Kinetics of the Acid Hydrolysis of Carboxylatopentammineruthenium(III) Complexes

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The kinetics of the hydrolysis of pentammineruthenium(III) complexes containing carboxylates and α-substituted acetates (glycolate and glycinate) have been studied. The experiments were carried out in a solution of $[H^+]=0.025$—0.1 M, at 40—70°C. For each complex, the rate law was found to be: rate=[complex]$(k_{H_2O}+k_H[H^+])$. The k_{H_2O} and k_H values for the formato, acetato, propionato, isobutyrato, glycolato, and glycinato complexes are, respectively (at $\mu=0.10$, 59—61°C): k_{H_2O}, 5.37×10^{-5}, 11.8×10^{-5}, 14×10^{-5}, 13.7×10^{-5}, 5.7×10^{-5}, and 6.75×10^{-5} sec^{-1}; k_H, 3.3×10^{-3}, 2.3×10^{-3}, 2.5×10^{-3}, 1.7×10^{-3}, 0.75×10^{-3}, and 3.1×10^{-3} M^{-1}sec^{-1}. The mechanisms of acid hydrolysis are discussed for the two reaction paths.

Recently, the kinetic studies of the hydrolysis of halogenopentammineruthenium(III)[1,2] and related complexes[2] have been reported. The kinetics of aquation have also been studied with some carboxylatopentammine complexes $[M(NH_3)_5OOCR]^{2+}$ (where M=Co(III), Rh(III), and Ir(III)) by Basolo *et al.*,[3,4] Kuroda,[5,6] and Saito *et al.*[7,8] These metal ions have six *d*-electrons, but Ru(III) has five. Therefore, it is of interest to study the aquation of a similar type of Ru(III) complexes and to compare them with d^6-metal complexes. In this paper, we will report on the kinetics of the aquation of several alkyl-, hydroxyl-, or amino-substituted-carboxylatopentammineruthenium(III) complexes.

Experimental

Reagents. All the chemicals used were of a reagent grade. Twice-distilled water was used in all the kinetic runs. The ionic strength and the acidity of the reaction solution were adjusted with *p*-toluenesulfonic acid and its sodium salt. The sodium salt was prepared by the neutralization of *p*-toluenesulfonic acid with sodium hydroxide.

Preparation of Complexes. *Chloropentammineruthenium(III) chloride* was prepared by the method of Allen *et al.*[9,10] from ruthenium trichloride and hydrazine hydrate.

Found: H, 5.08; N, 23.75%. Calcd for $[RuCl(NH_3)_5]Cl_2$: H, 5.19; N, 23.98%.

Aquopentammineruthenium perchlorate was prepared by the method of Endiccot and Taube.[11]

Found: H, 3.20; N, 13.74%. Calcd for $[Ru(H_2O)(NH_3)_5](ClO_4)_3$: H, 3.42; N, 13.94%.

Formatopentammineruthenium and other carboxylatopentammineruthenium perchlorates were prepared by the method of Stritar and Taube[12] from chloropentammineruthenium chloride, a carboxylate buffer solution, and a zinc amalgam.

Found: C, 3.00; H, 3.62; N, 16.39%. Calcd for $[Ru(NH_3)_5OOCH](ClO_4)_2$: C, 2.79; H, 3.75; N, 16.28%.

Found: C, 5.37; H, 3.86; N, 15.61%. Calcd for $[Ru(NH_3)_5OOCCH_3](ClO_4)_2$: C, 5.41; H, 4.08; N, 15.77%.

Found: C, 7.90; H, 4.29; N, 15.15%. Calcd for $[Ru(NH_3)_5OOCC_2H_5](ClO_4)_2$: C, 7.86; H, 4.41; N, 15.28%.

Found: C, 10.44; H, 4.32; N, 14.70%. Calcd for $[Ru(NH_3)_5OOCCH(CH_3)_2](ClO_4)_2$: C, 10.17; H, 4.70; N, 14.83%.

Found: C, 5.47; H, 3.75; N, 14.97%. Calcd for $[Ru(NH_3)_5OOCCH_2OH](ClO_4)_2$: C, 5.22; H, 3.94; N, 15.22%.

Found: C, 4.37; H, 3.80; N, 14.84%. Calcd for $[Ru(NH_3)_5OOCCH_2NH_3](ClO_4)_3$: C, 4.28; H, 3.60; N, 14.99%.

