The Acid and Base Hydrolysis of
Sulfatopentamminecobalt(III) and Rhodium(III) Complexes

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The aquation reaction of $[M(NH_3)_5SO_4]^+$ (M = Co and Rh) and the base hydrolysis of $[Rh(NH_3)_5SO_4]^+$ have been studied kinetically.

In acid solution and in the absence of added sulfate ion, the aquation rate follows the equation: $R/[complex] = k+k'_H[H^+]$, at constant ionic strenght $\mu = 1.0$ M $(NaClO_4)$, with the rhodium complex being slightly more labile. The activation parameters are $\Delta H^* = 22.7$ (Co) and 21.4 (Rh) kcal/mole, $\Delta S^* = -10.0$ (Co) and -13.3 (Rh) e.u., $\Delta H_H^* = 28.4$ (Co) and 28.5 (Rh) kcal/mole, $\Delta S_H^* = 9.2$ (Co) and 9.0 (Rh) e.u. The rate constants at 25°C are: $k = 8.9 \times 10^{-7}$ (Co) and 1.6×10^{-6} (Rh) sec^{-1}, $k'_H = 9.5 \times 10^{-7}$ (Co) and 1.1×10^{-6} (Rh) sec^{-1} M^{-1}.

The spontaneous and acid-catalysed aquation of both sulfatopentamminemetal complexes appear to be essentially dissociative processes.

The constant k, for the rhodium compound, increases with the increasing $[SO_4^{2-}]$ above 0.3 M, at $\mu = 4.0$ M and 65°C. This effect is discussed in connection with the equilibrium ratios Q = [aquocomplex] / [sulfatocomplex]. For both the cobalt and the rhodium compound, k decreases when $[NaClO_4]$ increases, possibly as a consequence of the decrease of water activity.

The rate of the base hydrolysis of $[Rh(NH_3)_5SO_4]^+$ follows the equation $R/[complex] = k_{OH}[OH^-]$. The activation parameters are $\Delta H_{OH}^* = 24.5$ kcal/mole and $\Delta S_{OH}^* = +10$ e.u.. Both S_N1 CB and S_N2 CB mechanisms are consistent with the data although the entropy of activation is in favour of the second.

Introduction

In a previous investigation[1] some data were reported on the rate of aquation of the complex ion [Rh(NH_3)_5SO_4]^+.

It was observed that the rate of this reaction is sensitive to SO_4^= ions while the reverse (anation) shows only the kinetic dependence on the sulfate concentration expected on the basis of an ion-pair equilibrium taking place before the substitution process.

In this paper a more complete investigation of the aquation of the above complex is described, with the scope of clarifying some aspects of the reactivity of the sulfatopentamminerhodium(III) cation in aqueous solutions.

In order to compare the behaviour of the rhodium complex with that of the cobalt(III) analogue, the aquation cf the latter was also considered. This reaction has been already studied by several workers.[2-5] However, a reinvestigation of this system was necessary since the experimental conditions previously chosen were in general so different from those adopted here that only few data from the literature could be used for a comparison. Data on the base hydrolysis of the sulfatopentamminerhodium(III) complex are also reported and discussed.

Experimental Section

Materials. All reagents were pure grade chemicals and were used without further purification except sodium perchlorate which was recrystallized once from water.

Aquopentamminecobalt(III), aquopentamminerhodium(III), sulfatopentamminecobalt(III) and sulfatopentamminerhodium(III) perchlorates were prepared and purified according to known procedures.[1,6-8]

Concentrated stock solutions of NaClO_4, HClO_4, and Na_2SO_4 were prepared by dissolving the compounds in degassed water. According to the nature of the solute, the concentration of each solution was determined by weighing the residue obtained by evaporation of a sample of known volume[1] or by titration with standard sodium hydroxide. This solution was prepared by diluting to the proper volume with degassed water a commercially available concentrated standard solution (Merck, Titrisol).

Kinetic Runs. The rate of release of SO_4^{2-} ions from the sulfatopentamminecobalt(III) and rhodium-(III) complexes was studied under varying pH and ionic strength (μ) conditions.

The rates were measured spectrophotometrically by following the change of optical density, A, of solutions containing the reactants in appropriate concentrations. For the acid hydrolysis the wavelengths chosen were 225-230 mμ (Rh) and 290 mμ (Co), where the varia-

(1) F. Monacelli, *Inorg. Chim. Acta,* 2, 263 (1968).
(2) B. Adell, *Z. anorg. all. Chemie,* 249, 251 (1942).
(3) H. Taube and F.A. Posey, *J. Am. Chem. Soc.,* 75, 1463 (1953).
(4) F.A. Posey and H. Taube, *J. Am. Chem. Soc.,* 78, 15 (1956).
(5) Ya.A. Fialkov and V.D. Panasyuk, *Zhur. Neorg. Khim.,* 2, 1007 (1957).
(6) Gemelins' Handbuch der Anorganischen Chemie, 58B, 94 (1932).
(7) Gmelins' Handbuch der Anorganischen Chemie, 64, 109 (1938).
(8) L.L. Po and R.B. Jordan, *Inorg. Chem.,* 3, 526 (1968).

Table I. Extinction coefficients of $[Rh(NH_3)_5SO_4]^+$ as a function of sulfate concentration. $T = 65°C$, $\lambda = 230$ mμ, $[H^+] = 10^{-2} M$. Ionic strength controlled with $NaClO_4$.

[Na₂SO₄] (M)	$\mu = 1.0\ M$ ε_i ($M^{-1} \times cm^{-1}$)	[Na₂SO₄] (M)	$\mu = 4.0\ M$ ε_i ($M^{-1} \times cm^{-1}$)
0.0190	353	0.0250	376
0.0250	367	0.0300	368
0.0324	361	0.0360	373
0.0500	350	0.0450	369
0.100	336	0.0625	359
0.200	313	0.200	345
0.333	286	0.500	317
		1.00	257
		1.33	239

tion of A due to the reaction was conveniently large. The base hydrolysis of $[Rh(NH_3)_5SO_4]^+$ was followed at 220 mμ.

