of monothiocyanatoiron(III) ion,[17] $(H_2O)_5FeNCS^{2+}$. The transition state of composition $\{(H_2O)_{5+x}Fe\text{-}NCS^{2+}\}^*$ (which almost certainly yields the products aquoiron(III) and thiocyanate ion, and not hydroxoiron(III) ion and thiocyanic acid) has an activation entropy for aquation of -9.6 ± 5 eu. Thus in the case of iron(III) the activation entropy difference $\Delta S^*_{FeN_3} - \Delta S^*_{FeNCS}$ is $+6 \pm 5$ eu. This value is positive, but it is substantially smaller than the analogous values for $(H_2O)_5Cr^{III}$ and $(NH_3)_5Co^{III}$.

The entropy of acid dissociation of aquoiron(III)[11] is 8 eu more positive than that of aquochromium(III).[18] It would appear that the expected value of $\Delta S^*_{MN_3} - \Delta S^*_{MNCS}$, assuming parallel mechanisms, should be still more positive for iron than for chromium, in view of the additional entropy developed in forming the hydroxoiron(III) species. The conclusion one would reach on the basis of entropy comparisons alone would probably be different from that presented earlier, namely, that this pathway represented reaction of $(H_2O)_6Fe^{3+} + N_3^-$ rather than $(H_2O)_5FeOH^{2+} + HN_3$.

This particular application of the entropy argument to the case of azidoiron(III) ion seems to contain a major weakness, however, especially in the extrapolation from comparisons of Cr(III) (d^3) and Co(III) (d^6) to Fe(III) (d^5), that renders it a less certain criterion of mechanism. The Cr(III) and Co(III) complexes (configurations t_{2g}^3 and t_{2g}^6, respectively) experience considerable ligand field stabilization, whereas Fe(III) ($t_{2g}^3e_g^2$) does not. The effect on relative ΔS^* values is not easy to predict, however. Changes in bond distances necessarily accompanying the activation process are likely to be somewhat different in the case of the d^5 configuration than for d^3 and d^6—possible intermediates are stabilized not at all or to different extents—so that values of ΔS^*, which depend strongly on ionic radii, cannot be assumed to have the same relative magnitudes even for mechanisms that are quite similar. The present status of theory with regard to the substitution process—indeed whether these substitutions pass through configurations of reduced or expanded coordination number—does not permit us to go farther at this time.

We conclude, therefore, that the evidence advanced by Seewald and Sutin[2] in favor of elementary reaction 16 corresponding to the transition state $\{(H_2O_{5+x}\text{-}FeN_3^{2+}\}^*$ is valid, that the sign of $\Delta S^*_{FeN_3} - \Delta S^*_{FeNCS}$ is consistent with this assignment, and that the magnitude of the ΔS^* difference does not detract from this formulation in any way.

[17] A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 438 (1966). These authors present convincing arguments for nitrogen-bonded thiocyanate ion in $(H_2O)_5FeNCS^{2+}$.

[18] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Kinetic Study on the Alkaline Hydrolysis of Oxalato, Fumarato, and Maleato Complexes of Pentaamminecobalt(III)

BY NEIL S. ANGERMAN AND ROBERT B. JORDAN

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The rate for the hydrolysis of the fumarato and maleato complexes of pentaamminecobalt(III) was found to be first order in hydroxide ion and in the complex. At 25° ($\mu = 1.0$, NaCl), for the fumarato complex k, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are 8.00×10^{-5} M^{-1} sec^{-1}, 28.5 kcal mole^{-1}, and 18.3 cal mole^{-1} deg^{-1}. These values for the maleato complex are 2.80×10^{-5} M^{-1} sec^{-1}, 28.0 kcal mole^{-1}, and 14.4 cal mole^{-1} deg^{-1}. The oxalato complex was found to have a term in the rate law first order in hydroxide ion (k_1) and a term second order in hydroxide ion (k_2). The kinetic parameters k_1, $\Delta H_1^{\ddagger}$, and $\Delta S_1^{\ddagger}$ (25°, $\mu = 1$, NaCl) are 2.45×10^{-4} M^{-1} sec^{-1}, 31.7 kcal mole^{-1}, and 32.2 cal mole^{-1} deg^{-1}; k_2, $\Delta H_2^{\ddagger}$, and $\Delta S_2^{\ddagger}$ (25°, $\mu = 1$, NaCl) are 0.61×10^{-4} M^{-2} sec^{-1}, 23.7 kcal mole^{-1}, and 2.5 cal mole^{-1} deg^{-1}.