These complexes were also characterized by their electronic and IR spectra.

Kinetic Runs. The rates of the reactions were followed spectrophotometrically. It was found that the usual inorganic acids were unsuitable for the study of acid hydrolysis. In perchloric and nitric acid solutions, the aquation and decomposition of the complex occurred simultaneously. Several hours later, the appearance of the reaction mixture changed from a transparent pale yellow to a turbid dark brown. These phenomena are probably due to the oxidation of ruthenium(III) by acid anions. In hydrochloric and sulfuric acid, ligand replacements were spectrophotometrically identified. *p*-Toluenesulfonic acid is the best for studying the kinetics of aquation. Since *p*-toluenesulfonate has a strong $\pi\leftrightarrow\pi^*$ absorption below 280 mμ, the rates of hydrolysis were followed by measuring the changes in the absorbances of the respective complex ion in the wavelength region of 290—300 mμ.

All the kinetic experiments were performed in a stoppered quartz cell placed in a cell compartment of HITACHI 124 spectrophotometer. The reaction mixture in the cell was kept at a constant temperature, ±0.2°C, by circulating water from a thermostated bath. After thermal equilibrium has been achieved, a weighed amount of the complex (about 1 mg) was rapidly dissolved in an aqueous solution of a given ionic strength and acid concentration. The absorbances of the complexes in the reaction mixtures were measured at appropriate intervals.

Identification of the Reaction Product. Since aquopentammineruthenium(III), which has an absorption maximum at 268 mμ,[5] can not be directly detected, as was mentioned above, it was separated and identified. About six half-lives

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[1] J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).

[2] J. A. Broomhead and C. Sutton, *ibid.*, **8**, 1544 (1969).

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

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

[5] K. Kuroda, *Nippon Kagaku Zasshi*, **82**, 572 (1961).

[6] K. Kuroda, *ibid.*, **82**, 1481 (1961).

[7] K. Ogino, T. Murakami, and K. Saito, This Bulletin, **41**, 1615 (1968).

[8] T. Murakami, K. Ogino, H. Kobayashi, H. Yamazaki, and K. Saito, *ibid.*, **44**, 120 (1971).

[9] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

[10] A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967).

[11] J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **84**, 4984 (1962).

[12] J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).

later, the reaction mixture was passed through a column of ion-exchange resin (Dowex 50X-8, 100—200 mesh). The column was washed several times with water until no *p*-toluenesulfonate ion was detected in the washings, and then a 3M sodium perchlorate solution (pH 1.0 with perchloric acid) was passed through the column. The electronic spectrum of this eluate was measured and compared with that of the authentic aquopentammine complex.

Results

The electronic spectrum of the reaction product coincided with that of the aquopentammineruthenium(III) ion prepared from chloropentammineruthenium(III) and ammonia water (Fig. 1). The extent of the absorbance of the reaction product contributing to that of the reactant was smaller than 3% at one half-life of the reaction. The changes in the spectrum during the acid hydrolysis of the acetatopentammine complex are exemplified in Fig. 2. The acid hydrolysis reaction is an irreversible one, for the plot of log C_t *vs.* the reaction time is linear over a period of approximately one half-life, as is shown in Fig. 3, where C_t denotes the concentration of the complex at the reaction time, t. As is shown in Fig. 3, the slopes of the first-order plots are independent of the initial concentration of the reactant complex at the same hydrogen-ion concentration, ionic strength, and reaction temperature.

The pseudo first-order rate constants, k_{obs}, for the acid hydrolysis of carboxylatopentammines as a function of the hygrogen-ion concentration are listed in Table 1. The values of k_{obs} have a precision of $\pm 5\%$ or better. As is shown in Fig. 4, the plots of k_{obs} *vs.* the hydrogen-ion concentration are linear for the formatopentammine complex, and similar relationships were obtained for the other five complexes. From these results, it is possible to estimate an acid-independent rate constant, k_{H_2O}, and an acid-dependent rate constant k_H. The observed rate constant, k_{obs}, can be expressed by Eq. (1):

