# Kinetic and Tracer Studies on the Alkaline Hydrolysis of $Co(NH_3)_5O_2C_2F_3^{2+}$

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**Abstract:** The rate law for the alkaline hydrolysis of the complex $Co(NH_3)_5O_2C_2F_3^{2+}$ has the form $-d \ln [\text{complex}]/dt = k_{1H}'[OH]^- + k_{2H}'[OH^-]^2$. At 25° and $\mu = 1.0$ (NaCl), $k_{1H}' = 2.1 \times 10^{-2}\ M^{-1}\ sec^{-1}$ and $k_{2H}' = 0.54\ M^{-2}\ sec^{-1}$; $\Delta H^*_1$ and $\Delta S^*_1$ are 22.7 kcal mole$^{-1}$ and 10 cal mole$^{-2}$ deg$^{-1}$; $\Delta H^*_2$ and $\Delta S^*_2$ are 6.8 kcal $M^{-1}$ and $-37$ cal mole$^{-1}$ deg$^{-1}$. Tracer studies have shown that the $k_{1H}'$ path takes place with Co–O bond breaking and the $k_{2H}'$ path with O–C bond breaking. During hydrolysis there is exchange of oxygen between $Co(NH_3)_5O_2C_2F_3^{2+}$ and the solvent. The mechanism of the exchange reaction has been elucidated by means of measurements of the exchange rate and the isotopic composition of the hydrolysis products.

Both kinetic and oxygen-18 tracer studies have already been done on the alkaline hydrolysis of $Co(NH_3)_5O_2C_2F_3^{2+}$.[1,2] This paper deals with the same subject, but the results as reported here[3] feature some unusual aspects not anticipated from the earlier work. Our study of the kinetics has considerably extended the the range of hydroxide ion concentration investigated and has thereby revealed a hydrolysis path second order in hydroxide ion. In the tracer experiments both the $Co(NH_3)_5OH^{2+}$ and $F_3C_2O_2^-$ products of the alkaline hydrolysis have been isolated and analyzed. The results established that exchange and both Co–O and O–C bond breaking occur during hydrolyis. Exchange and Co–O bond breaking involve activated complexes of the same composition but probably different geometry; no measurable exchange occurs by a path having an activated complex of the composition of that corresponding to C–O bond breaking.

Tracer studies can help in determining whether the carboxylate ligand has both oxygens bonded equivalently to the cobalt or if only one oxygen is directly bonded to the metal atom. Interpretation of the infrared spectra of several carboxylatopentaamminecobalt(III) complexes has led to conflicting opinions on this point.[4,5] Fraser's interpretation indicates two equivalent oxygens, while Nakamoto, *et al.*, picture the bonding as analogous to that in an organic ester with a distinct carbonyl oxygen. The problem has been settled in the solid state by Fleischer's[6] X-ray study which shows that the oxygens are not equivalent, but evidence bearing on the structure in solution is still needed.

## Experimental Section

**Preparation of Complex Salts.** $[Co(NH_3)_5O_2C_2F_3](ClO_4)_2$ was prepared by heating $[Co(NH_3)_5OH_2](ClO_4)_3$ with $F_3C_2O_2H$ in water at 70° for 3–4 hr. *Anal.* Calcd: $ClO_4^-$, 43.5; Co, 12.9; N, 17.4. Found: $ClO_4^-$, 43.4; Co, 12.7; N, 17.5. The molar extinction coefficients for $[Co(CH_3)_5O_2C_2F_3](ClO_4)_2$ were 63.5 (500 mμ) and 51.0 (350 mμ).

$[Co(NH_3)_5O_2C_2F_3]Br_2$ was prepared by adding a saturated aqueous solution of the perchlorate salt of the complex to an equal volume of a saturated solution of LiBr in methanol. The resultant mixture was cooled and stirred vigrously. The product was washed with iced methanol and dried under vacuum. Analysis gave 37.9% Br (calculated, 38.2%).