Introduction

The series of carboxylatopentaamminecobalt(III) complexes presents a favorable system for studies of the effect of ligand properties on hydrolysis rates. The atom bound to cobalt is the same in all cases but the properties of the ligand may be varied in a systematic way as judged from their organic chemistry.

Previous studies have shown that these complexes may undergo both Co–O and O–C bond breaking.[1] Subsequent work on halo-substituted acetato complexes[2] has confirmed the prediction of Basolo, Bergman, and Pearson[3] that Co–O bond breaking should be easier the smaller the pK of the carboxylic acid.

The present results extend this study to a series of dicarboxylic acids and further indicate the factors influencing the ease of cobalt–oxygen and carbon–oxygen bond breaking.

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[1] R. B. Jordan and H. Taube, *J. Am. Chem. Soc.*, **88**, 4406 (1966).

[2] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **6**, 379 (1967).

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

Experimental Section

Preparation and Analysis of Complex Salts.—Each of the cobalt(III) complexes was prepared by heating an aqueous solution of the half-neutralized dicarboxylic acid with $(NH_3)_5CoOH_2(ClO_4)_3$ at 70° for 2 hr. The organic acid was in about 10-fold molar excess. The crude product which separates on cooling was redissolved in water and recrystallized by adding concentrated perchloric acid.

The complexes were analyzed for ammonia by the method of Horan and Eppig.[4] The equivalent weight of the maleato and fumarato complexes was determined by titration with sodium hydroxide to the phenolphthalein end point. The oxalate content of the oxalate complex was determined by permanganate titration as described by Andrade and Taube.[5]

Anal. Calcd for fumarato complex: NH_3, 18.48; equiv wt, 458.1. Found: NH_3, 18.43; equiv wt, 456.2. Calcd for maleato complex: NH_3, 18.48; equiv wt, 458.1. Found: NH_3, 18.50; equiv wt, 457.1. Calcd for oxalato complex: NH_3, 16.21; $C_2O_4^{2-}$, 20.35. Found: NH_3, 16.19; $C_2O_4^{2-}$, 20.35.

Base-Hydrolysis Kinetics.—The reactions were sufficiently slow in all cases that the solid complex could be dissolved in the reaction solution containing appropriate amounts of sodium hydroxide and sodium chloride to give an ionic strength of 1.0. Reaction solutions were equilibrated at the required temperature for at least 0.5 hr before adding the solid complex. All solutions were prepared in water redistilled from alkaline permanganate. The reaction solutions were protected from light by wrapping them with aluminum foil.

Spectral measurements were made on a Bausch and Lomb Spectronic 505 spectrophotometer. Temperatures were controlled to ±0.10° with a standard constant-temperature bath.

Several methods were used to follow the hydrolysis of $(NH_3)_5CoC_2O_4^+$. The main problem is to avoid or eliminate the colloidal cobaltic oxide which forms in 3–10% yield on decomposition of the oxalato complex. One analytical method found to be satisfactory involved quenching aliquots from the hydrolysis reaction, then placing the sample on an ion-exchange column of Dowex 50-X12 resin and eluting with four column volumes of water. The column served to filter out cobaltic oxide and adsorbed all cobalt–ammine species. The eluent contained the hydrolyzed oxalate ion which was titrated with 0.01 *N* potassium permanganate.

An alternative procedure was to quench the reaction with 2 ml of concentrated HCl. The cobaltic oxide is reduced by HCl to Co^{2+}. The quenched solution was diluted to volume and the optical density was recorded at 280 mμ. Blank experiments showed that $Co(NH_3)_5OH_2^{2+}$, Co^{2+}, and HCl mixtures have negligible absorbance at this wavelength compared to that of the oxalatopentaamminecobalt(III). Rate constants calculated from both methods agreed to within ±2%.

For the fumarato and maleato complexes, aliquots were quenched with excess perchloric acid and the cobalt oxide was removed by filtration through a 0.45-μ Millipore filter (Millipore Filter Corp., Bedford, Mass.). Samples were diluted to volume and the optical density was recorded at 304 and 298 mμ for the fumarato and maleato complexes, respectively.