$$k_{obs} = k_{H_2O} + k_H[H^+] \qquad (1)$$

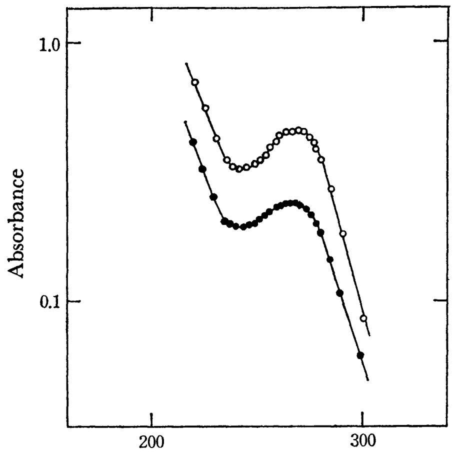


Fig. 1. Identification of the reaction product.
A: Spectrum of $[Ru(H_2O)(NH_3)_5]^{3+}$ prepared from $[RuCl(NH_3)_5]^{2+}$ in 0.1M $HClO_4$.
B: Spectrum of the reaction product eluted from cation exchange resin.
Reactant complex=$[Ru(NH_3)_5OOCH]^{2+}$

The calculated k_{H_2O} and k_H values are listed in Table 2, together with the pK_a values of the carboxylic acids.

The influence of the ionic strength on the rate of the hydrolysis was also investigated, the results are given in Table 3. The rates of hydrolysis increase with an increase in the ionic strength. This fact indicates that there is a positive kinetic salt effect.

The activation parameters for the reactions were evaluated from the kinetic data at 40—70°C and at an ionic strength of 0.1. The results are listed in Table 4.

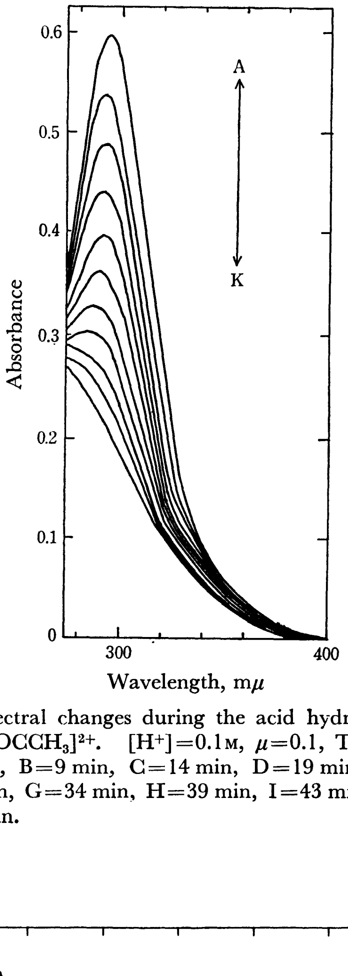


Fig. 2. Spectral changes during the acid hydrolysis of $[Ru(NH_3)_5OOCCH_3]^{2+}$. $[H^+]=0.1M$, $\mu=0.1$, Temp=60.2°C. A=4 min, B=9 min, C=14 min, D=19 min, E=20 min, F=29 min, G=34 min, H=39 min, I=43 min, J=49 min, K=54 min.

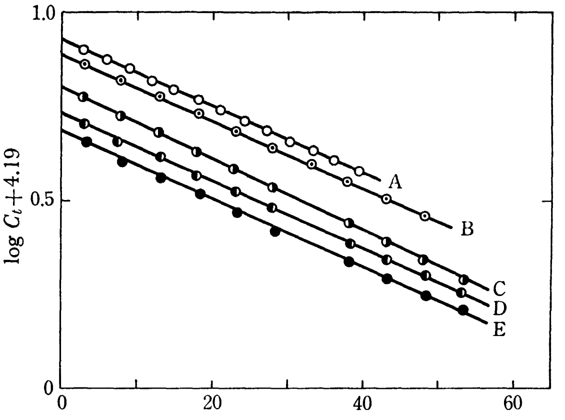


Fig. 3. The rates of hydrolyses of $[Ru(NH_3)_5OOCCH_3]^{2+}$ Temp=60.2°C, 0.1M *p*-toluenesulfonic acid, $\mu=0.1$. Initial concentrations: A=5.36×10^{-4}M, B=5.05×10^{-4}M, C=4.05×10^{-4}M, D=3.40×10^{-4}M, E=3.08×10^{-4}M.