**Procedures for Isotopic Analysis.** The $F_3C_2O_2^-$ product from the alkaline hydrolysis of $[Co(CH_3)_5O_2C_2F_3]Br_2$ was isolated by neutralizing the solution with dilute HCl. Then the solution was passed through an ion-exchange column (Bio-Rad Dowex 50-X12, $Na^+$ form) at 0° to remove cobalt-containing products. The water was evaporated from the eluent by vacuum distillation. The remaining white solid mixture of NaCl and $NaO_2C_2F_3$ was rigorously dried under high vacuum at 70°, then heated with *o*-phenylenediamine dihydrochloride at 300°[7] to give $H_2O$. The sample was cooled to −78° and volatile impurities were pumped off. After warming to room temperature the water product was condensed into a break-seal tube containing $Hg(CN)_2 + HgCl_2$. This sample was heated for 3–4 hr at 400°[8] and the $CO_2$ product purified by gas chromatography[9] prior to isotopic analysis. Blank experiments carried out by dissolving $NaO_2C_2F_3$ in $O^{18}$-enriched NaOH and analyzing by the above procedure indicated less than 0.2% enrichment induced by analysis at 25°, and 0.5% at 60°.

The $Co(NH_3)_5OH^{2+}$ product of the alkaline hydrolysis was isolated by adding the reaction solution to iced 50% HBr. The resulting $[Co(NH_3)_5OH_2]Br_3$ was collected, dried, and then heated at 110° for 4 hr. The water given off was collected in a break-seal tube containing $Hg(CN)_2$–$HgCl_2$ and decomposed, purified, and analyzed as described previously.

The rate of oxygen exchange with solvent during the alkaline hydrolysis of $Co(NH_3)_5O_2C_2F_3^{2+}$ was followed by quenching the reaction solution of complex in $O^{18}$-enriched NaOH solution with acid to make the resultant mixture 0.1 to 0.05 $M$ in $H^+$. The solution was then deoxygenated and 1 $M$ $Cr^{2+}$ in 0.1 $M$ $HClO_4$ was added to make the resultant solution 0.1 $M$ in $Cr^{2+}$. The $Co(NH_3)_5OH_2^{3+}$ is reduced 50-fold[10] faster than the $Co(NH_3)_5O_2C_2F_3^{2+}$ under these conditions. After 30 sec, the reduction was stopped by sucking air through the solution. A saturated solution of $NaClO_4$ was added dropwise to the solution and $[Co(NH_3)_5O_2C_2F_3](ClO_4)_2$ collected. This salt was dissolved in water at ice temperature and the solution was made 1 $M$ in NaOH. Hydrolysis under these conditions gives completely O–C bond breaking with no exchange. After 10 min the solution was poured into an equal volume of cold 50% HBr and the $[Co(NH_3)_5OH_2](Br_3)$ collected and analyzed as described previously. The enrichment of samples taken at various intervals extrapolates to that expected for time zero, thus indicating that the method of analysis does not cause significant exchange.

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[1] C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, 1692 (1953).

[2] F. Basolo, J. G. Bergman, and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).

[3] Our results were reported in part in a more general paper: R. B. Jordan, C. Andrade, and H. Taube, Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964, ppp 381–395.

[4] R. T. M. Fraser, *Nature*, **202**, 691 (1964).

[5] K. Nakamoto, J. Fujita, S. Tanaka, and K. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).

[6] E. B. Fleischer and R. Frost, *ibid.*, **87**, 3998 (1965).

[7] H. Dohn, M. Moll, and R. Manasse, *Helv. Chim. Acta*, **42**, 1225 (1954).

[8] M. Anbar and S. Guttman, *J. Appl. Radiation Isotopes*, **5**, 223 (1959).

[9] A. L. Odell and R. B. Jordan, to be published.

[10] E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

The solvent water in all cases was analyzed by heating with $HgCN_2$–$HgCl_2$ followed by purification of the $CO_2$ product by gas chromatography. All isotopic analyses were carried out on an Atlas M-86 mass spectrometer.

**Base Hydrolysis Kinetics.** Two methods were used to follow the rate of hydrolysis. The rate of formation of $Co(NH_3)_5OH^{2+}$ was determined by following the increase in optical density at 370 mμ. The reaction could only be followed for two to three half-lives because of formation of colloidal cobaltic oxide.

In the second method the reaction was quenched by adding acid and the decrease in $Co(NH_3)_5O_2C_2F_3^{2+}$ determined from the optical density change at 270 mμ. When possible, reactants were mixed in a volumetric flask and aliquots withdrawn periodically, quenched, and analyzed. For reactions with half-times less than 1 min, solutions of complex and NaOH, at the same ionic strength, were placed in respective sides of an erlenmeyer flask with a divided bottom. The solutions were brought to temperature in the flask, and mixed by swirling. Acid was added from a needleless syringe to quench the reaction.

