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Anation Reaction of $[Rh(NH_3)_5OH_2]^{3+}$ Ion. Evidence for the Nucleophilic Attack of the Entering Group*

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The anation by Cl^-, Br^-, and SO_4^{2-} of the complex ion $[Rh(NH_3)_5OH_2]^{3+}$ has been kinetically studied at 65°C, in water solutions of controlled ionic strength. The reactions with Cl^- and Br^- were complete while a definite equilibrium was reached with SO_4^{2-} in the sulfate concentration range 0.05-1.33 M. *In the latter case equilibrium measurements were carried out in order to separate the observed rate constants into the aquation (k_{aq}) and anation (k_{an}) rate constants. In all cases k_{an} was found to follow the equation $k_{an}=\frac{k\,.\,K_a[X^{m-}]}{1+K_a[X^{m-}]}$ (X^{m-}=anion) consistent with a mechanism involving a fast 1:1 ion association (K_a being the «conditional» equilibrium constant) followed by a slow interchange of the water and the anionic ligands (k being the rate constant of this process). The comparison of k values with the water exchange rate constant k_e of the aquo-complex under comparable conditions, ($k/k_e \geqslant 1$), suggests for the interchange process a transition state where the incoming anion is appreciably bonded to the metal. Complications, possibly due to medium effects, were observed in the reaction with SO_4^{2-}.*

Introduction

The anation reaction in octahedral complexes has been the subject of several kinetic investigations, mainly with inert Cr^{III}, Co^{III}, and Rh^{III} compounds.[1]

Though the rates have been generally found dependent upon the entering anion concentration, the actual role of the latter in the mechanism could not be established unambigously since the observed results were consistent with both associative and dissociative mechanisms.

Furthermore, there is direct evidence that, when the complex is positively charged, the reacting species is the ion-pair formed between the comlpex and the entering anion.[2] Hence, the observed dependence on the concentration of the latter could reflect its influence in determining the concentration of the reactive ion-pair, according to the following scheme

$$ROH_2^{n+} + X^{m-} \overset{K_a}{\rightleftarrows} ROH_2^{n+}, X^{m-} \qquad (1)$$

$$ROH_2^{n+}, X^{m-} \xrightarrow{k} RX^{(n-m)+} + H_2O \qquad (2)$$

(R is a radical, which includes the metal and the inert ligands of an octahedral complex cation).

Consequently, the pseudo first-order rate constants, k_{an}, for the disappearance of the aquocomplex, in the presence of an excess of X^{m-}, are expected to follow the equation

$$k_{an} = \frac{k\,.\,K_a\,.\,[X^{m-}]}{1+K_a\,.\,[X^{m-}]} \qquad (3)$$

apart from possible deviations due to changes of the activity coefficients.

Recently, the above reaction scheme received further support by the anation reaction results of $[Co(NH_3)_5OH_2]^{3+}$ ion.[3] It was also shown in this system, that for a variety of entering anions, their rate constants, k, for the ion-pair interchange are all about one fifth of the exchange rate constant of the aquocomplex. This fact is evidence for a mechanism where the primary factor controlling the rate is the loss of the coordinated water, with the immediate capture of the ligand available in the surroundings, this last process being governed mainly by statistical factors.

In a recent paper, Monacelli and Viel[4] reported a kinetic study on the water exchange of $[Rh(NH_3)_5OH_2]^{3+}$. The results were such as to suggest a more pronounced nucleophilic participation of the incoming water to the transition state, in comparison with $[Co(NH_3)_5OH_2]^{3+}$, where an essentially dissociative mechanism operates.[5]

It seemed useful to extend this study to the anation of $[Rh(NH_3)_5OH_2]^{3+}$ in the search for some other evidence supporting the nucleophilic attack of the entering group on this substrate. In particular, the factor separating water exchange and ion-pair interchange rates was expected to be different from that found for $[Co(NH_3)_5OH_2]^{3+}$.

The results presented in this paper concern the reaction of $[Rh(NH_3)_5OH]_2^{3+}$ with Cl^-, Br^-, and SO_4^{2-}. They indeed show a difference between the behaviour of aquopentamminecobalt(III) and rhodium(III) ions in the expected sense.