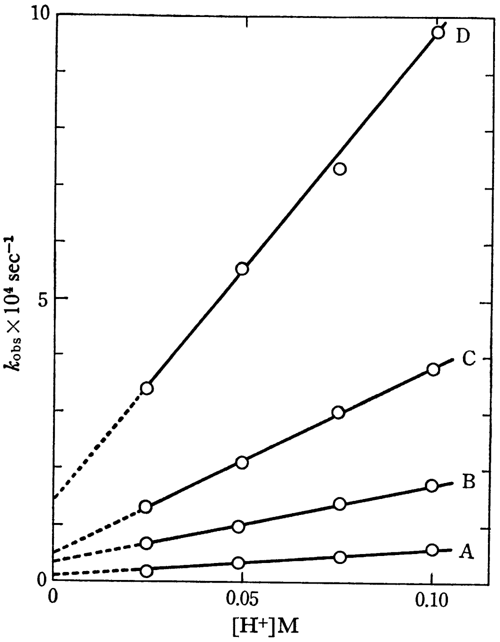


Fig. 4. The rate constant of hydrolysis *vs.* [H+] Complex; $[Ru(NH_3)_5OOCH]^{2+}$, μ=0.1. Temp=A; 40.0°C, B; 51.0°C, C; 61.0°C, D; 71.0°C.

TABLE 1. THE RATES OF HYDROLYSIS OF CARBOXYLATOPENTAMMINERUTHENIUM(III) AT VARIOUS HYDROGEN ION CONCENTRATIONS AND μ=0.10

Complexes	Temp °C	[H+]M	$k_{obs}\times 10^4$sec^{-1}
Formato-	61.0	0.0244	1.36
		0.0499	2.13
		0.0745	3.03
		0.0996	3.80
Acetato-	60.2	0.0260	1.78
		0.0511	2.35
		0.0767	2.92
		0.1020	3.53
Propionato-	60.0	0.0244	1.98
		0.0500	2.76
		0.0756	3.24
		0.0998	3.88
iso-Butyrato-	61.0	0.0252	1.80
		0.0487	2.20
		0.0748	2.60
		0.0995	3.07
Glycolato-	61.0	0.0200	0.70
		0.0400	0.90
		0.0800	1.15
		0.0995	1.32
Glycinato-	59.0	0.0247	0.68
		0.0494	0.69
		0.0741	0.70
		0.0988	0.71

Discussion

Equation (1) shows that the rate of hydrolysis of the complex is dependent on the hydrogen-ion concentration and that the two reaction paths are involved in the reaction mechanism of the hydrolysis. This can be expressed by Eq. (2) for one path and by Eqs. (3) and

TABLE 2. RATE CONSTANT OF ACID-CATALYZED AND UNCATALYZED PATH OF THE HYDROLYSIS OF CARBOXYLATOPENTAMMINERUTHENIUM(III) at μ=0.10

Complexes	Temp °C	pK_a	$k_{H_2O}\times 10^5$sec^{-1}	$k_H\times 10^4$M^{-1}sec^{-1}
Formato-	40.0	3.75	0.38±0.08	5.7±0.1
	51.0		3.19±0.04	14 ±1
	61.0	3.81	5.37±0.04	33 ±1
	71.0		13.8 ±1.9	83 ±3
Acetato-	40.0	4.76	0.99±0.07	3.5±0.1
	51.0		4.1 ±0.1	9.6±0.2
	60.2	4.81	11.8 ±0.1	22.9±0.2
	68.0		25 ±2	46 ±3
Propionato-	40.0	4.89	0.7 ±0.2	3.6±0.2
	50.0		4.2 ±0.5	11 ±1
	60.0	4.94	14 ±1	25 ±1
	70.0		40 ±4	61 ±4
iso-Butyrato-	40.6	4.92	1.0 ±0.8	2 ±1
	51.0		4.4 ±0.4	7.5±0.5
	61.0	4.99	13.7 ±0.2	16.9±0.5
	71.5		42.3 ±0.5	35 ±1
Glycolato-	50.0	4.85	2.1 ±0.1	2.0±0.2
	61.0		5.7 ±0.2	7.5±0.5
	65.0		9.6 ±0.2	10.1±0.3
	70.0		16.7 ±0.5	15.4±0.8
Glycinato-	59.0	2.32	6.75±0.01	0.31±0.02
	66.0		15.21±0.1	1.4 ±0.2
	70.0		22.6 ±0.1	1.5 ±0.9

TABLE 3. INFLUENCE OF IONIC STRENGTH (μ) ON THE RATE OF HYDROLYSIS OF CARBOXYLATOPENTAMMINERUTHENIUM(III) at [H+]=0.1M AND Temp=60.0±0.2°C