Infinite time absorbancies were determined from the spectrum of the aquo or hydroxo product in the same ionic medium as that in which the kinetic samples were measured. Spectrophotometric measurements were carried out on a Cary Model 14 spectrophotometer.

## Results and Discussion

The results of the kinetic study of the alkaline hydrolysis of $Co(NH_3)_5O_2C_2F_3^{2+}$ are shown in Table I. It was found that the observed rates conform to a rate law with both a first- and second-order dependence on $OH^-$.

$$\frac{-d \ln [\text{complex}]}{dt} = k_{\text{obsd}} = k_{1H}'[OH^-] + k_{2H}'[OH^-]^2$$

Values of $k_{1H}'$ and $k_{2H}'$ were obtained from the intercept and slope of a plot of $k_{\text{obsd}}/[OH^-]$ *vs.* $[OH^-]$. In Table I experimental values of $k_{\text{obsd}}/[OH^-]$ are compared to values calculated using $k_{1H}' = 2.1 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$ and $k_{2H}' = 0.54\ M^{-2}\ \text{sec}^{-1}$, at 25°. At other temperatures values of $k_{\text{obsd}}/[OH^-]$ were calculated using the experimentally determined activation parameters $\Delta H^*_1 = 22.7$ kcal mole$^{-1}$, $\Delta S^*_1 = 10$ cal mole$^{-1}$ deg$^{-1}$, $\Delta H^*_2 = 6.8$ kcal mole$^{-1}$, and $\Delta S^*_2 = -37$ cal mole$^{-1}$ deg$^{-1}$. These values were all determined at ionic strength (μ) 1.0 adjusted with NaCl.

Table I. Kinetic Results[a] on the Hydrolysis of $Co(NH_3)_5O_2C_2F_3^{2+}$

| NaOH, *M* | Temp, °C | $k_{\text{obsd}}/[OH^-] \times 10^2\ M^{-1}\ \text{sec}^{-1}$ Obsd | Calcd | Method |
|---|---|---|---|---|
| 0.0094 | 25 | 2.02 | 2.55 | Spectral 370 mμ |
| 0.0293 | | 3.70 | 3.64 | Spectral 370 mμ |
| 0.0586 | | 5.08 | 5.20 | Spectral 370 mμ |
| 0.117 | | 7.60 | 6.67 | Spectral 370 mμ |
| 0.176 | | 11.7 | 11.5 | Spectral 370 mμ |
| 0.235 | | 14.8 | 14.7 | Quench 270 mμ |
| 0.293 | | 19.5 | 17.8 | Spectral 370 mμ |
| 0.40 | | 23.0 | 23.5 | Quench 270 mμ |
| 0.50 | | 27.2 | 28.8 | Quench 270 mμ |
| 0.010 | 35 | 7.66[b] | 7.00 | Quench 270 mμ |
| | | 7.48[b] | | Quench 270 mμ |
| 0.050 | | 9.15 | 10.2 | Quench 270 mμ |
| | | 10.0 | | Quench 270 mμ |
| 0.10 | | 14.4 | 13.8 | Quench 270 mμ |
| | | 13.3 | | Quench 270 mμ |
| 0.20 | | 20.5 | 20.5 | Quench 270 mμ |
| 0.010 | 15.5 | 0.52[b] | 0.50 | Quench 270 mμ |
| 0.10 | | 2.97 | 3.42 | Quench 270 mμ |
| 0.25 | | 7.70 | 7.80 | Quench 270 mμ |
| 0.40 | | 12.0 | 12.1 | Quench 270 mμ |
| 0.40 | | 13.0 | 12.1 | Quench 270 mμ |

[a] μ = 1.00 adjusted with NaCl. [b] Equivalent concentrations of complex and NaOH; second-order plot gives $k_{1H}'$ (approximate).