(*) Research supported by the Italian Consiglio Nazionale delle Ricerche.

(1) For a survey on the argument see: F. Basolo and R. G. Pearson, «Mechanisms of Inorganic Reactions», p. 193 *et seq.*, J. Wiley, New York (1967).

(2) See ref. 1 and refs. therein.

(3) C. H. Langford and W. R. Muir, *J. Am. Chem. Soc.*, *89*, 3141 (1967).

(4) F. Monacelli and E. Viel, *Inorg. Chim. Acta*, *1*, 467 (1967).

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

When this research was already completed, a paper was published concerning the reaction of $[Rh(NH_3)_5OH_2]^{3+}$ with Cl^-, Br^-, and I^-.[6] However, present experiments tend to clarify a different aspect of the anation reaction and different experimental conditions have been chosen.

Experimental Section

Materials. All reagents were pure grade chemicals and were used without further purification.

The aquo- and chloropentamminerhodium(III) perchlorates were prepared as described in the literature.[7-9]

The preparation of $[Rh(NH_3)_5SO_4]^+$ has not been reported before. An attempt to prepare this complex by reacting the aquocomplex with an excess of Na_2SO_4 in water solution was unsuccessful since only a small amount of $[Rh(NH_3)_5OH_2]ClO_4.SO_4$ was obtained upon addition of concentrated $HClO_4$. This indicated, however, that the reaction was not complete. A better procedure was the following. An amount of $[Rh(NH_3)_5OH_2](ClO_4)_3$ was treated with a strong anionic exchanger, in OH^- form, and the resulting solution was neutralized with the stoichiometric amount of H_2SO_4. After exaporation to dryness, a yellowish solid (largely $[Rh(NH_3)_5OH_2]1.5SO_4$) was obtained. This was kept for several hours at 110°C under vacuum and in the presence of P_2O_5. The product was dissolved in a small volume of water containing the amount of $Ba(ClO_4)_2$ required for complete precipitation of ionic SO_4^{2-}, assuming for the complex the formula $[Rh(NH_3)_5SO_4]0.5SO_4$. After filtration, methanol was added to the solution and a white powder precipitated. This last was collected on a filter, washed with methanol, air dried and recrystallized from water. The elemental analysis gave the following results: $H\% = 4.09$, $N\% = 18.41$, $SO_4^{=}\% = 24.90$. Calcd. for $[Rh(NH_3)_5SO_4]ClO_4$: $H\% = 3.9$, $N\% = 18.25$, $SO_4^{=}\% = 25.1$. The spectrum of the complex is reported in Figure 1.

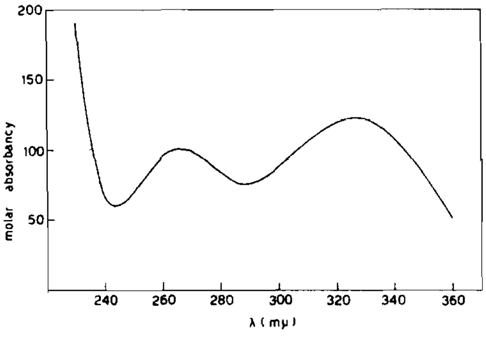

Figure 1. Spectrum of $[Rh(NH_3)_5SO_4]ClO_4$.

Sodium and lithium perchlorates were prepared by reacting saturated solutions of the carbonates with the required amounts of concentrated $HClO_4$. After partial evaporation and cooling, the precipitated salts were collected on a filter and recrystallized twice from water.

Concentrated solutions of $NaClO_4$, $LiClO_4$, LiCl, NaCl, NaBr, and Na_2SO_4 were prepared by dissolving each salt in $1 \times 10^{-1} M$ aqueous $HClO_4$. The concentrations were determined by evaporating to dryness (140-180°C) several samples of known volumes and weighing the residues. The results so obtained were reproducible within ±0.5%.

Also a $2 \times 10^{-2} M$ solution of $[Rh(NH_3)_5OH_2](ClO_4)_3$ was prepared by dissolving the complex in $1 \times 10^{-2} H$ $HClO_4$.