Results

The rate of hydrolysis of the fumarato and maleato complexes at ionic strength $\mu = 1.0$ (NaCl) was found to be first order in hydroxide ion, obeying the rate law

$$\frac{-\mathrm{d} \ln [\text{complex}]}{\mathrm{d}t} = k_{\text{obsd}} = k_1[\text{OH}^-]$$

Tables I and II record the values of k_1 at various hydroxide ion concentrations and temperatures for the fumarato and maleato complexes, respectively.

TABLE I

RATE OF HYDROLYSIS OF FUMARATOPENTAAMMINECOBALT(III)[a]

Temp, °C	$[OH^-]$, *M*	10^4k_1, M^{-1} sec^{-1}
25	0.60	0.815
	0.80	0.780
	0.90	0.800
	1.00	0.805
35	0.60	3.18
	0.80	3.17
	1.00	3.01
45	0.40	16.3
	0.60	16.8
	0.80	16.6

[a] Ionic strength 1.0 *M* adjusted with NaCl.

TABLE II

RATE OF HYDROLYSIS OF MALEATOPENTAAMMINECOBALT(III)[a]

Temp, °C	$[OH^-]$, *M*	10^4k_1, M^{-1} sec^{-1}
25	0.60	0.278
	0.80	0.282
	0.90	0.280
35	0.60	1.04
	0.80	0.97
	1.00	0.99
40	0.40	2.40
	0.60	2.38
	0.80	2.41
45	0.40	5.85
	0.50	6.02
	0.60	6.03
	0.80	5.81

[a] Ionic strength 1.0 *M*, adjusted with NaCl.

The results for the oxalato complex are given in Table III. It was found that there is a consistent though small trend in the values of $k_{\text{obsd}}/[\text{OH}^-]$ indicating a higher than first-order dependence of the rate on hydroxide ion. Although the maximum deviation from first-order hydroxide dependence is only about 15%, since it is not observed in the maleato and fumarato complexes, it is assumed to be due to an added term in the rate law rather than to activity coefficient or ion-pair effects. Therefore, the rate constants have been fitted to a rate law analogous to that found for the halo-substituted acetato complexes of pentaamminecobalt(III); that is

$$\frac{-\mathrm{d} \ln [(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+]}{\mathrm{d}t} = k_{\text{obsd}} = k_1[\text{OH}^-] + k_2[\text{OH}^-]^2$$

The best fit values of k_1 and k_2 are given in Table IV. Table II presents values of $k_{\text{obsd}}/[\text{OH}^-]$ calculated from the values of k_1 and k_2 for comparison to the observed values of $k_{\text{obsd}}/[\text{OH}^-]$.

Values of $\Delta H^{\ddagger}$ were determined from plots of ln (k/T) *vs.* $1/T$ and $\Delta S^{\ddagger}$ was calculated from the transition state theory equation. The respective values are given in Table V. $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ refer to the $k_1[\text{OH}^-]$ path and $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ refer to the $k_2[\text{OH}^-]^2$ path as defined above.

Discussion

The previous results[2] on the alkaline hydrolysis of halogen-substituted acetato complexes of pentaammine-

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(4) H. A. Horan and H. J. Eppig, *J. Am. Chem. Soc.*, **71**, 581 (1949).

(5) C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966).

Table III

Rate of Hydrolysis of $(NH_3)_5CoC_2O_4^{+}$ [a]

Temp, °C	$[OH^-]$, M	$10^4k_{obsd}/[OH^-]$, M^{-1} sec^{-1}	
		Obsd[b]	Calcd
15.0	0.10	0.371	0.377
	0.40	0.420	0.413
	0.80	0.455	0.461
25.0	0.10	2.50	2.51
	0.50	2.75	2.76
	1.00	3.05	3.06
35.2	0.20	15.1	15.0
	0.50	15.5	15.6
	0.70	16.1	15.9
	0.99	16.5	16.5

[a] Ionic strength 1.0 M, adjusted with NaCl. [b] Duplicate runs indicate a reproducibility of ±2% in the values of k_{obsd}.

Table IV

Rate Constants for the Hydrolysis of $(NH_3)_5CoC_2O_4^{+}$ [a]

Temp, °C	10^4k_1, M^{-1} sec^{-1}	10^4k_2, M^{-2} sec^{-1}
15	0.365	0.12
25	2.45	0.61
35.2	14.6	1.9

[a] Fitting of the experimental rate constants to the proposed rate law indicates an error of about ±3% in k_1 and ±15% in k_2.