The tracer results on the base-catalyzed hydrolysis of $Co(NH_3)_5O_2C_2F^{2+}$ are summarized in Table II. Several values in Table II are of particular importance to the interpretation of the results. The reaction

$$Co(NH_3)_5O_2C_2F_3^{2+} + OH^- = Co(NH_3)_5OH^{2+} + F_3C_2O_2^-$$

requires that one solvent oxygen be incorporated into the products to satisfy stoichiometry; oxygen incorporation in excess of this indicates that exchange has occurred during the reaction. Since it is known[11,12] that neither product exchanges significantly during the reaction, any exchange must occur in the reactant prior to or in the act of hydrolysis. The results at 1.0 *M* $OH^-$ and 0°, where more than 99% of the reaction occurs by the path second order in $OH^-$, show that by this path there is O–C bond fission but no detectable exchange. At 0.02 *M* $OH^-$ and 60°, the reaction proceeds >98% by the path first order in $OH^-$ and involves primarily Co–O bond fission. But because considerable exchange accompanies the reaction, only a lower limit of 90% on the extent of Co–O bond breaking can be set. It is assumed in the quantitative treatment of the results which follows that the first-order path goes completely with Co–O bond breaking.

Table II. Tracer Results[a] on the Hydrolysis of $Co(NH_3)_5O_2C_2F_3^{2+}$

| NaOH, *M* | Temp, °C | Fraction of solvent oxygen in $Co(NH_3)_5$-$OH^{2+}$ | $F_3C_2O_2^-$ | Excess incorporation of solvent O |
|---|---|---|---|---|
| 0.03 | 25 | 0.86[b] | 0.82[b] | 1.50 |
| 0.10 | 25 | 0.63 | 0.72, 0.71 | 1.06 |
| 0.20 | 25 | 0.52 | | . . . |
| 0.30 | 25 | 0.36 | 0.65 | 0.66 |
| 0.45 | 25 | 0.29 | | . . . |
| 0.02 | 60 | 0.97 | 0.47 | 0.91 |
| 0.40 | 15.5 | 0.15 | | . . . |
| 1.00 | 0 | 0.013 | 0.49 | 0.00 |

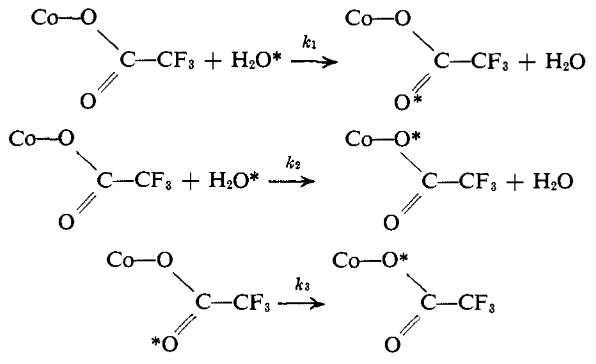
[a] All reactions at μ = 1.0 in NaCl. [b] Lack of isotopic balance due to exchange during hydrolysis.

The rate of exchange of the oxygens in $Co(NH_3)_5$-$O_2C_2F_3^{2+}$ was studied at 0.10 and 0.05 *M* NaOH (25°, μ = 1.0, NaCl). It was found during work on the acid-catalyzed exchange of this complex that the oxygens were interequilibrated during precipitation of the perchlorate salt. Therefore the rate measured will be the total exchange rate for both oxygens. The observed half-times are 65 and 150 sec at 0.10 and 0.05 *M* NaOH, respectively, giving second-order rate constants of 0.107 and 0.094 $M^{-1}$ sec$^{-1}$, respectively, for the exchange of the oxygens in $Co(NH_3)_5O_2C_2F_3^{2+}$.

The tracer results have been interpreted in terms of the general reaction scheme

[11] H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).

[12] D. R. Llewellyn and C. O'Connor, *J. Chem. Soc.*, 4400 (1964).



(where $k_1$, $k_2$, and $k_3$ may be functions of $[OH^-]$) together with the two hydrolytic processes, one proceeding at the rate $k_{1H}'[OH^-]$ and leading only to Co-O bond rupture, and the other at the rate $k_{2H}'[OH^-]^2$ leading only to C-O bond rupture. On this basis it is possible to solve for the percentage of solvent oxygen, $F_1$ and $F_2$, in the products $Co(NH_3)_5OH^{2+}$ and $F_3C_2O_2^-$, respectively, in terms of the rate constants $k_{1H}'$, $k_{2H}'$, $k_1$, $k_2$, and $k_3$. From the experimental values of $F_1$, $F_2$, $k_{1H}'$, and $k_{2H}'$, values of $k_1$, $k_2$, and $k_3$ can be calculated. If the interpretation is correct $k_1$, $k_2$, and $k_3$ should be consistent with the measured exchange rates and should also show a reasonable dependence on $OH^-$.