These stock solutions were used to prepare the reacting mixtures and $HClO_4$ was present in order to prevent the acid dissociation of the aquocomplex.[6]

Ion-pair Formation. The formation of ion-pairs $[Rh(NH_3)_5OH_2]^{3+}$, X^{m-} ($X^{m-} = Cl^-$, Br^-, and SO_4^{2-}) was directly proved by the absorption increase of the aquocomlpex in the electron transfer band region in the presence of the anions.

All spectrophotometric measurements, including kinetics (see below), were carried out by means of a Beckman DU instrument adapted for the thermal control of the samples as described elsewhere.[10]

The measurements were made at 25°C, the anation being so slow that fairly constant absorption values were obtained.

The procedure for determining the conditional association constants was as follows: a weighed amount of the complex was vigorously shaken with 10.0 ml of a solution containing the anion at the desired concentration, adjusted to ionic strength 4 *M* with $NaClO_4$. The absorptions of both solutions, with and without the complex, were measured against water, at a given wavelength, and the contribution due to the complex species was obtained by subtracting the second from the first. The wavelengths were 210 mμ (SO_4^{2-}), 215 mμ (Cl^-), and 240 mμ (Br^-).

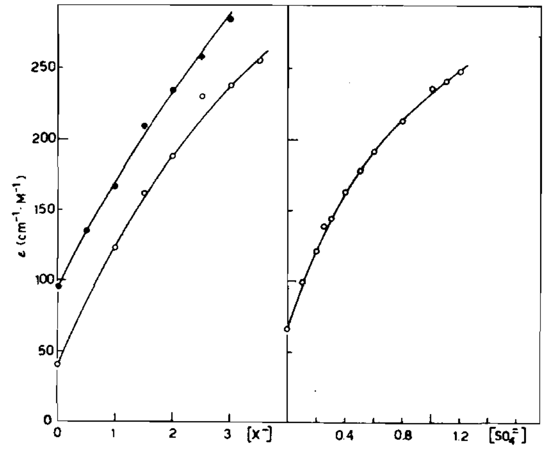

Figure 2. Apparent extinction coefficient of $[Rh(NH_3)_5OH_2]^{3+}$ ion *vs.* anion concentration. $X^{m-} = Br^-$ (●), Cl^- (○). For $X^- = Br^-$ ε values are shifted upwards on the vertical axis by 50 units. Lines are calculated according to equation (4).

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(6) A. J. Poë, K. Shaw, and M. J. Wendt, *Inorg. Chim. Acta, 1*, 371 (1967).

(7) *Gmelins' Handbuch der Anorganischen Chemie, 64*, 109 (1938).

(8) S. N. Anderson and F. Basolo. *Inorg. Synthesis, 7*, 216 (1963).

(9) S. C. Chan, *Austr. J. Chem., 20*, 61 (1967).

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

In Figure 2 are reported the apparent extinction coefficients, ε (units are $cm^{-1}M^{-1}$), of $[Rh(NH_3)_5OH_2]^{3+}$ as a function of the concentration of each anion. Assuming that only a 1:1 outer sphere association was formed in each case the experimental data were analyzed on the basis of the equation

$$\frac{\varepsilon - \varepsilon_o}{[X^{m-}]} = K_a \cdot \varepsilon_{ip} - K_a \cdot \varepsilon \qquad (4)$$

where ε_o and ε_{ip} are the molar extinctions of $[Rh(NH_3)_5OH_2]^{3+}$ and $[Rh(NH_3)_5OH_2]^{3+}$, X^{m-}, respectively.

By the method of least-squares the association constants given in Table III as K_a (25°) were obtained. As an estimate, for the lowest values ($X^{m-} = Cl^-$ and Br^-) the error may be as large as ±25 while for $X^{m-} = SO_4^{2-}$ it should be considerably smaller.

In all cases the agreement between the experimental points and the curves calculated by means of equation (4) (see Figure 2) may be considered satisfactory.