The reaction mixture was usually prepared by mixing at room temperature the proper volumes of the stock solutions with a weighed amount of the sulfato complex.

This solution was then poured in a 1-cm quartz cell and kept in the cell compartment of a Beckman DU2 spectrophotometer, adjusted to the desired temperature by circulating water from a thermostat. This procedure required about 15 minutes for the solution to reach the thermal equilibrium and for most of the runs this was a sufficiently short time compared with the reaction half-life. For the fastest reacting systems, however, the following procedure was adopted. A known volume (~ 2.7 ml) of a solution containing all the reagents except the complex, was allowed to equilibrate thermally in the quartz cell placed in the temperature controlled compartment of the spectrophotometer. The necessary amount of complex (1-3 mg) was weighed in a capillary tube which was then immersed in the solution with a little stirring. With this simple technique the temperature of the solution was only little disturbed and the time required for riequilibration was practically less than 5 minutes.

In all cases the complex was the minor component of the reaction mixture ($1-2 \times 10^{-3} M$) so that the concentration of all other species *initially present* could be considered constant regardless to their participation to the overall reaction stoichiometry.

The concentrations were corrected for the thermal expansion of the solutions, measured separately.

The observed optical changes were assumed to be due only to the substitution of water or hydroxide ion for the sulfate ligand.

When treated according to a pseudo first-order scheme the absorption data gave linear plots over more than two half-periods, except for the first minutes needed for the thermal equilibration (see above). However, for the aquation runs at low acid concentration a correction was introduced in order to account for the reverse reaction (see further).

Equilibrium Experiments. When the aquation of both sulfatopentamminecobalt(III) and rhodium(III) cations was carried out in the presence of added sulfate or at low acid concentration a definite equilibrium was reached as indicated by the fact that the

infinite time absorbancy, A_∞, was higher than expected for completion.

In these cases the equilibrium ratios $Q = $ [aquo complex]/[sulfato complex] were calculated by the formula

$$Q = \frac{\varepsilon_s - \varepsilon_e}{\varepsilon_e - \varepsilon_a}$$

where ε_s, ε_e and ε_a are the extinction coefficients of the sulfato complex, the equilibrium mixture and the aquo complex, respectively. The first two values were calculated from the zero time (*) and equilibrium absorbancies, while ε_a was assumed to be identical to that measured with the aquo complex in the absence of sulfate ions.[1]

At 230 mμ the extinction coefficient of the sulfatopentamminerhodium(III) complex was found to *decrease* markedly with the sodium sulfate concentration, as shown in Table I. An analogous effect has been reported by Posey and Taube for the sulfatopentamminecobalt(III) complex.[9]

Results and Discussion

A - Aquation. Acid dissociation of the hydrogensulfate ion. Some of the reactions here discussed were carried out in solutions containing sulfate and hydrogen ions in comparable concentrations. In these cases it was important to know the equilibrium constant of the following reaction:

$$HSO_4^- \overset{K_d}{\rightleftharpoons} H^+ + SO_4^{2-} \tag{1}$$
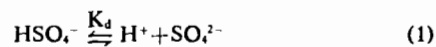
in order to evaluate the actual concentration of the ions involved.

Equilibrium (1) has been extensively investigated[10] but no data are available at the conditions chosen in the present study. Since K_d appears to be dependent on both the ionic strength and the nature of the

(*) Since the optical density of the reaction solution, at the wavelength used, increases with temperature and decreases as the aquation proceeds, after about 12 minutes from the start, A_t reaches a maximum value and remains virtually constant for 3-4 minutes before decreasing. This maximum was taken as zero time absorbancy though it is obviously lower than that. However, the error thus introduced was estimated to be small and unimportant in the calculations for Q.

(9) F.A. Posey and H. Taube, *J. Am. Chem. Soc.*, 79, 255 (1957).
(10) L.G. Sillén, « Stability constants of metal ion complexes », The Chemical Society special publication n. 17, London, 1964, p. 232 and foils.
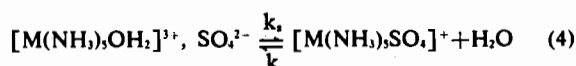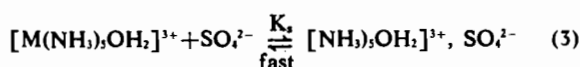
electrolytes,[11-14] the medium conditions should be carefully considered.

The most extensive investigations carried out in Na_2SO_4 - $NaClO_4$ mixtures of low acidity are those of Reynolds and Fukushima[13] and of Vdovenko, et al.[15] whose data are in moderate agreement with each other. Since those of ref. 15 allow the extrapolation to different temperatures, they were used to calculate K_d at 65°C. At this temperature K_d was calculated to be $2.7 \times 10^{-2} M$ ($\mu = 1.0\ M$) and $5.0 \times 10^{-2}\ M$ ($\mu = 4.0\ M$), the latter value being a reasonable extrapolation from values at lower ionic strengths.
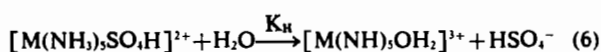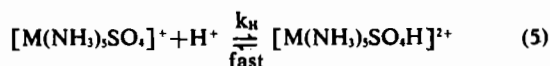
Rates of aquation of $[Co(NH_3)_5SO_4]^+$ *and* $[Rh-(NH_3)_5SO_4]^+$. The overall reaction may be represented by the following equilibrium (M = Co, Rh):

$$[M(NH_3)_5SO_4]^+ + H_2O \underset{k_{an}}{\overset{k_{aq}}{\rightleftharpoons}} [M(NH_3)_5OH_2]^{3+} + SO_4^{2-} \quad (2)$$
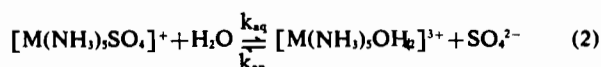
The reverse reaction is known to take place through the following steps[1,4]:

$$[M(NH_3)_5OH_2]^{3+} + SO_4^{2-} \underset{fast}{\overset{K_2}{\rightleftharpoons}} [NH_3)_5OH_2]^{3+}, SO_4^{2-} \quad (3)$$

$$[M(NH_3)_5OH_2]^{3+}, SO_4^{2-} \underset{k}{\overset{k_1}{\rightleftharpoons}} [M(NH_3)_5SO_4]^+ + H_2O \quad (4)$$