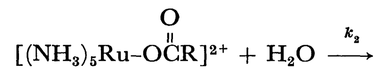
Complexes	μ	$k_{obs}\times 10^4$sec^{-1}
Formato-	0.10	3.80
	0.28	5.76
	0.55	6.91
	0.88	8.56
	1.01	8.90
Acetato-	0.10	3.53
	0.33	4.76
	0.55	5.87
	0.77	6.71
	1.00	7.56
Propionato-	0.10	3.88
	0.28	5.03
	0.55	6.37
	0.82	6.99
	1.00	8.06
iso-Butyrato-	0.10	2.36
	0.33	3.30
	0.55	3.95
	0.78	4.51
	1.00	5.15
Glycolato-	0.10	0.90
	0.24	1.13
	0.50	1.33
	1.00	1.49
Glycinato-	0.10	0.71
	0.50	0.64
	1.00	0.62

Table 4. Activation parameters for carboxylatopentammine complexes $\mu=0.1$

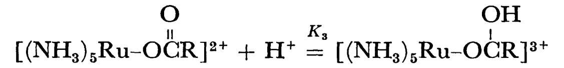
Complexes	k_{H_2O}		k_H	
	E_a kcal/mol	$\Delta S^{\ddagger}$ e.u.	E_a kcal/mol	$\Delta S^{\ddagger}$ e.u.
$[Ru(NH_3)_5OOCH]^{2+}$	24	−9	19	−16
$[Ru(NH_3)_5OOCCH_3]^{2+}$	24	−7	20	−15
$[Ru(NH_3)_5OOCC_2H_5]^{2+}$	25	−5	20	−15
$[Ru(NH_3)_5OOCCH(CH_3)_2]^{2+}$	25	−4	16	−26
$[Ru(NH_3)_5OOCCH_2OH]^{2+}$	22	−11	22	−6
$[Ru(NH_3)_5OOCCH_2NH_3]^{3+}$	26	−2	—	—
$[Co(NH_3)_5OOCH]^{2+,a)}$	—	—	25.2	—
$[Co(NH_3)_5OOCCH_3]^{2+,b)}$	25.3	−8	25	+2
$[Rh(NH_3)_5OOCCH_3]^{2+,b)}$	26.3	—	23	−4
$[Ir(NH_3)_5OOCCH_3]^{2+,b)}$	—	—	25	−8
$[Co(NH_3)_5OOCC_2H_5]^{2+,a)}$	—	—	25.4	—
$[Co(NH_3)_5OOCCH_2NH_3]^{3+,c)}$	22.6	−20	29.6	+3

a) Results from Ref. 6. b) Results from Ref. 4.
c) Resluts from Ref. 7.

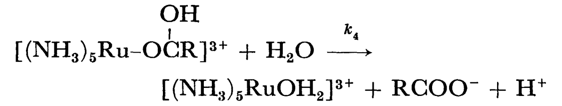
(4) for the other path:



$$[(NH_3)_5Ru\text{-}O\overset{O}{\overset{\|}{C}}R]^{2+} + H_2O \xrightarrow{k_2} [(NH_3)_5RuOH_2]^{3+} + RCOO^- \quad (2)$$



$$[(NH_3)_5Ru\text{-}O\overset{O}{\overset{\|}{C}}R]^{2+} + H^+ \overset{K_3}{=} [(NH_3)_5Ru\text{-}O\overset{OH}{\overset{|}{C}}R]^{3+} \quad (3)$$



$$[(NH_3)_5Ru\text{-}O\overset{OH}{\overset{|}{C}}R]^{3+} + H_2O \xrightarrow{k_4} [(NH_3)_5RuOH_2]^{3+} + RCOO^- + H^+ \quad (4)$$

The rate constant of an uncatalysed path [Eq. (2)], k_2, corresponds to k_{H_2O}. Equations (3) and (4) indicate an acid-catalysed path, the rate constant, k_H, of which can be expressed by Eq. (5):

$$k_H = k_4K_3 \quad (5)$$

these relationships for the hydrolyses of similar complexes of Co(III), Rh(III), and Ir(III) have previously reported.[4-8] However, it should be noted that the values of k_{H_2O} and k_H for ruthenium(III) complexes are greater than those of the Co(III), Rh(III), and Ir(III) complexes. In view of the electrostatic attraction between the metal and the ligand ion, the aquation of the d^5-metal complex should proceed faster than that of the d^6-metal complex if the break of the metal-ligand bond is the rate-determining step.