Kinetics. The rate of the overall reaction

$$[Rh(NH_3)_5OH_2]^{3+} + X^{m-} \underset{k_{aq}}{\overset{k_{an}}{\rightleftharpoons}} [Rh(NH_3)_5X]^{(3-m)+} + H_2O \qquad (5)$$

was studied spectrophotometrically by following the increase of optical density due to the formation of the acidocomplex.

The temperature 65°C was chosen since the reaction was conveniently fast and because the rate of water exchange in the presence of Cl^- has been measured at this temperature.[4]

As a general procedure, a solution containing the aquocomplex, $NaClO_4$ (or $LiClO_4$) and the reacting anion, as the sodium (or lithium) salt, was prepared by mixing the proper volumes of stock solutions. The complex concentration was in the range $1\text{-}5 \times 10^{-4}$ *M*. The wavelength was chosen, in the u.v. region, so as to provide a suitably large change in the absorption as a consequence of the reaction.

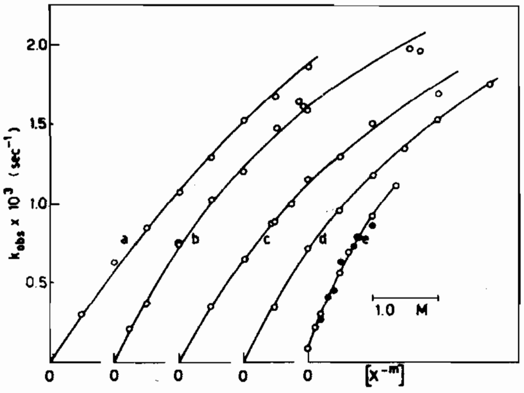

Figure 3. Observed rate constants of reaction (5) *vs.* anion concentration. (a) 4.0 *M* Na(Br, ClO_4); (b) 5.0 *M* Na(Cl, ClO_4); (c) 4.0 *M* Li(Cl, ClO_4); (d) 4.0 *M* Na(Cl, ClO_4); (e) Na_2SO_4, $NaClO_4$, $\mu = 4.0$ *M*, runs carried out starting from the aquocomplex, (○), and from the sulfatocomplex, (●). Lines (a) to (d) are calculated by means of equation (3). Temperature 65°C.

The plots of $\log(D_\infty - D)$ *vs.* time were all linear up to more than 80% of completion, except for the first minutes needed for the thermal equilibration.

The observed first-order constants, k_{obs}, are listed in Table I and graphically shown in Figure 3. Duplication of the runs gave a reproducibility better than ±3%.

Table I. Observed rate constants for the reaction
$[Rh(NH_3)_5OH_2]^{3+} + X^{m-} \rightleftharpoons [Rh(NH_3)_5X]^{(3-m)+} + H_2O$
Temperature 65°C, ionic strength 4 *M*

X^{m-}	$[X^{m-}]$ (*M*)	$k_{obs} \times 10^3$ (sec^{-1})	X^{m-}	$[X^{m-}]$ (*M*)	$k_{obs} \times 10^3$ (sec^{-1})
Cl^-	0.50	0.35	Br^-	0.50	0.30
(NaCl)	1.00	0.65	(NaBr)	1.00	0.63
	1.45	0.88		1.50	0.85
	1.50	0.89		2.00	1.08
	1.50	0.91		2.00	1.07
	1.75	1.00		2.50	1.29
	2.00	1.15		3.00	1.52
	2.50	1.30		3.50	1.67
	3.00	1.51		4.00	1.85
	4.00	1.70			
			SO_4^{2-}	0.12	0.21
Cl^-	0.25	0.22	(Na_2SO_4)	0.20	0.29
(NaCl) [a]	0.50	0.38		0.20 [b]	0.27
	1.00	0.76		0.30 [b]	0.40
	1.00	0.75		0.40 [b]	0.45
	1.50	1.03		0.49	0.56
	2.00	1.20		0.50 [b]	0.63
	2.50	1.48		0.62	0.69
	2.86	1.65		0.71 [b]	0.73
	2.94	1.61		0.75	0.79
	3.00	1.59		0.80 [b]	0.79
	4.56	1.98		0.98	0.92
	4.75	1.97		1.00 [b]	0.85
				1.00 [b,c]	0.91
Cl^-	0.50	0.34		1.33	1.11
(LiCl)	1.00	0.73			
	1.50	0.96			
	2.00	1.18			
	2.50	1.45			
	3.00	1.54			
	3.81	1.77			

[a] Ionic strength 5.0 *M*. [b] Runs carried out starting from the sulfatocomplex. [c] $(NH_4)_2SO_4$ added (0.5 *M*).