At $\mu = 1.0\ M$ the rate of reaction (2) was found to increase with the hydrogen ion concentration, in the range 5×10^{-3} - $1.0\ M$, suggesting for the aquation of both metal complexes an acid catalysed path. This may be accounted for by including the following reactions:

$$[M(NH_3)_5SO_4]^+ + H^+ \underset{fast}{\rightleftharpoons} [M(NH_3)_5SO_4H]^{2+} \quad (5)$$

$$[M(NH_3)_5SO_4H]^{2+} + H_2O \overset{K_H}{\longrightarrow} [M(NH)_5OH_2]^{3+} + HSO_4^- \quad (6)$$

Moreover, the infinite time absorbancy of the reacting solutions indicated that at the lowest hydrogen ion concentrations a small but detectable fraction of the starting sulfato complex was still present at equilibrium while above $\sim 0.2\ M$ the aquation could be considered virtually complete. This behaviour may be explained by considering the conversion of SO_4^{2-} ions to the less reactive HSO_4^- ions, through the equilibrium (1).

On the basis of reactions (3) to (6), if the concentrations of the ion-pair and the protonated species are negligible and if the hydrogen ion concentration may be considered constant within each run, the following equation holds:[16]

$$\ln \frac{X_\infty + X_t \frac{1}{1+Q}}{X_\infty - X_t} = (k + k_H K_H[H^+]) \frac{2+Q}{Q} \times t \quad (7)$$

where X_t and X_∞ are the instantaneous and equilibrium concentration of the aquo complex formed and Q the equilibrium ratio defined above. In all cases Q was a quantity so large to allow equation (7) to be expanded in the form:

$$\ln(A_t - A_\infty) + \frac{A_o - A_t}{A_o - A_\infty}\left(\frac{1}{1+Q}\right) = -(k + K_H k_H[H^+])\frac{2+Q}{Q} \times t + \ln(A_o - A_\infty) \quad (8)$$

using optical densities instead of concentrations. The term $\frac{A_o - A_t}{A_o - A_\infty}\left(\frac{1}{1+Q}\right)$ was always small compared to $\ln(A_t - A_\infty)$ and was considered only when it introduced a correction greater than 1% to the slope of the pseudo first-order $\ln(A_t - A_\infty)$ vs time plots. The term $\frac{Q}{2+Q}$, though close to unity, was instead more important.

The aquation rate constants $k_{aq} = k + k_H K_H[H^+]$, calculated according to (8) are listed in Table II. Figure 1 shows the dependence of k_{aq} on $[H^+]$ for both M = Rh and Co, at 74°C. As expected, the plots are linear within the experimental accuracy ($\pm 3\%$). For each temperature, the intercept (k) and the slope ($k_H' = k_H K_H$) were calculated by a least-square treatment of the experimental data and are reported in Table III. The Arrhenius plots were linear over the whole temperature range. The activation parameters obtained by least-square analysis are reported in Table IV.
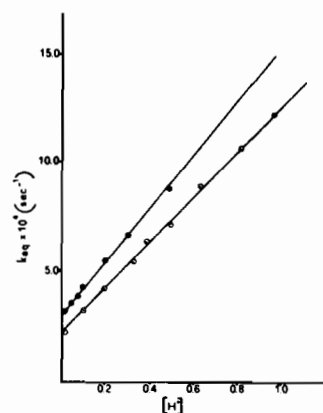

Figure 1. Aquation rate constants of $[M(NH_3)_5SO_4]^+$ as a function of hydrogen ion concentration. T = 74°C, μ = 1.0 M, ⊙ M = Co, ● M = Rh.

A set of aquation runs was carried out, at 65°C and in conditions where $k'_H[H^+]$ was negligible compared to k ($[H^+] = 0.01\ M$), at different ionic strengths ranging from 0.01 to 4.1 M. The uncatalyzed aquation rate constants of both sulfato complexes were found to decrease and the reactions were shifted

(11) M. Kerker, *J. Am. Chem. Soc.*, 79, 3664 (1957).
(12) R.W. Ramette and R.F. Stewart, *J. Phys. Chem.*, 65, 243 (1961).
(13) W.L. Reynolds and S. Fukushima, *Inorg. Chem.*, 2, 176 (1963).
(14) W.L. Marshall and E.V. Jones, *J. Phys. Chem.*, 70, 4028 (1966).
(15) V.M. Vdovenko, L.N. Lazarev, and Ya.S. Khoorostin, *Zhur. Neorg. Khim.*, 12, 1152 (1967).
(16) A. Frost and R.G. Pearson, « Kinetics and Mechanism » 2nd Ed., John Wiley, N.Y., p. 186.

towards completion with increasing perchlorate concentration, being virtually complete when $[NaClO_4] \geqslant$ 1 M (see Figure 2 and Table V).

Table II. Aquation rate constants of $[M(NH_3)_5SO_4]^+$ at constant ionic strength $1.00 \pm 0.05 M$ $(NaClO_4)$.