The expressions for $F_1$ and $F_2$ were obtained by first solving for the concentrations of $Co(NH_3)_5O^*OC_2F^{2+}$ and $Co(NH_3)_5OO^*C_2F^{2+}$ and integrating with respect to time. Using the limiting conditions that the concentration of products at $t = 0$ is 0, the integration constant can be found and this gives the solvent oxygen content of $Co(NH_3)_5OH^{2+}$ and $F_3C_2O_2^-$ at $t = \infty$ or after the reaction has gone to completion.

The resulting general expressions for $F$ are, for $Co(NH_3)_5OH^{2+}$

$$F_1 = \frac{k_{1H}}{k_H} + \frac{k_{2H}k_2}{k_H}\left[\frac{b_1 + k_H}{k_H{}^2 + k_H(a_1 + a_2) + a_1a_2}\right]$$

and for $F_3C_2O_2^-$

$$2F_2 = \frac{k_{2H}}{k_H} + k_1\left[\frac{b_2 + k_H}{k_H{}^2 + k_H(a_1 + a_2) + a_1a_2}\right] + \frac{k_{1H}k_2}{k_H}\left[\frac{b_1 + k_H}{k_H{}^2 + k_H(a_1 + a_2) + a_1a_2}\right]$$

where

$$a_1 + a_2 \equiv k_1 + k_2 + 2k_3$$
$$a_1a_2 \equiv k_1k_2 + k_2k_3 + k_1k_3$$
$$b_1 \equiv k_1 + k_3 + k_1k_3/k_2$$
$$b_2 \equiv k_2 + k_3 + k_2k_3/k_1$$
$$k_{1H} \equiv k_{1H}'(OH^-)$$
$$k_{2H} \equiv k_{2H}'(OH^-)^2$$
$$k_H \equiv k_{1H}'[OH^-] + k_{2H}'[OH^-]^2$$

Several special conditions can be imposed to conform to various mechanisms for exchange. Three such cases will be discussed.

**Case I. Let $k_1 = k_2 = k_3$.** Corresponding to this case all the exchange rates could be equal or all the oxygens in the complex could be equivalent and therefore exchange at the same rate. The equations derived also correspond to the case in which the oxygen atoms become equivalent by rapid internal exchange (*i.e.*, $k_3 \gg k_1$ or $k_2$).

$$F_1 = 1 - \left(\frac{k_{2H}}{k_H + k_1}\right)$$

$$2F_2 = \frac{k_{2H}}{k_H} + \frac{k_1}{(k_H + k_1)} + \frac{k_{1H}k_1}{k_H(k_H + k_1)}$$

Values of $k_1$ were calculated from the rearranged expression for $F_1$

$$k_1 = \left(\frac{k_{2H}}{1 - F_1}\right) - k_H$$

Then these values of $k_1$ were used to calculate the values of $F_2$ at various $OH^-$ concentrations. The results are shown in Table III.

**Table III.** Calculated Values for Case I, $k_1 = k_2 = k_3$

| NaOH, $M$ | $k_1 \times 10^3$ $sec^{-1}$, calcd | $F_2$ | |
|---|---|---|---|
| | | Calcd | Found |
| 0.030 | 2.9 | 0.77 | 0.82 |
| 0.10 | 7.1 | 0.67 | 0.72 |
| 0.20 | 19 | | |
| 0.30 | 26 | 0.61 | 0.65 |
| 0.445 | 35 | | |

The calculated values of $k_1$ show a first-order dependence on $[OH^-]$ giving a second-order rate constant $k_1' = 0.082$ $M^{-1}$ $sec^{-1}$. However, the deviation of the calculated value of $k_1'$ from the average experimental value (0.098 $M^{-1}$ $sec^{-1}$) and especially the deviation of the calculated $F_2$ values from the experimental ones indicate that the exchange is faster than calculated; that is, the carbonyl oxygen in the complex is more enriched than this assumed scheme permits.