Reaction (5) is known to be an equilibrium process[9,11] and, hence, $k_{obs} = k_{an} + k_{aq}$. Data on the aquation of chloro- and bromopentamminerhodium(III) ions have been published by different authors.[6,9,12] From Poë's data, which seem to be the most accurate, the acid hydrolysis rate constants for both complexes are about 6×10^{-6} sec^{-1}, at 65°C and $\mu = 0.2$ *M*. This value is negligible compared with the k_{obs} values obtained for reaction (5), even at the lowest anion concentration, thus suggesting the completion of this reaction under the conditions chosen. As confirmation, solutions of chloropentamminerhodium(III), containing variable amounts of NaCl were kept at 65°C in the cell compartment of the spectrophotometer. Even at the lowest $[Cl^-]$ used for the kinetics and over a period of time corresponding to 3 or more half-lives of the anation reaction, no change in the readings was observed, the wavelength being the same as that used to follow the anation.

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(11) A. B. Lamb, *J. Am. Chem. Soc.*, *61*, 699 (1938).
(12) G. B. Schmidt, *Z. Phys. Chem.* (Frankfurt), *41*, 26 (1964); *ibid.*, *50*, 222 (1966).

The aquation of $[Rh(NH_3)_5SO_4]^+$ has not been studied before. The results obtained in the attempt to prepare this complex in water solution indicated that k_{aq} is not negligible compared with k_{obs} for reaction (5). Indeed, it was found that, at 65°C, the sulfatocomplex aquates, in $1 \times 10^{-2}\,M$ $HClO_4$ and 4 *M* $NaClO_4$, with an observed first-order rate constant of $8 \times 10^{-5}\,sec^{-1}$. The reaction was followed spectrophotometrically, at 230 mμ, and was nearly complete (~90% of aquation).

Equilibrioum Ratios. For the reaction between the aquocomplex and SO_4^{2-}, the equilibrium ratio $Q = \frac{\varepsilon_s-\varepsilon_e}{\varepsilon_e-\varepsilon_a}$ (ε_s, ε_e, and ε_a are the extinction coefficients of the sulfatocomplex, the equilibrium mixture and the aquocomplex, respectively) was measured at different ion concentrations, in order to separate k_{obs} into k_{aq} and k_{an}.

Each experiment was carried out starting from a solution of $[Rh(NH_3)_5SO_4]^+$ of known concentration, containing the proper amounts of $NaClO_4$ and $HClO_4$ ($\mu = 4\,M$ and $[HClO_4] = 1 \times 10^{-2}\,M$). The absorption of the solution was measured at 65°C against a reference solution containing all the reagents except the complex. The wavelength was usually 230 mμ where the difference $\varepsilon_s-\varepsilon_a$ is sufficiently large and ε_a ($25\ cm^{-1}$. M^{-1}) is practically insensitive to SO_4^{2-} and temperature.

Since ε_s was found to decrease with increasing $[SO_4^{2-}]$, it was determined in any experiment using the optical density measured soon after the attainement of the thermal equilibrium (about 10 minutes). The aquation reaction was allowed to reach the equilibrium and the final absorption value registered.

Some of these experiments were used to measure the rate of approaching equilibrium (5) from the right. The k_{obs} values so obtained, though less accurate, were found in agreement with those measured starting from the aquocomplex, as described.

