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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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 $k_1 = 9 \times 10^{-2}$ sec^{-1}, $k_2 = 3.5 \times 10^{-3}$ sec^{-1}, and $k_3 = 4.3 \times 10^{-1}$ 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.

TABLE I

CALCULATED HYDROLYSIS RATE CONSTANTS FOR $Co(en)_2CO_3^+$

pH	10^4k, sec^{-1}
5	0.90 (0.67)[a]
4	1.57 (1.74)
3	7.3 (7.4)
2	51 (50)
1	443 (445)

[a] Calculated from the best fit parameters of Harris and Sastri.[1]

to the k (in parentheses) calculated from the parameters of Harris and Sastri; see Table I.

The fitting of the proposed rate constants is quite good and could be improved by adjustment of the equilibrium constants to take into account ionic strength and temperature effects.

However it is only the purpose of this note to show that the pH dependence of the hydrolysis rate fits the proposed mechanism using independently determined equilibrium constants. Also the values of k_1 and k_2 are in reasonable agreement with the analogous hydrolysis rate constant for $Co(NH_3)_5CO_3H^{2+}$.

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