M	T (°C)	[HClO₄] (M)	$k_{aq} \times 10^4$ (sec⁻¹)
Co	55.3	0.0050	0.345
		0.0050	0.341
	65.1	0.0195	1.04
		0.0976	1.31
		0.195	1.70
		0.293	1.92
		0.391	2.24
		0.488	2.59
		0.701	3.31
		0.830	3.68
		0.976	4.19
	74.3	0.0050	2.36
		0.0972	3.36
		0.194	4.39
		0.321	5.64
		0.389	6.46
		0.486	7.34
		0.632	9.00
		0.728	9.47
		0.826	11.1
		0.972	12.3
	83.7	0.0050	6.01
		0.0484	7.33
		0.0968	9.14
		0.194	11.6
		0.242	13.4
		0.290	14.6
		0.339	16.2
		0.387	17.4
		0.436	19.3
		0.484	21.0
Rh	55.3	0.0050	0.516
	66.4	0.00978	1.50
		0.0391	1.66
		0.0684	1.79
		0.246	2.73
		0.490	3.80
		0.683	4.65
	74.6	0.00972	3.28
		0.0389	3.71
		0.0680	4.02
		0.0972	4.42
		0.194	5.58
		0.292	6.75
		0.488	8.98
	83.1	0.0197	8.03
		0.0485	8.96
		0.0975	11.0
		0.145	12.6
		0.242	15.7
		0.338	19.1
		0.435	23.0
		0.532	26.1

Equilibria in the presence of added sulfate ions $(M = Rh)$. The equilibrium ratios Q for the aquation reaction of $[Rh(NH_3)_5SO_4]^+$ have been already measured[1] at 65°C and $\mu = 4.0$ M $(NaClO_4)$. Additional

Table III. Spontaneous and hydrogen ion-catalysed aquation of $[M(NH_3)_5SO_4]^+$. Rate constants k and k'_H as a function of temperature. Ionic strength $1.0 M$ $(NaClO_4)$.

| M	T (°C)	$k \times 10^4$ (sec⁻¹)	$k_H' \times 10^3$ (sec⁻¹ × M⁻¹)
Co	55.3	0.343	—
	65.1	0.994	0.327
	74.3	2.36	1.03
	83.6	5.86	3.06
Rh	55.3	0.516	—
	66.4	1.49	0.469
	74.6	3.23	1.19
	83.1	7.35	3.53

experiments have been carried out in the present study with a more careful control of the reaction conditions. In addition, a set of experiments at 65°C and $\mu = 1.0$ M has been performed.

The concentration of perchloric acid, necessary to suppress the dissociation of the aquo complex, was kept as low as 4.0×10^{-3} in order to make negligible the contribution of the hydrogen ion- induced aquation of the sulfato complex. Furthermore, at the lowest sulfate ion concentrations, allowance was made for both the release of SO_4^{2-} ions from the acido complex and the effect of equilibrium (1).

The equilibrium ratios Q are reported in Table VI. Figure 3 shows the dependence of Q on the reciprocal sulfate concentration. At $\mu = 4.0$ M, Q is linearly dependent on $[SO_4^{2-}]^{-1}$ when $[SO_4^{2-}] \leqslant$ 0.3 M while above this value the points show an upward deviation. This confirms previous observations[1] which are reported in the same plot for comparison.

The data at $\mu = 1.0$ M follow a similar pattern but, because of the lower ionic strength, the region above $[SO_4^{2-}] = 0.33$ M could not be explored and a clear evidence of curvature was not found.

Values of Q at $\mu = 4.0$ M, interpolated on the solid
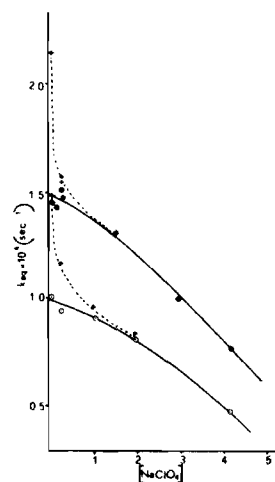
Figure 2. Effect of added $NaClO_4$ on the spontaneous aquation of $[M(NH_3)_5SO_4]^+$. Constant hydrogen ion concentration 0.010 M, T = 65°C. ● M = Rh; ⊙ M = Co; + observed rate constants, $k_{aq}(\frac{2+Q}{Q})$.

Table IV. Aquation of $[ML_5SO_4]^+$ cations. Activation parameters.

ML_5	spontaneous aquation			acid-catalysed aquation			Ref.
	$k \times 10^{7~a}$ (sec^{-1})	ΔH^* (kcal/mole)	ΔS^* (e.u.)	$k'_H \times 10^{7~a}$ (sec$^{-1} \cdot M^{-1}$)	ΔH_H^* (kcal/mole)	ΔS_H^* (e.u.)	
$Cr(H_2O)_5$	7.6	21.9	—13.0	1.1	26.5	—1.3	17
$Co(NH_3)_5$	12	18.7	—24	—	—	—.	3
$Co(NH_3)_5$	8.9	22.7	—10.0	9.5	28.4	9.2	This work
$Rh(NH_3)_5$	16	21.4	—13.3	11	28.5	9.9	This work

^{a} Rate constants at 25°C.

Table V. Spontaneous aquation of $[M(NH_3)_5SO_4]^+$. Effect of $NaClO_4$ concentration. T = 65°C, $[H^+]$ = 0.01 M (as $HClO_4$).

M	$[NaClO_4]$ (M)	$k_{aq} \times \dfrac{2+Q}{Q} \times 10^4$ (sec^{-1})	$k_{aq} \times 10^4$ (sec^{-1})
Co	0.00	1.49	1.01
	0.244	1.17	0.94
	0.98	0.92	0.92
	1.95	0.84	0.82
	4.15	0.48	0.48
Rh	0.00	2.14	1.45
	0.098	1.69	1.43
	0.244	1.57	1.47
	0.244	1.55	1.51
	1.46	1.30	1.30
	2.93	1.00	1.00
	4.15	0.77	0.77