Table II. Equilibrium ratios Q as a function of $[SO_4^{2-}]$. Temperature 65°C, ionic strength 4.0 *M*, λ = 230 mμ

$[SO_4^{2-}]$ (*M*)	Q
0.046	1.39
0.057	1.17
0.075	0.94
0.100	0.78
0.100	0.68
0.133	0.57
0.226	0.37
0.25	0.37
0.30	0.34
0.34	0.28
0.35	0.31
0.37	0.32
0.40 [a]	0.30
0.50	0.34
0.50 [a]	0.31
0.50	0.30
0.71	0.30
0.80	0.36
1.00 [b]	0.35
1.1	0.40

[a] λ = 229 mμ. [b] Solution 0.50 *M* Na_2SO_4 and 0.50 *M* $(NH_4)_2SO_4$.

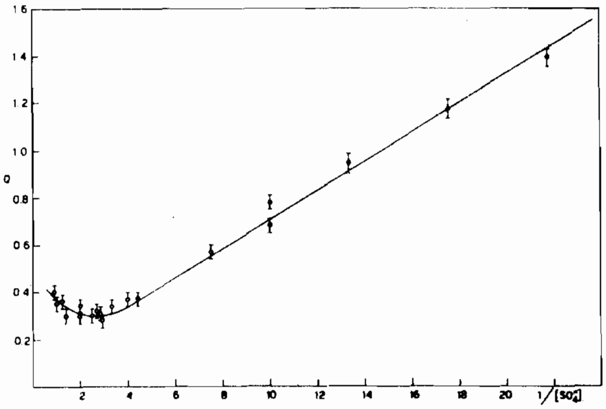

Figure 4. Equilibrium ratios Q *vs.* $1/[SO_4^{2-}]$. Temperature 65°C, $\mu = 4.0\,M$ ($NaClO_4$). The error is calculated assuming a ±1% error on the extinction coefficients.

The equilibrium ratios Q are quoted in Table II and shown in Figure 4.

Results

Ion-pair Formation. The ion-pair association constants K_a (25°) of Table III follow the order $SO_4^{2-} > Cl^- > Br^-$, as expected if both ionic charges and radia are taken as the most important factors determining the extent of ion association, in a given medium.[13]

However, it is worth noting that the constants are definitely lower than those of the corresponding Co^{III} and Cr^{III} systems.[3,14,15] Outer sphere associations have been found to be sensitive to the medium,[14,16,17] and the different ionic strength of the compared systems may partially account for the differences. Furthermore, the relation between ion-pair formation thermodynamics and substrate structure is not always clear,[17] expecially when complex ions are concerned, so that comparative differences may not be readily rationalized.

Cl^- and Br^- Anation. As Figure 3 shows, a distinct curvature appears in all cases when the observed rate constants for reaction (5) are plotted against $[X^-]$. Equation (3) was found to be closely followed and the K_a and k values, obtained by the least-squares analysis of the data, are reported in Table III. The agreement between the kinetically derived K_a constants and those independently measured at 25°C is satisfactory and confirms the low enthalpy of ion associations.[3] Neither K_a nor k appear to be greatly affected by moderate changes of the medium.

SO_4^{2-} Anation. The observed first-order constants of approaching equilibrium (5) can be separated into

(13) H. S. Harned and B. B. Owen, «The Physical Chemistry of Electrolytic Solutions», pp. 70 and 306, Reinhold, New York (1958).
(14) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, *78*, 15 (1956).
(15) N. V. Duffy and J. E. Earley, *J. Am. Chem. Soc.*, *89*, 272 (1967).
(16) V. E. Mironov and V. A. Fedorov, *Zhur. Neorg. Khim.*, *7*, 2524 (1962).
(17) V. A. Fedorov, V. E. Mironov, and F. Ya. Kul'ba, *Zhur. Neorg. Khim.*, *7*, 2528 (1962).

Table III. Ion-pair formation constants and reactivities. Temperature 65°C except for the constants K_a (25°). Ionic strength 4.0 *M* ($NaClO_4$) unless otherwise indicated. R denotes $Rh(NH_3)_5$

Ion-pair	K_a (25°) (M^{-1})	K_a (M^{-1})	$k \times 10^3$ (sec^{-1})	k/k_e [a]
ROH_2^{3+}, Br^-	0.10	0.08	7.9±0.1	4.9
ROH_2^{3+}, Cl^-	0.16	0.18	4.2±0.1	2.6
		0.25 [b]	3.6±0.3	2.2
		0.22 [c]	4.1±0.2	2.5
ROH_2^{3+}, SO_4^{2-}	1.0	0.71	1.7	1.0_5