**Case II. If $k_2 = 0$.** This assumption would correspond to an exchange mechanism in which only the carbonyl oxygen of the complex exchanges directly with the solvent. The oxygen bound to cobalt can exchange by interchange with the carbonyl oxygen. For this case

$$F_1 = \frac{k_{1H}}{k_H} + \frac{k_{2H}}{k_H}\left(\frac{k_H + k_1 + 2k_3}{k_H{}^2 + k_H(k_1 + 2k_3) + k_1k_3}\right)$$

$$2F_2 = \frac{k_{2H}}{k_H} + k_1\left(\frac{k_3 + k_H}{k_H{}^2 + k_H(k_1 + 2k_3) + k_1k_3}\right) + \frac{k_{1H}}{k_H}\left(\frac{k_1k_3}{k_H{}^2 + k_H(k_1 + 2k_3) + k_1k_3}\right)$$

Rearranging and combining these two expressions

$$A = \left(\frac{2F_2 - k_{2H}/k_H}{F_1 - k_{1H}/k_H}\right) = \frac{k_H(k_3 + k_H) + k_{1H}k_3}{k_{2H}k_3}$$

Further rearrangement gives

$$k_3 = \left(\frac{k_H{}^2}{k_{2H}A - (k_H + k_{1H})}\right)$$

Thus $k_3$ can be calculated using the values of $F_1$ and $F_2$ at the same $OH^-$ concentration. The values of $k_3$ obtained can be used in the expression for $F_1$ to calculate $k_1$.

$$k_1 = \frac{(k_HF_1 - k_{1H})k_H(k_H + 2k_3)}{k_{2H}k_3 - (k_HF_1 - k_{1H})(k_H + k_3)}$$

The resulting calculated values of $k_1$ and $k_3$ are shown in Table IV.

Table IV. Calculated Values for Case II, $k_2 = 0$

| NaOH, *M* | $k_1 \times 10^3$ sec$^{-1}$, calcd | $k_3 \times 10^3$ sec$^{-1}$, calcd |
|---|---|---|
| 0.03 | 0.21 | 7.6 |
| 0.10 | 19 | 38 |
| 0.30 | 67 | 240 |

We found that neither of the calculated rate constants can be fitted to a function of the form $k = p(OH^-) + q(OH^-)^2$, and furthermore that the measured exchange rate is more than a factor of 2 less than that calculated at 0.10 *M* NaOH.

The data require that the cobalt-bonded oxygen exchanges directly with the solvent and does not wait for labeled oxygen to accumulate in the carbonyl position.

**Case III.** Let $k_3 = 0$. For this case

$$F_1 = \frac{k_{1H}}{k_H} + \frac{k_{2H}}{k_H}\left(\frac{k_2}{k_H + k_2}\right)$$

$$2F_2 = \frac{k_{2H}}{k_H} + \left(\frac{k_1}{k_H + k_1}\right) + \frac{k_{1H}}{k_H}\left(\frac{k_2}{k_H + k_2}\right)$$

Substituting in the expression for $F_1$ the relations $k_{1H} = k_{1H}'[OH^-]$ and $k_{2H} = k_{2H}'[OH^-]^2$ and assuming that $k_2 = k_2'[OH^-]$ gives

$$\left(\frac{1 - F_1}{F_1}\right) = \left(\frac{k_{2H}'}{k_{1H}' + k_2'}\right)[OH^-]$$

Therefore, if the assumptions are correct a plot of $(1 - F_1)/F_1$ *vs.* $OH^-$ should be linear and pass through the origin. The plot, shown in Figure 1, is found to be linear with a slope $k_{2H}'/(k_{1H}' + k_2') = 5.49$; $k_{2H}' = 5.4 \times 10^{-1} M^{-2}$ sec$^{-1}$, $k_{1H}' = 2.1 \times 10^{-2} M^{-1}$ sec$^{-1}$; then $k_2' = 7.7 \times 10^{-2} M^{-1}$ sec$^{-1}$. The values of $k_1'$ can be calculated from $F_2$, $k_{1H}$, $k_{2H}$, and this value of $k_2'$. The results are shown in Table V. Values in parenthesis show the high sensitivity of the calculated $k_1'$ values to errors in the $F_2$ values.

Table V. Calculated $k_1'^a$ for Case III, $k_3 = 0$

| NaOH, *M* | $k_1' \times 10$ $M^{-1}$ sec$^{-1}$ |
|---|---|
| 0.03 | 1.7 (2.3–1.3)$^b$ |
| 0.10 | 0.93 (1.2–0.87) |
| 0.30 | 1.2 (1.3–0.93) |

$^a$ $k_1' = k_1[OH^-]$. $^b$ Values in parentheses are calculated extremes assuming ±0.02 error in experimental values of $F_2$.