As is shown in Table 2, the k_{H_2O} values in a solution of $\mu=0.1$ at 59—61°C decrease in the order of isobutyrato-, (≃propionato-), acetato-, glycinato-, glycolato-, and formatocomplex. This suggests that the rate becomes faster, the greater the size of the leaving group, and that the reactions proceed through a dissociation-type mechanism.

The rates of the aquation of some carboxylatopentammineruthenium(II) complexes have been reported by Stritar and Taube.[12] In the acid-independent path, the values of the rate constants are 1.28 sec^{-1} and <5 sec^{-1} for the formato- and acetatocomplexes at 25°C and an ionic strength of 0.1. The values for the corresponding ruthenium(III) complexes which are obtained from the present experiments and extrapolated to the same experimental conditions are 1×10^{-5} and 7×10^{-6} sec^{-1} respectively. The ratios of the rate constants of the Ru(II) complexes to those of the Ru(III) complexes are 10^5 and 10^6. The effect of the positive charge of the complex on the rate could be interpreted as follows. The separation of a negative charge in the form of the carboxylate ion is more difficult as the remaining charge on the complex increases. These facts may indicate that the bond break is important and that we are dealing with an S_N1 mechanism in the present reactions.

The rate constant of hydrolysis, k_{obs}, increases with the increase in the ionic strength of the acidic solution (Table 3). This indicates that both of the reactants have same kinds of charge. When $[H^+]=0.1$ M, we can assume k_{H_2O} to be much smaller than k_H; thus, k_{obs} is nearly equal to k_4K_3. As may be seen from Eqs. (3) and (4), a positive kinetic salt effect can be expected in Eq. (3), the equilibrium constant of which is K_3. Therefore, it can be concluded that K_3 is the more effective fraction in the acid-dependent path.

Basolo *et al.*[4] reported that the k_{H_2O} values of carboxylatopentamminecobalt(III) complexes tend to decrease with an increase in the pK_a values of the ligand acids. The results in Table 2 do not indicate that such a relation fits the ruthenium(III) complexes. On the contrary, the k_H values for the ruthenium(III) complexes decrease with the increase in the pK_a values. The pK_a values affect the equilibrium constant, K_3, of Eq. (3), and hence the k_H values. The k_H values of the glycolato- and glicinatocomplexes are smaller than those of the other complexes. Concerning the glicinatocomplex of cobalt(III), Saito *et al.*[8] described the small k_H value as being due to the difficulty with which the protonated species are formed. For the similar complex of ruthenium(III), the same effect seems to be exhibited. The influence of the substituting hydroxyl group in the glycolatocomplex is not very clear, but it may be considered that there are some interactions between the hydroxyl and the carboxylate groups such as those in the aminoacid complex.

With regard to the hydrolysis of acetatopentamminecobalt(III), Monacelli *et al.*[4] reported that the acid-independent path proceeds by means of metal-oxygen bond fission and that the acid-dependent path takes place through the breaking of the acyl-oxygen bond. Bunton and Llewllyn[13] found that the aquation of this complex proceeds by means of metal-oxygen bond cleavage on the basis of a tracer study with oxygen-18.

The k_{H_2O} values for Co(III)[4] and Ru(III) acetatopentammine are, respectively, $8.0\times10^{-1}sec^{-1}$ and $2.9\times10^{-4}sec^{-1}$ at 70°C and an ionic strength of 0.1. Thus, the ratio of the rate constants, k_{H_2O}, for these complexes is 1 : 36, while the ratio of k_H is 1 : 5 under the same experimental conditions.