[a] $k_e = 1.6 \times 10^{-3}$ sec^{-1} in the presence of 4 *M* NaCl, ref. 4. [b] Experiments in 4 *M* Li(Cl,ClO_4). [c] Experiments in 5 *M* Na(Cl,ClO_4).

k_{an} and k_{aq} by means of the formula:

$$k_{an} = k_{obs}\frac{1}{1+Q}$$

In the calculations, the Q values interpolated on the curve of Figure 4 were used and the results appear in Table IV. In Figure 5 the $1/k_{an}$ *vs.* $1/[Na_2SO_4]$ plot is reported. As expected if equation (3) is followed, the plot is fairly linear over the whole sulfate concentration range. From the slope and the intercept of the line drawn through the most reliable points (runs carried out starting from the aquocomplex), the constants k and K_a have been calculated and their values appear in Table III. As for the previously discussed reactions, K_a and K_a (25°) are in a satisfactory agreement with each other.

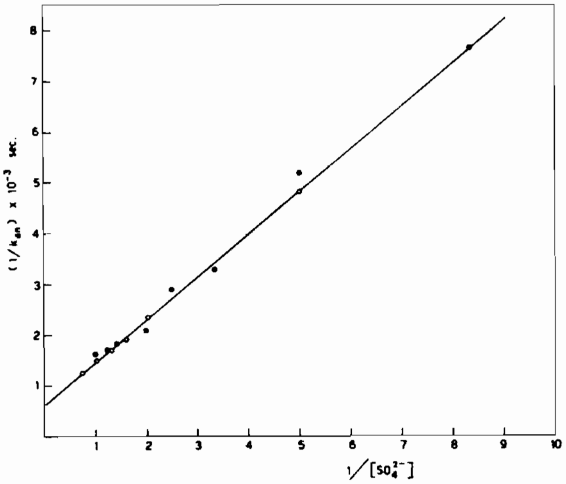

Figure 5. Plot of $1/k_{an}$ *vs.* $1/[SO_4^{2-}]$. Runs carried out starting from the aquocomplex (○) and from the sulfatocomplex (●). The line has been drawn considering only the first set of points (○), which are the most accurate.

The Q *vs.* $1/[Na_2SO_4]$ plot (see Figure 4) is expected to be linear according to the reaction scheme (1) and (2).[14] The actual shape of the plot is a consequence of the marked increase of k_{aq} with sulfate concentration, as appears from the data of Table IV. An analogous effect was observed in the Cl^- anation of $[Co(NH_3)_5OH_2]^{3+}$ but there is no simple explanation for that.* Certainly, the double negative charge of SO_4^{2-} makes the reacting system intrinsically more complicated, and possible changes of the medium properties, when ClO_4^- is replaced by SO_4^{2-} though at constant μ, could account for the observations. However, it is not clear why only k_{aq} should be sensitive to such factor.

Table IV. Anation and aquation rate constants for the reaction $[Rh(NH_3)_5OH_2]^{3+} + SO_4^{2-} \rightleftharpoons [Rh(NH_3)_5SO_4]^+ + H_2O$

$[SO_4^{2-}]$ (*M*)	Q [a]	$k_{an} \times 10^3$ (sec^{-1})	$k_{aq} \times 10^3$ (sec^{-1})
0.12	0.60	0.13_1	0.08
0.20	0.40	0.20_3	0.08
0.20 [b]	0.40	0.19_3	0.08
0.30 [b]	0.31	0.30_5	0.09
0.40 [b]	0.30	0.34_6	0.10
0.49	0.31	0.42_7	0.13
0.50 [b]	0.31	0.48_1	0.15
0.62	0.32	0.52_3	0.17
0.71 [b]	0.34	0.54_5	0.18
0.75	0.34	0.59_4	0.20
0.80 [b]	0.35	0.58_5	0.20
0.98	0.37	0.67_1	0.25
1.00 [b]	0.37	0.62_0	0.23
1.00 [b]	0.37	0.66_5	0.25
1.33	0.39	0.80_0	0.31

[a] Q values interpolated on the curve of Figure 4. [b] Runs carried out starting from the sulfatocomplex.