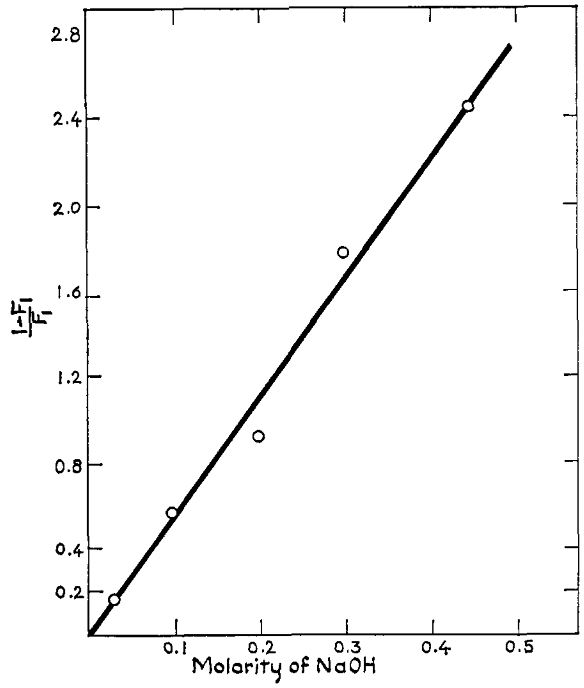


Figure 1. $(1 - F_1)/F_1$ *vs.* molarity of NaOH for case III.

The best calculated second-order exchange rate constants are then $k_1' = 0.12$ $M^{-1}$ sec$^{-1}$ and $k_2' = 0.077$ $M^{-1}$ sec$^{-1}$ at 25°, $\mu = 1.0$ (NaCl). The calculated average rate constant of 0.098 $M^{-1}$ sec$^{-1}$ compares with the experimental value of 0.10 $M^{-1}$ sec$^{-1}$ much better than might be expected.

It can be concluded that the assumption that $k_3 = 0$ leads to a set of exchange rate constants which have a first-order dependence on $[OH^-]$ and agree quite well with the experimentally measured exchange rate.

From the single experiment at 15.5° the calculated exchange rate constant $k_2' = 1.9 \times 10^{-2}$ $M^{-1}$ sec$^{-1}$. This value and that at 25° lead to a calculated $\Delta H^*$ of 25 kcal mole$^{-1}$. Although these values cannot be considered accurate it is reassuring that the calculated exchange rate decreases with decreasing temperature and has a reasonable enthalpy of activation.

The case corresponding to a large value of $k_3$ is excluded by the data, but mechanisms in which $k_3$ is finite but small compared to $k_2$ are not. These possibilities, however, do not account for the data better than the simple case considered in III and are not considered in detail here.

## Conclusions

Our results can only be compared semiquantitatively with those of previous work. Our value of $k_{1H}'$ is consistent with that of Basolo, *et al.*[2] ($0.73 \times 10^{-1}$ $M^{-1}$ sec$^{-1}$), measured at lower ionic strength. The tracer results of Bunton and Llewellyn[1] are compatible with those presented here if the exchange rates are insensitive to the difference in ionic strength and the hydrolysis rate increases with increasing ionic strength. The latter effect has been noted but no data are available for the exchange rates.

The new feature of the base hydrolysis of cobalt(III)–pentaammine complexes revealed here is the term in the rate law second order in $[OH^-]$. Tracer results have shown that this path involves only C–O bond fission.

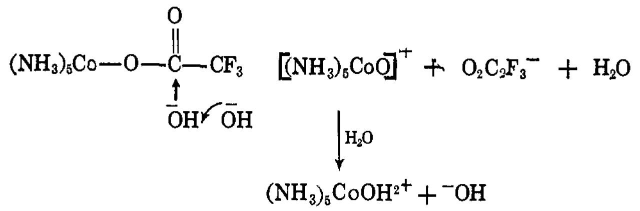


Figure 2.

One possible mechanism for this path features initial formation of the conjugate base $Co(NH_3)_4NH_2O_2C_2F_3^+$ followed by attack of $OH^-$ at the carbonyl carbon of the $F_3C_2O_2^-$ ligand with subsequent O-C bond cleavage. However, this mechanism seems unlikely firstly because removal of the proton from $NH_3$ is not expected to increase the rate of attack on the carbon atom of the carboxylate ligand, and secondly because deuterium-exchange studies[13] indicate an activation energy of 14.5 kcal $mole^{-1}$ for formation of the conjugate base. Since this is considerably higher than the observed value of 6.8 kcal $mole^{-1}$, the conjugate base can be eliminated as an intermediate for the $[OH^-]^2$ path.