Table VI. Equilibrium ratios Q for the reaction:
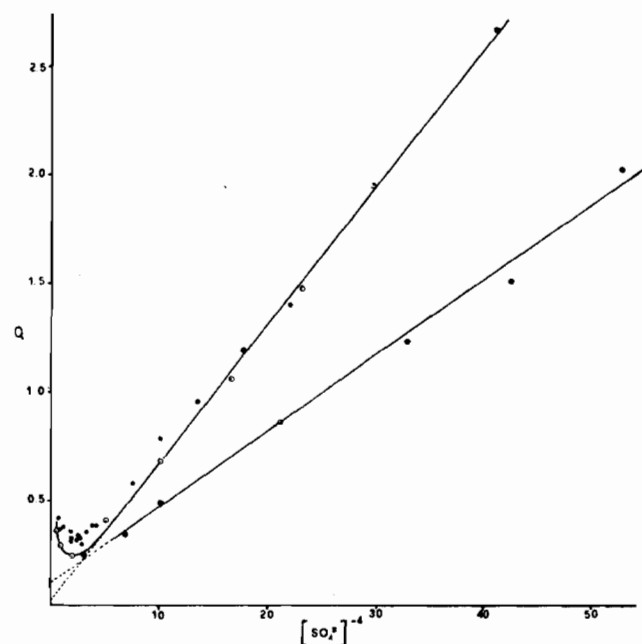$[Rh(NH_3)_5SO_4]^+ + H_2O \rightleftharpoons [Rh(NH_3)_5OH_2]^{3+} + SO_4^{2-}$.

$\mu = 1.0~M$		$\mu = 4.0~M$	
$[SO_4^{2-}]^{-1~a}$ (M^{-1})	Q	$[SO_4^{2-}]^{-1~a}$ (M^{-1})	Q
52.9	2.01	41.2	2.66
42.7	1.49	29.8	1.93
33.1	1.21	23.3	1.46
21.3	0.84	16.8	1.04
10.6	0.47	10.2	0.67
7.0	0.33	5.2	0.39
3.1	0.24	2.0	0.23
		1.0	0.27
		0.75	0.34

^{a} Corrected for the release of SO_4^2 from the complex and for the formation of HSO_4.

Table VII. Base hydrolysis of $[Rh(NH_3)_5SO_4]^+$. Ionic strength 1.0 M ($NaClO_4$).

T (°C)	$[NaOH]$ (M)	$k_{obs} \times 10^4$ (sec^{-1})	$k_{OH} \times 10^2$ (sec$^{-1} \cdot M^{-1}$)
41.5	0.025	3.08	1.23
	0.050	6.04	1.21
	0.070	8.63	1.23
		Ave.	1.22
50.6	0.010	3.86	3.86
	0.030	10.7	3.57
	0.050	17.9	3.58
		Ave.	3.67
59.5	0.010	10.8	10.8
	0.030	33.1	11.0
	0.050	55.5	11.1
		Ave	11.0

Table VIII. Base hydrolysis of $[M(NH_3)_5SO_4]^+$. Activation parameters.

M	$k_{OH} \times 10^{2~a}$ (sec$^{-1} \cdot M^{-1}$)	ΔH_{OH}^* (Kcal/mole)	ΔS_{OH}^* (e.u.)
Co ^{b}	4.9	26.3	24.6
Rh ^{c}	0.13	24.5	10

^{a} Rate constants at 25°C. ^{b} Data from ref. 8. ^{c} Estimated uncertainties are $\pm$ 0.5 kcal/mole (ΔH_{OH}^*) and $\pm$ 2 e.u. (ΔS_{OH}^*).

Figure 3. Equilibrium ratios Q vs $[SO_4^{2-}]^{-1}$ for the reaction: $[Rh(NH_3)_5SO_4]^+ + H_2O \rightleftharpoons [Rh(NH_3)_5OH_2]^{3+} + SO_4^{2-}$. T = 65°C, $[H^+]$ = $4.0 \times 10^{-3} M$ (as $HClO_4$). ⊙, μ = 4.0 M; ●, μ = 4.0 data from ref. 1; ◓, μ = 1.0 M.

curve drawn in Figure 3, have been used to recalculate the aquation and the anation rate constants, k and k_{an}, from the observed rate constants, k_{obs}, reported in Table I of ref. 1 (sulfate ion anation). Figure 4 shows the dependence of k on the sulfate ion concentration. The rate constants k_{an} are close to those previously calculated and the k_{an}^{-1} vs $[SO_4^{2-}]^{-1}$ plot is again a straight line only slightly shifted from that reported in Figure 5 of ref. 1. The intercept is 5.2 $\times$ 10^2 sec (previous value 6.0 $\times$ 10^2 sec) while the slope is practically coincident with that calculated previously (8.3 $\times$ 10^2 sec $\times$ M).

B - Base hydrolysis. The rate constants for the reaction

$$[Rh(NH_3)_5SO_4]^+ + OH^- \rightarrow [Rh(NH_3)_5OH]^{2+} + SO_4^{2-} \quad (9)$$

are reported in Table VII. The observed rate constants, k_{obs}, are related to the hydroxyde ion concentration by the equation $k_{obs} = k_{OH} [OH^-]$ as shown by the constancy of the ratio $k_{obs}/[OH^-]$ at any given temperature. Second order constants, k_{OH}, were found to fit the Arrhenius equation and a least-square analysis of the data yielded the activation parameters shown in Table VIII, where they are compared with those concerning the analogous Co^{III} complex.

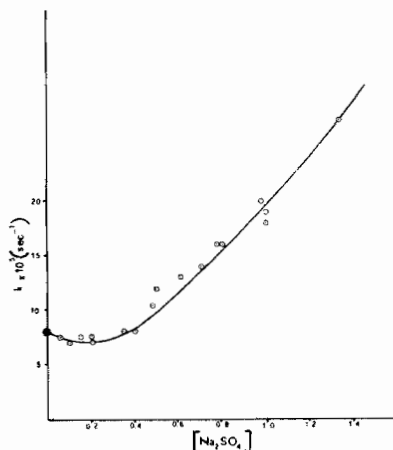Figure 4. The aquation rate constant, k, of $[Rh(NH_3)_5SO_4]^+$ as a function of sulfate concentration. T = 65°C, μ = 4.0 H (NaClO₄). ● Interpolated on upper curve of Fig. 2 at $[NaClO_4] = 4.0$ M.

Conclusions

Spontaneous and acid catalysed aquation. The spontaneous aquations of sulfatopentamminecobalt-(III) and rhodium(III) complexes follow a similar pattern with the rhodium compound being more labile by a factor of about 2. This difference is due to a more favourable activation enthalpy which is not fully compensated by a slightly less favourable entropy term.

