and Schwarzenbach

$$cis\text{-}(en)_2CoOHCO_3H^+ \rightleftharpoons cis\text{-}(en)_2CoOHCO_3 + H^+ \qquad pK_1 = 8.75$$

$$cis\text{-}(en)_2CoOH_2CO_3H^{2+} \rightleftharpoons cis\text{-}(en)_2CoOHCO_3H^+ + H^+ \qquad pK_2 = 5.32$$

The original workers gave the pK values interchanged for these reactions. The pK_1 is consistent with the value we have found for $Co(NH_3)_5CO_3H^{2+}$ and pK_2 is consistent with values given by Tobe[7] in various aquobis(ethylenediamine)cobalt(III) complexes.

The mechanism proposed for the hydrolysis reaction is outlined by the reactions

$$Co(en)_2CO_3^+ + OH^- \rightleftharpoons Co(en)_2OHCO_3 \qquad K_0$$

$$Co(en)_2OHCO_3 + H^+ \rightleftharpoons Co(en)_2OHCO_3H^+ \qquad 1/K_1$$

$$Co(en)_2OHCO_3H^+ + H_2O \longrightarrow Co(en)_2OHOH_2^{2+} + HCO_3^- \qquad k_1$$

$$Co(en)_2OHCO_3H^+ + H^+ \rightleftharpoons Co(en)_2OH_2CO_3H^{2+} \qquad 1/K_2$$

$$Co(en)_2OH_2CO_3H^{2+} + H_2O \longrightarrow Co(en)_2(OH_2)_2^{3+} + HCO_3^- \qquad k_2$$

$$Co(en)_2OH_2CO_3H^{2+} + H_3O^+ \longrightarrow Co(en)_2(OH_2)_2^{3+} + H_2CO_3 \qquad k_3$$

It is assumed, as indicated by our study of the pentaammine system, that the bicarbonato complexes are much more reactive than the carbonato complexes. The acid-dependent k_3 path was originally proposed by Harris and Sastri and has some precedent in the aquation of the carboxylatopentaammine complexes studied by Monacelli, Basolo, and Pearson.[8]

Assuming all reactions written as equilibria are rapid, the above mechanism gives the rate of hydrolysis as

$$\text{rate} = \frac{k_1K_0K_2K_w + k_2K_0K_w[H^+] + k_3K_0K_w[H^+]^2}{K_1K_2 + K_1K_2K_0[OH^-] + K_0K_2K_w + K_0K_w[H^+]}[\text{complex}]$$

in which $K_w = [H^+][OH^-]$.

From the known values of K_0, K_1, and K_2 and for the pH range 1–5 this expression can be simplified to

$$\text{rate} = \frac{k_1K_2 + k_2[H^+] + k_3[H^+]^2}{\dfrac{K_1K_2}{K_0K_w} + [H^+]}[\text{complex}] = k[\text{complex}]$$

Using the values K_0, K_1, and K_2 of 1.6 × 10^2, 1.8 × 10^{-9}, and 5 × 10^{-6}, respectively, as given in ref 6,[9] the rate constants calculated from the equation of Harris and Sastri were fitted to the above rate law. The values obtained were k_1 = 9 × 10^{-2} sec^{-1}, k_2 = 3.5 × 10^{-3} sec^{-1}, and k_3 = 4.3 × 10^{-1} M^{-1} sec^{-1}. The calculated values of k at various pH values are compared

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[1] G. M. Harris and V. S. Sastri, *Inorg. Chem.*, **4**, 263 (1965).

[2] G. Lapidus and G. M. Harris, *J. Am. Chem. Soc.*, **85**, 1223 (1963).

[3] D. J. Francis and R. B. Jordan, to be published.

[4] J. P. Hunt, A. C. Rutenberg, and H. Taube, *J. Am. Chem. Soc.*, **74**, 268 (1952).

[5] F. A. Posey and H. Taube, *ibid.*, **75**, 4099 (1953).

[6] H. Scheidegger and G. Schwarzenbach, *Chimia* (Aarau), **19**, 166 (1965).

[7] M. L. Tobe, *Sci. Progr.* (London), **58**, 483 (1960).

[8] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

[9] These values were determined at 20°; however, their temperature dependence is expected to be small and they have been applied at 25° without correction.