Table V

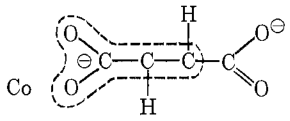
Activation Parameters for the Hydrolysis of Carboxylate Pentaamminecobalt(III) Complexes

Carboxylic acid ligand	$\Delta H_1^{\ddagger}$, kcal mole^{-1}	$\Delta H_2^{\ddagger}$, kcal mole^{-1}	$\Delta S_1^{\ddagger}$, eu	$\Delta S_2^{\ddagger}$, eu	Ref
Fumarate	28.5	...	18.3	...	This work
Maleate	28.0	...	14.4	...	This work
Oxalate	31.7	23.7	32	2.5	This work
Dichloroacetate	28.9	20.8	28.8	0.3	2
Trichloroacetate	23.3	22.3	12.5	8.5	2
Trifluoroacetate	22.7	6.8	10	−37	1

cobalt(III) indicate that the activation energy decreases with decreasing pK_a of the carboxylic acid. This correlation predicts, contrary to observation, that the oxalato complex will have a lower activation energy than the fumarato or maleato complex. It is expected that the fumarato and maleato complexes will be similar in spite of their large pK_a differences, because these differences are due to intramolecular hydrogen bonding in the bimaleate ion. This failure emphasizes the fact that the simple correlation found for the series of acetate complexes, which are similar in charge and size, cannot be extended to other systems in a simple way. It was part of the purpose of this work to determine what effect, if any, changing the size, charge, and shape of the carboxylate ligand will have on the hydrolysis rate.

The previous correlation was based on the idea that the cobalt–ligand bond strength depended on the amount of negative charge on the oxygen next to the cobalt. Electron-withdrawing substituents decrease this charge and give a weaker bond. The present results can be interpreted in a similar way; however, the factors influencing the amount of negative charge on the oxygen next to cobalt are more complex.

In the fumarato and maleato complexes some stability may be gained by negative charge delocalization from the carboxylate group next to the cobalt atom onto the –CH═CH– group



This delocalization will reduce the Co–O bond strength but will increase the C–O bond strength and give some added stability due to the delocalization of charge, considered relative to the case with the negative charge localized on the oxygen atom next to the cobalt. This effect cannot stabilize the oxalate complex because there are no carbon atoms, onto which charge can be delocalized, between the carboxylate groups. The result will be a weakening of the cobalt–carboxylate bond in the fumarato and maleato complexes relative to that expected from the simple pK_a correlation.

A term second order in hydroxide ion has been observed previously in the hydrolysis of the trifluoro-, trichloro-, and dichloroacetato complexes of pentaamminecobalt(III).[2] Tracer results on the trifluoroacetato complex have shown that this path involves O–C bond breaking.[1] Also oxygen-18 tracer studies on the oxalato complex[6] indicate that this complex undergoes some O–C bond breaking and that substitution at cobalt has a higher activation energy than substitution at carbon. The results of the kinetic study presented here are, therefore, consistent with the previous tracer work, if the $[OH^-]^2$ path involves O–C bond breaking.

Two of the tracer values given by Andrade and Taube can be used in conjunction with the hydrolysis rates to calculate the rate of oxygen exchange between complexed oxalate and water during the alkaline hydrolysis. The method used for this calculation is given in ref 1. Making the assumption that only the oxygens next to the cobalt are exchanging and that they both exchange at the same rate (case I of ref 1), then the rate constant for the exchange is

$$k_e = \left(\frac{4F_2(k_1 + k_2[OH^-]) - k_2[OH^-]}{2 - 4F_2}\right)[OH^-]$$

where F_2 is the fraction of solvent oxygen in the oxalate product after complete reaction and k_1 and k_2 are the hydrolysis rate constants defined previously. At 25° the results of Andrade and Taube are $F_2 = 0.0855$ at 0.25 M NaOH and $F_2 = 0.14$ at 1.4 M NaOH. Assuming k_e is first order in hydroxide ion, these values give the specific first-order rate constant k_e' of 0.44×10^{-4} and 0.40×10^{-4} M^{-1} sec^{-1} at 0.25 and 1.4 M NaOH, respectively. The constancy of the calculated k_e' at two widely different hydroxide ion concentrations shows that the hydrolysis and tracer studies are consistent with a hydrolysis mechanism similar to that found for $(NH_3)_5CoO_2C_2F_3^{2+}$.[1]