Table IV shows the activation parameters pertaining to the systems under study, together with previous data on $[Co(NH_3)_5SO_4]^+$ and the activation parameters of the aquation of $CrSO_4^+$ ion.[17]

There is an evident discrepancy between the activation enthalpy quoted by Taube and Posey[3] for the sulfatopentamminecobalt(III) complex and that found with the present study, the latter being about 4 kcal/mole higher. Since the rate constants are relatively close to each other, also the activation entropies are different. A reason for this discrepancy might be that Taube's activation parameters were obtained from measurements at only 2 temperatures over a range as narrow as 13°C.

On the other hand, the activation data of both the

Co^{III} and the Rh^{III} complex ions are close to those of $[Cr(H_2O)_5SO_4]^+$, suggesting for the aquation of all three complexes a common mechanism.

However, the kinetic parameters themselves do not allow a clear-cut distinction between a dissociative and an associative type of activation. The large negative value of ΔS^* could be due, in fact, either to the formation of an activated complex of increased coordination number or to the « freezing » of solvent molecules around the $+3$ and -2 ions formed from a $+1$ complex through a dissociative process. However, there are now strong indications that the substitution reactions on acidoamminecobalt(III) complexes are essentially dissociative interchange processes[18,19] in the sense defined by Langford and Gray.[20]

Though direct information on the relative metal-ligand bond strength is not available, it is often believed that the overall energy involved in a dissociative activation would increase in going from a Co^{III} to a Rh^{III} complex of the same structure, mainly because of the greater crystal field stabilization energy loss.[21] In the present case this trend is reversed since sulfatopentamminerhodium(III) aquates with e sligtly but definitely lower activation enthalpy than sulfatopentamminecobalt(III). This fact could indicate for the first e greater degree of metal-water interaction in the transition state as suggested also by the slightly lower ΔS^*. Thus, while the process seems essentially dissociative, a partial associative character previously proposed for the rhodium complex[1] is still consistent with present findings.

The decrease of reactivity in the presence of sodium perchlorate (Figure 2) is in agreement with a predominantly dissociative mechanism insofar as the addition of the salt decreases the activity of the solvent water necessary to stabilize the strongly dipolar activated complex.

The aquation of both sulfatopentamminecobalt(III) and rhodium(III) complexes is catalysed by hydrogen ions as shown in Figure 1 and Table II. This effect was expected because it was observed for $[Cr(H_2O)_5SO_4]^{+17}$ and for $[Co(NH_3)_5SO_4]^+$ though, for the latter, a quantitative study was not completed.[3] An acid-promoted path for the aquation of metal complexes is a common feature among compounds containing basic ligands[22] and it is generally explained in terms of a protonation equilibrium followed by the slow solvolytic step of the conjugate acid produced, as summarized by reactions (5) and (6).

Since $k'_H = k_H K_H$ is a composite quantity the corresponding activation parameters, listed in Table IV, cannot be readily rationalized. However, it is interesting to note that the differencies between the activation entropies of acid-catalysed and spontaneous aquation of both sulfatocomplexes are close to the difference $S°_{HO_4} - S°_{SO_4^{2-}}$. (26 e.u.).[23] Thi would

(17) J.E. Finholt and S.N. Deming, *Inorg. Chem.*, 6, 1533 (1967).
(18) W.E. Jones and T.W. Swaddle, *Chem. Comm.*, 17, 998 (1969).

(19) (a) C.H. Langford, *Inorg. Chem.*, 2, 265 (1965). (b) A. Haim, *Inorg. Chem.*, 9, 426 (1970).
(20) C.H. Langord and H.B. Gray, « Ligand Substitution Processes », W.A. Benjamin, New York, 1965.
(21) F. Basolo and R.G. Pearson, « Mechanisms of Inorganic Reactions » 2nd Ed., John Wiley, New York, (1967) p. 169.
(22) F. Basolo and R.G. Pearson, « Mechanisms of Inorganic Reactions » 2nd Ed. John Wiley, New York (1967) p. 216.
(23) W.M. Latimer, « Oxidation Potentials » 2nd Ed., Prentice-Hall, New York, (1952) p. 72.

be the expected value if the mechanisms were both predominantly dissociative with the anions almost fully solvated in the transition state.

Influence of sulfate ions on the rate and the equilibrium of the aquation of $[Rh(NH_3)_5SO_4]^+$. At low acid concentration, the aquation rate constant of $[Rh(NH_3)_5SO_4]^+$ is sensitive to the presence of sulfate ions as shown in Figure 4.

On the other hand, the above mentioned linearity of the k_{an}^{-1} *vs* $[SO_4^{2-}]^{-1}$ plot suggests that the anation rate constant follows instead the simple trend expected on the basis of reactions (3) and (4) which lead to the well known equation:

$$\frac{1}{k_{an}} = \frac{1}{k_s} + \frac{1}{k_s K_s} \times \frac{1}{[SO_4^{2-}]} \qquad (10)$$

where k_s and K_s are unaffected by the presence of sulfate ions. From the intercept and the slope reported above the values $k_s = 1.9 \times 10^{-3}$ sec^{-1} and $K_s = 0.63$ M^{-1} are obtained at 65°C and $\mu = 4.0$ M.

The nature of the influence of sulfate ions on k is not completely clear. Often, the effect of anions on the aquation rate constant of acido complex cations is ascribed to the formation of ionic associations.[24] In this case, the formation of the species [Rh-(NH₃)₅SO₄]⁺, SO₄²⁻ is possible and has been suggested previously[4,9] for the cobalt analogue. The decrease of u.v. absorbancy shown by this complex in the presence of SO₄²⁻ ions has been taken as a supporting evidence for the association between the anion and the complex cation. The rhodium compound shows a similar behaviour (see Table I). However, the *shape* of the curve reported in Figure 4 cannot be explained *only* in terms of an ion-pair formation, since a different type of curvature should be observed. In addition, since the solvolysis of the above ion-pair would lead to the ion-triplet [Rh(NH₃)₅OH₄]³⁺, 2SO₄²⁻, this latter should contribute to the rate constant of the reverse reaction, k_{an}. However, no evidence of such a species has been found, as pointed out above. Thus, it is likely that non-specific salt effects are responsible, at least in part, for the change of k with the composition of the medium when NaClO₄ is replaced with Na₂SO₄ at constant μ. In this respect it is worth noting that since both aquation and anation are largely dissociative processes, the first reaction should be more sensitive to medium effects because it brings about a charge separation while the second does not since the leaving group is a neutral molecule. However, it is not clear why the presence of sulfate ions should favour the formation of a dipolar transition state.