These facts suggest that the influence of the central metal ion on the rate of aquation is larger for the acid-independent path than for the acid-dependent path. Therefore, it may be supposed that the bond fission occurs at a position farther from the central metal ion

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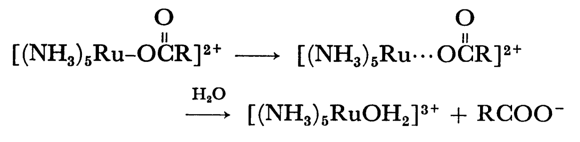
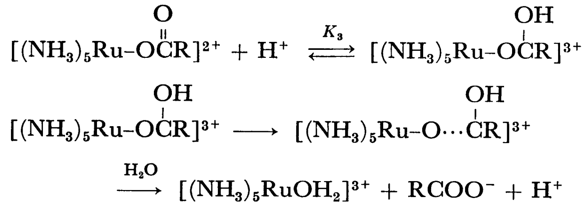
[13] C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, **1953**, 1692.

in the acid-dependent path than that in the acid-independent path. Thus, we believe that the acid-dependent path proceeds *via* acyl-oxygen bond fission and that the acid-independent reaction takes place through the breaking of the ruthenium-oxygen bond. These reaction mechanism are shown in Eq. (8) and (9):



$$[(NH_3)_5Ru\text{-}O\overset{O}{\overset{\|}{C}}R]^{2+} \longrightarrow [(NH_3)_5Ru\cdots O\overset{O}{\overset{\|}{C}}R]^{2+} \xrightarrow{H_2O} [(NH_3)_5RuOH_2]^{3+} + RCOO^- \quad (8)$$



$$[(NH_3)_5Ru\text{-}O\overset{O}{\overset{\|}{C}}R]^{2+} + H^+ \xrightleftharpoons{K_3} [(NH_3)_5Ru\text{-}O\overset{OH}{\overset{|}{C}}R]^{3+}$$

$$[(NH_3)_5Ru\text{-}O\overset{OH}{\overset{|}{C}}R]^{3+} \longrightarrow [(NH_3)_5Ru\text{-}O\cdots\overset{OH}{\overset{|}{C}}R]^{3+} \xrightarrow{H_2O} [(NH_3)_5RuOH_2]^{3+} + RCOO^- + H^+ \quad (9)$$

As another possibility, the attack of the water molecule on the carboxyl group may be considered; this would also lead to the acyl-oxygen bond cleavage.[13] We have, however, not yet obtained any experimental evidence to confirm this mechanism.

As is shown in Table 4, the activation energies for the acid-independent paths are generally larger than those for the acid-dependent paths. These values are independent of the substituting group in carboxylic acids except for the acid-dependent path of isobutyratocomplex. The activation energies for the k_{H_2O} values of d^5-(Ru^{III}) metal complexes are nearly the same as those of the d^6-(Co^{III}, Rh^{III}, and Ir^{III}) metal complexes. However, it was found that the activation energies for the k_H values of d^5-metal complexes are less than those of the d^6-metal complexes. The difference between the values of the formatocomplexes amounted to 6.2 kcal/mol.

The entropies of activation for k_H are more negative than those for k_{H_2O}. This suggests that the difference in the extent of hydration between the transition state and the ground state is larger in the acid-dependent path than in the acid-independent path. As is shown in Eqs. (8) and (9), there is an increase of +1 unit charge in the acid-dependent path, while no variation of the charge arises in the acid-independent path.

In the acid-dependent path, the entropy of activation, $\Delta S^{\ne}$, obtained may be expressed as follows:

$$\Delta S^{\ne} = \Delta S_{K_3} + \Delta S_{K_4}^{\ne}$$

where ΔS_{K_3} is the change of entropy for the process of protonation to the complex cation with the equilibrium constant K_3, and where $\Delta S_{K_4}^{\ne}$ is the entropy of activation with respect to the rate constant, K_4, described in Eq. (9). When reactions take place between two ions, an important contribution to the entropy of activation arises from the electrostatic force. For a reaction between two ions, A (Z_A charge) and B (Z_B charge), in a dilute aqueous solution, the entropy of activation is approximately $-10\ Z_A Z_B$ e.u./mol.[14] Considering that $Z_A Z_B$ is +2 in the process of protonation, the value of −20 e.u./mol can be calculated for ΔS_{K_3}. This is comparatively close to the observed values of activation entropies, and they are nearly the same for the cases of the formato-, acetato-, and propionatocomplexes. Therefore, it may be considered that a large part of $\Delta S^{\ne}$ consists of ΔS_{K_3} in these cases. The values of the activation entropies for k_H are considerably different in the case of the isobutyrato- and glycinatocomplexes. This indicates that the extent of the contribution of ΔS_{K_3} to $\Delta S^{\ne}$ may not be the same as in the other cases.

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14) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes" McGraw-hill book company, Inc., New York and London (1941), p. 433.