The above arguments indicate that the path second

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[6] C. A. Andrade and H. Taube, *J. Am. Chem. Soc.*, **86**, 1328 (1964).

order in hydroxide involves O–C bond breaking in the oxalato complex. The lack of such a path for the fumarato and maleato complexes is consistent with the previous statements on the bonding in these complexes. Both are proposed to have more charge delocation giving greater carbon–oxygen double-bond character and placing more negative charge on the carboxyl carbon. These effects will make O–C bond rupture and OH^- attack at the carboxyl carbon more difficult.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

Rates and Mechanism of Formation of Some Nickel(II) Complexes in Methanol

BY RALPH G. PEARSON AND PAUL ELLGEN

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Neutral ligands react with nickel(II) to form complexes at a slower rate in methanol than in water. Monovalent anions react at about the same rate in methanol as in water. Divalent anions react faster in methanol than in water. These results are in very good agreement with the ion-pair interchange mechanism for complex formation reactions. The agreement can be made reasonably quantitative. Small amounts of water added to methanol markedly accelerate the rates of complex formation.

Introduction

The development of techniques for kinetic study of rapid reactions has resulted in an extensive accumulation of rate data for reactions of the type

$$M(H_2O)_6^{n+} + L^{z-} \longrightarrow M(H_2O)_5L^{(n-z)+} + H_2O \qquad (1)$$

The results for these systems have been reviewed by several authors.[1-3] Because many of its reactions proceed at rates accessible to stopped-flow investigation, hexaaquonickel(II) has been a favorite substrate for these studies. The behavior which has been observed for nickel(II) is typical of that for a large class of aquometal ions. The characteristic kinetic features of these reactions can be summarized briefly. (i) The rate law for formation of $M(H_2O)_5L$ is second order over-all, first order in metal ion, and first order in ligand. (ii) For a given metal ion, large variation in formation rates can be observed with different ligands. In general, ligands bearing a large negative charge react rapidly, while those bearing a more positive charge react more slowly. Ligands having the same charge tend to react at about the same rate; such variations as are observed fail to correlate with expected relative nucleophilicities. (iii) For a range of metal ions, ligand-substitution rates parallel the rates of water exchange.

These observations are accounted for by a mechanism in which the ligand and the aquated metal ion are in rapid equilibrium with an outer-sphere complex in which the incoming group occupies a position in the second coordination sphere. The rate-determining step is the collapse of this outer-sphere complex to give the inner-sphere complex

$$M(H_2O)_6^{n+} + L^{z-} \overset{K_0}{\rightleftharpoons} [M(H_2O)_6,L]^{(n-z)+} \qquad (2)$$

$$[M(H_2O)_6,L]^{(n-z)+} \xrightarrow{k_0} M(H_2O)_5L^{(n-z)+} + H_2O \qquad (3)$$

The rate law predicted by this mechanism is, for excess metal ion

$$\frac{d[M(H_2O)_5L^{(n-z)+}]}{dt} = \frac{K_0k_0[M(H_2O)_6^{n+}][L^{z-}]}{1 + K_0[M(H_2O)_6^{n+}]} \qquad (4)$$

In the usual event that $1 >> K_0[M(H_2O)_6^{n+}]$, this becomes

$$\frac{d[M(H_2O)_5L^{(n-z)+}]}{dt} = K_0k_0[M(H_2O)_6^{n+}][L^{z-}] \qquad (5)$$

As pictured here, the rate step (3) is an interchange process characterized, in the classification scheme of Langford and Gray,[4] by "dissociative activation." In this scheme the mechanism for step 3 would be assigned the symbol I_d.

The rate of reaction 3 is expected to be close to the rate of solvent exchange. This has been repeatedly confirmed (see below), particularly for nickel(II). The rate at which $Ni(H_2O)_6^{2+}$ exchanges water molecules in the inner coordination sphere is known to be 3.0×10^4 sec^{-1}.[5] The rate for methanol exchange on

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(1) R. G. Wilkins and M. Eigen, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

(2) M. Eigen, IUPAC 7th International Conference on Coordination Chemistry, Butterworth and Co. Ltd., London, 1963.

(3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

(4) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 3.

(5) R. E. Connick and D. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).