On the basis of reactions (3) and (4) the equilibrium ratio, Q, defined above may be related to the constants K_s, k_s and k by the equation:

$$Q = \frac{k}{k_s} + \frac{k}{k_s K_s} [SO_4^{2-}]^{-1} \qquad (11)$$

(24) (a) T.P. Jones and J.K. Phillips. *J. Chem. Soc.* (A), 674 (1968). (b) F. Basolo and R.G. Pearson, « Mechanisms of Inorganic Reactions », 2nd Ed. (1967), John Wiley, N.Y. p. 178 and refs. therein.

Thus, a plot of Q *vs* $[SO_4^{2-}]^{-1}$ should be linear, provided that K_s, k_s and k are independent of the sulfate ion concentration, at a given ionic strength. As it is shown in Figure 3, at $\mu = 4.0$ M and 65°C, the plot is actually linear, within the experimental errors, up to $[SO_4^{2-}] \simeq 0.3$ M while above this value it shows a minimum.

A least-square treatment of the points (open circles) below $[SO_4^{2-}] = 0.3$ M yields $\dfrac{k}{k_s} = 0.02 \pm 0.02$ and $\dfrac{k}{k_s K_s} = 0.065 \pm 0.001$ M where the uncertainties are probable errors. While the large error on the intercept, precludes a meaningful comparison, the slope is in good agreement with the one calculated by means of the constants k, k_s and K_s obtained kinetically. In fact, taking for k the value 8.0×10^{-5} sec^{-1} *in the absence of sulfate*, obtained by interpolation of the upper curve of Figure 2 at $\mu = 4.0$ M, and using for k_s and K_s the values calculated above, the ratio $\dfrac{k}{k_s.K_s}$ is 6.7×10^{-2} M. Also, the ratio $\dfrac{k}{k_s} = 4.1 \times 10^{-2}$ is not in contrast with the value obtained from equilibrium measurements.

It should be stressed that the ratios Q used to calculate k_s and K_s from kinetic data (see Results and Discussion) were mostly outside the linear part of the Q *vs* $[SO_4^{2-}]^{-1}$ plot so that the two calculations are actually independent, and since they lead to a common result when the change of k whit $[SO_4^{2-}]$ is not considered, this effect appears entirely responsible for the minimum shown in Figure 3.

The least-square analysis of the points at unit ionic strength (Figure 3, half-filled circles) yields $\dfrac{k}{k_s} = 0.10 \pm 0.30$ and $\dfrac{k_s K_s}{k} = 0.034 \pm 0.001$ M, where uncertainties are again probable errors.

If K and K₁ are the equilibrium costants (conditional) of reactions (2) and (4), respectively, the following equations hold:

$$\text{(a)} \quad K = \frac{1}{K_1 K_s} \qquad \text{and} \qquad \text{(b)} \quad K_1 = \frac{k_s}{k} \qquad (12)$$

Table 9 lists the values of K, K_s, K_1, k and k_s for the rhodium system, at 65°C. When available, the corresponding values for the cobalt system have been included for comparison. These data suggest some interesting observations. The equilibrium constant of the overall aquation reaction, K, does not depend greatly on the nature of the metal ion; however, both K_1 and K_s change appreciably going from Co to Rh. As the ionic strength increases the aquation [Rh-(NH₃)₅SO₄]⁺ becomes more complete. This is due to the decrease of K_s that is not compensated by the increase of K_1. The change of K with μ explains the shift towards completion of the aquation reaction of both sulfatopentamminemetal complexes, indicat-

Table IX. Equilibrium and rate constants for the reversible reactions (2), (3) and (4). T= 65°C.

M	μ = 4.0 M					μ = 1.0 M				
	K (M)	K_s (M^{-1})	K_1	$k \times 10^3$ (sec^{-1})	$k_s \times 10^3$ (sec^{-1})	K (M)	K_s (M^{-1})	K_1	$k \times 10^5$ (sec^{-1})	$k_s \times 10^5$ (sec^{-1})
Co	—	—	—	—	—	0.038 [a]	11.2 [b]	2.4 [b]	9.2 [c]	0.22 [d]
Rh	0.065 [a]	0.63 [i]	24 [d]	7.8 [g]	1.9 [h]	0.034 [f]	2.9 [a]	10 [e]	13.2 [c]	1.32 [d]

[a] Calculated according to equation 12b. [b] From ref. 4. [c] Calculated from data reported here. [d] Calculated according to equation 12a. [e] From the intercept of equation (11). [f] From the slope of equation (11). [g] Interpolated on the upper curve of Fig. 2. [h] From the intercept of equation (10). [i] From the slope of equation (10).

ed by the tendency of the ratio $\dfrac{2+Q}{Q}$ to unity as μ increases (see Table V and Figure 2).

The interchange rate constant k_s is only slightly changed by changing the ionic strength, as expected for an outer-sphere - inner-sphere interchange process.

Perchlorate ion-pairing and association of Na$^+$ with SO$_4^{2-}$. In the preceeding discussion it has been implicitly assumed that ClO$_4^-$ does not associate with any of the complex cations present in the reacting solutions studied. This is a widely accepted statement which has never been proved to be generally correct.* The data discussed in the present work do not show any evidence for perchlorate association but do not preclude their existence.