A detailed study of the aquation reaction of $[Rh(NH_3)_5SO_4]^+$ is under way in this laboratory.

Discussion

Anation reactions generally show a marked kinetic dependence on anion concentration and are known to be complicated by the formation of ion-pairs, when the substrate is positively charged. There is now a sufficient experimental ground to consider this a general phenomenon and the overall reaction is best regarded as an ion-pair equilibrium followed by a slow interchange** between ligands in the first and second coordination sphere.[1]

Nevertheless, an interchange mechanism may still be an associative or a dissociative process, according to the relative importance of bond making over bond

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(*) Complications due to decomposition of the complex by loss of ammonia[6] were excluded by a single experiment where a considerable amount of $(NH_4)_2SO_4$ was added to the reaction mixture without any significant effect.

(**) The definition of interchange or I process is that given in ref. 18.

breaking in the transition state[18] and an operational test for making this distinction may be found in the comparison between the water exchange reaction and reaction (2).

For a dissociative interchange, I_d, it is expected that anation rate will not exceed the rate of water exchange. Furthermore, reaction (2) will be insensitive to the nature of the entering group, which needs only to be present in a favourable position when the stretch of the metal-water bond occurs.

It follows that the ratio k/k_e (k_e being the water exchange rate constant) should be governed only by the probability that the anion is in the immediate neighborhood of the outgoing H_2O.

On the other hand, if the formation of the bond to the incoming ligand is an important factor contributing to the energy content of the transition state, the complex would be expected to select the incoming group from the second coordination shell. As a consequence the anation need not be slower than the water exchange and the rate constants for the various nucleophiles need not be similar.

From an inspection of Table III two main points arise. First, k values are not lower than k_e in comparable conditions and, second, they differ for different nucleophiles.

According to above, these observations cannot be easily explained in terms of a dissociative interchange but they are consistent with an associative mechanism with the incoming ligand largely bonded in the activated state.

The k/k_e ratios are strongly indicative in this respect since, even for an associative interchange, water is still the statistically favoured ligand.

The selectivity shown by the substrate towards the nucleophiles, including water, is not large. However, it is worth noting that the reactivity order $H_2O \simeq SO_4^{2-} < Cl^- < Br^-$ goes in the direction of increasing softness, in agreement with the idea that Rh^{III} be a relatively soft centre.[6,19]

Present conclusions are not in contrast with previous hypotheses about substitution reactions on Rh^{III} complexes. The water exchange of $[Rh(NH_3)_5OH_2]^{3+}$, as already mentioned, seems to take place with the nucleophilic contribution of the incoming water molecule to the transition state.[4] On the basis of a comparative study of the aquation as well as base hydrolysis of halopentamminerhodium(III) ions, Chan[9] stated that an associative pattern would explain better the observed reactivity sequence. Poë and coworkers,[20] in their study of the *trans* effect on substitution reactions of bis-ethylenediaminerhodium(III) complexes, came to the conclusion that an associative character of these reactions could not be excluded. They also pointed out, on the other hand, that earlier arguments in favour of a nucleophilic displacement on Rh^{III} compounds, based on the insensitivity of aquation rates on the complex charge,[21] were inconclusive in view of more extended investigations.

Evidence of bimolecular substitutions has been presented by Robb and coworkers,[22,23] with their studies on chlororhodium(III) complexes.

It is known that the ratio k_{OH}/k_{aq}, where k_{OH} is the base hydrolysis rate constant, is lower for Rh^{III} complexes than for the corresponding Co^{III} complexes by a factor of about 10^3. This has been explained mainly in terms of a different labilizing effect by the amido group (S_N1CB mechanism operating) upon the two substrates.[21] In view of the present results, which can be extended to aquation reactions as well from the principle of microscopic reversibility, a lower k_{OH}/k_{aq} ratio could be due also to the fact that substitution reactions in acid medium for Co^{III} and Rh^{III} complexes are not mechanistically comparable, being for the latter metal more associative in character.

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