A possible mechanism, shown in Figure 2, involves attack of an $OH^-$ at the carbonyl carbon followed by a second $OH^-$ removing an $H^+$ from the first. This process is considered to be concerted, the low activation energy being consistent with strong bond making in the activated complex. If the product of attack of the first $OH^-$ were sufficiently long-lived to permit proton transfer between oxygens, this process would contribute 6-8 kcal $mole^{-1}$ to the activation enthalpy[14,15] and would require the activation enthalpy for the remaining steps to be unreasonably small.

Hydrolytic processes at the carbonyl position second order in $[OH^-]^2$ have been observed for other cases, among them amide hydrolysis[14,16,17] and hydrolysis of β-diketones.[17] Our reaction has this in common with the others that a "poor leaving group" is involved but is unusual because of the low activation energy.

The $k_{1H}'$ hydrolysis path presumably involves a conjugate base mechanism

$$(Co(NH_3)_5O_2C_2F_3^{2+} + OH^- \rightleftharpoons Co(NH_3)_4NH_2O_2C_2F_3^+ + H_2O$$

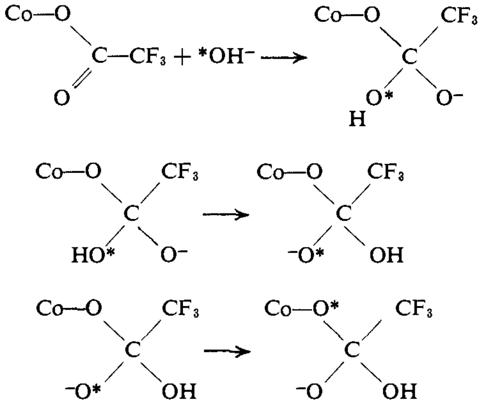
$$Co(NH_3)_4NH_2O_2C_2F_3^+ \longrightarrow Co(NH_3)_4NH_2OH_2^{2+} + F_3C_2O_2^-$$

$$Co(NH_3)_4NH_2OH_2^{2+} = Co(NH_3)_5OH^{2+}$$

It should be mentioned explicitly that though the composition of the activated complex for exchange and hydrolysis by the path first order in $OH^-$ are the same, the geometries need not be the same, and in fact in the following we propose a quite different geometry for the activated complex for exchange compared to that for hydrolysis.

The exchange rate of the oxygens in $Co(NH_3)_5O_2C_2F_3^{2+}$ during alkaline hydrolysis has been found to be first order in $OH^-$. The oxygen bound to cobalt exchanges at a rate about one-half that of the carbonyl oxygen. The fact that these rates are different shows that these oxygens are bonded differently in the complex, as has been shown for the solid phase containing the acetate complex.

The results prove that exchange into the Co-O-C position does not wait for accumulation of solvent oxygen into the carbonyl group. However, they do not exclude the possibility that exchange at the two positions proceeds through a common intermediate. The mechanism



with the intermediate decomposing by expelling $OH^-$ or $*OH^-$ accounts for the observations. The fact that $k_1$ and $k_2$ are so nearly alike implies that O is almost completely randomized at the three positions, and speaks for transfer of $(NH_3)_5Co^{3+}$ between adjacent oxygens at nearly the rate of proton transfer.

The factors which favor hydrolysis by a path involving two $OH^-$ ions are not completely delineated by the results presented here. The work on the hydrolysis rates of the analogous formate and oxalate complexes shows that for the former the $[OH^-]^2$ path has not been detected, but for the latter there is a small $[OH^-]^2$ dependence.[3] Thus it appears that strongly electron-withdrawing groups such as $-CF_3$ are required for $OH^-$ attack to occur at the carbonyl carbon of the carboxylate ligand.

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[13] J. S. Anderson, H. V. A. Brisco, and N. L. Spoor, *J. Chem. Soc.*, 361 (1943).

[14] M. L. Bender and R. J. Thomas, *J. Am. Chem. Soc.*, **83**, 4184 (1961).

[15] A. Moffat and H. Hunt, *ibid.*, **81**, 2082 (1959).

[16] S. S. Buchler and R. W. Taft, Jr., *ibid.*, **79**, 4927 (1957).

[17] R. G. Pearson and E. A. Mayerle, *ibid.*, **73**, 926 (1951).