One serious complication arising from perchlorate ion-pairing concerns the sulfate anation of the aquo-pentamminerhodium(III) complex which is also the most likely ion- pair partner on a coulombic ground. In fact, k_s and K_s would no longer be the "true" interchange rate constant and ion-pair formation constant,[25] respectively.

It has been shown that the association of ClO$_4^-$ ions with [Ir(NH$_3$)$_5$OH$_2$]$^{3+}$ is only limited,[25] if any, in agreement with the observation that the rate of water exchange of this complex is insensitive to the presence of sodium perchlorate up to 3.0 M while it increases measurably when a comparable amount of NaCl is added.[25] The close analogy of structure between the iridium and the rhodium complex makes it likely that perchlorate association may not be important also for the latter. Unfortunately, there is no simple way to check this hypothesis independently of kinetics since the optical methods commonly used to detect ionic associations with metal complexes cannot be applied in this case because the accessible spectrum of [Rh(NH$_3$)$_5$OH$_2$]$^{3+}$ is practically unaffected by the addition of Na ClO$_4$. This fact is, however, an additional indication against perchlorate association.

Also, an extensive formation of the ion-pair Na$^+$, SO$_4^{2-}$ would affect some of the constants reported on Table IX. It can be shown that in a sodium sulfate-sodium perchlorate mixture, at the formal

ionic strength μ, the concentration of free sulfate ion, [SO$_4^{2-}$]$_f$, is related to the total sulfate concentration, [SO$_4^{2-}$], through the equation:

$$\frac{1}{[SO_4^{2-}]_f} = \frac{1}{[SO_4^{2-}]}(1+K_2\mu) + K_2(\frac{[SO_4^{2-}]_f}{[SO_4^{2-}]} - 2) \quad (13)$$

where K_2 is the conditional equilibrium constant of the reaction:

$$Na^+ + SO_4^{2-} \rightleftharpoons Na^+, SO_4^{2-}. \quad (14)$$
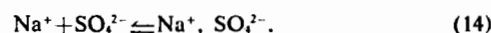
Equilibrium (14) has been studied previously[10] but no experimental values of K_2 are available for the ionic medium conditions of the present investigation. Peterson[27] found $K_2 \leqslant 0.13$ M^{-1} at μ = 4.5 M (1.5 M Na$_2$SO$_4$) and 25°C, and calorimetric measurements indicate that reaction (14) is practically insensitive to temperature variations.[28] If the above value is accepted for the experiments at μ = 4.0 M and 65°C reported in this paper, it can be calculated that the ratio $\dfrac{[SO_4^{2-}]_f}{[SO_4^{2-}]}$ changes only from 0.66 to 0.76 when [SO$_4^{2-}$] is varied from 0.01 M to 1.2 M.

Thus, equation (13) may be approximate to

$$\frac{1}{[SO_4^{2-}]_f} = 1.52\frac{1}{[SO_4^{2-}]} - 0.17 \quad (15)$$

where the ratio $\dfrac{[SO_4^{2-}]_f}{[SO_4^{2-}]}$ is set equal to 0.70 and K_2 and μ are substituted by the proper values.

Since $[SO_4^{2-}]_f^{-1}$ is linearly related with $[SO_4^{2-}]^{-1}$, equation (10) and (11) are still linear when [SO$_4^{2-}$] is substituted with [SO$_4^{2-}$]$_f$; however the constants k_s and K_s change their values. Straightfoward calculations yield $k_s = 1.6 \times 10^{-3}$ sec^{-1} and $K_s = 1.1$ M^{-1} and, consequently, $K_1 = 20.5$ and $K = 0.044$ M. This shows that the knowledge of the value of K_2 is important in order to assess reliable values to the above constants. Nevertheless, the *trends* above discussed should be left unchanged.

Base hydrolysis of sulfatopentamminerhodium(III) cation. The rate of release of SO$_4^{2-}$ ions from the complex, in basic solution, shows a first-order dependence on [OH$^-$]. There is now little doubt that, when the substrate contains acidic protons (like ammonia protons), this kinetic dependence is related

(*) M.G. Burnett[31] has shown that kinetic and equilibrium data of substitution reactions of Co^{III} complexes bearing close analogy to those reported in this paper, can be described by equations where extensive ion-pairing by perchlorate is assumed. However, in view of the large number of constants which are to be assessed in order to fit the experimental data, the ability of ClO$_4^-$ to form ionic associations does not seem sufficiently supported.

(25) E. Borghi, F. Monacelli, and T. Prosperi, *Inorg. Nucl. Chem. Letters, 6,* 667 (1970).

(26) E. Borghi and F. Monacelli, *Inorg. Chim. Acta, 5,* 211 (1971).

(27) A. Peterson, *Acta Chem. Scand., 15,* 101 (1961).

(28) J.M. Austin and A.D. Mair, *J. Phys. Chem., 66,* 519 (1962).

to the formation of a conjugate base through an acid-base equilibrium, according to the well known CB mechanism.

Recently, the subject of the base hydrolysis mechanism of octahedral complexes has been reviewed by Tobe[29] who pointed out the large positive value of ΔS^{*}_{OH} observed for such a reaction. This argument will be more fully developed in a forthcoming review[30] and shown to be a definitive proof in favour of the conjugate base mechanism.

The activation parameters of the reaction here discussed (see Table VIII) may not be very accurate expecially because of the relatively narrow temperature range; however ΔS^{*}_{OH} is definitely lower than the activation entropy shown by the analogous Co^{III} complex, which falls in the « normal » range. Unless such difference originates in the conjugate base formation equilibrium, it may indicate for the rhodium complex some degree of nucleophilic interaction of a water molecule with the conjugate base, i.e. a S_N2CB mechanism. However no clear distinction can be made between S_N1CB and S_N2CB mechanism on the basis of the present data.

(29) M.L. Tobe, *Accounts Chem. Res.*, 3, 377 (1970).
(30) J.O. Edwards, F. Monacelli, and G. Ortaggi, unpublished review.

(31) M.G. Burnett, *J. Chem. Soc.*, (A), 2480-2486-2490 (1970).