Contribution from the Department of Chemistry,
The University of Rome, 00185 Rome, Italy

The Exchange Reaction between $[Rh(NH_3)_5OH_2]^{3+}$ and Solvent Water (*)

F. Monacelli and E. Viel

Received September 30, 1967

The water exchange reaction of $[Rh(NH_3)_5OH_2]^{3+}$ ion has been kinetically studied by means of an ^{18}O tracer technique. Rates were found to be independent of pH and addition of NaCl. The activation enthalpy and entropy are 23.9 kcal/mole and –3 e.u., respectively. A comparison with the analogous reactions of aquopentamminechromium(III) and cobalt(III) ions suggests for the rhodium system a significant participation of the incoming water molecule as a nucleophile in the transition state. The activation parameters are in agreement with such hypothesis. Attempts have been made to measure the rate of exchange of $[Rh(NH_3)_5OH]^{2+}$ ion, but, even at 60°C and 0.1 M *NaOH, no appreciable exchange was noticed.*

Introduction

Most of the studies of nucleophilic substitution reactions of inert octahedral complexes have been limited to those of Co^{III} and Cr^{III} systems, which can be prepared from unexpensive materials and according to well-known procedures.

However, there has been increasing interest on Rh^{III} compounds, which provide further data for a comparative analysis of the reactivity of related octahedral structures.

Among the reactions studied, those concerning the acidopentamminerhodium(III) ions have been the subject of several papers. After the early study by Lamb[1] on the reversible reaction:

$$[Rh(NH_3)_5X]^{2+} + H_2O \rightleftharpoons [Rh(NH_3)_5OH_2]^{3+} + X^-$$

where X = Cl, Br, the reactivity of halopentamminerhodium(III) systems has been investigated by other authors in both acidic and basic water solutions.[2,3,4]

However, no data (except those of Lamb have been reported on the anation or water exchange of $[Rh(NH_3)_5OH_2]^{3+}$.

The usefulness of a comparative study of aquation, anation and water exchange reactions has been pointed out.[5-9] As a further development of our research on the reactivity of pentamminerhodium(III) complexes, we started with a kinetic investigation of the replacement of the coordinated water of $[Rh(NH_3)_5OH_2]^{3+}$ by solvent water and anionic ligands.

In this paper we present the kinetics of the oxygen exchange reaction of $[Rh(NH_3)_5OH_2]^{3+}$ with solvent water.

Experimental Section

Materials. Oxygen-18 enriched water (1.5% ^{18}O) was supplied by Yeda Research and Developments Co., Rehovoth, Israel, and was used without further purification.

A concentrated solution (48%) of HBr in enriched water was prepared by dissolving gaseous hydrobromic acid in 1.5% ^{18}O water and collecting the azeotropic mixture (b.p. 126°C under normal pressure). Gaseous HBr was prepared according to the method reported by Vogel.[10]

The aquopentamminerhodium(III) perchlorate was prepared and purified according to a procedure described in Gmelin.[11] The ^{18}O enriched complex was prepared by dissolving at 100°C 3.0 g of $[Rh(NH_3)_5OH_2](ClO_4)_3$ of normal composition with 13 ml of an acid solution ($10^{-3}M$ $HClO_4$) of enriched water. After two hours of refluxing, the solution was cooled to 0°C. The precipitated enriched complex was collected on a filter and washed several times with acetone. After prolonged drying in a vacuum dessicator, 2.0 g of the complex were obtained.

Other reagents were all pure grade.

Kinetic runs and mass analysis. The general procedure was essentially that of Posey.[12] Either ^{18}O enriched or normal complex was made to react with normal or enriched water, respectively.

For each run a water solution of $[Rh(NH_3)_5OH_2](ClO_4)_3$ containing known amounts of complex, salts and $HClO_4$ or NaOH was allowed to exchange in a bath at the desired temperature, controlled within ±0.1°C. Independent samples were prepared by dissolving a weighed amount of the complex in a known volume of water (2-10 ml) adjusted to the

---

(*) This research was supported by the Italian Consiglio Nazionale delle Ricerche.

(1) A. B. Lamb, *J. Am. Chem. Soc.*, *61*, 699 (1939).

(2) S. A. Johnson, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, *85*, 1741 (1963).

(3) S. C. Chan, *Aust. J. Chem.*, *20*, 61 (1967).

(4) G. B. Schmidt, *Z. Phys. Chem.*, *41*, 26 (1964).

(5) J. P. Hunt and H. Taube, *J. Chem. Phys.*, *19*, 602 (1951).

(6) H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, *75*, 1463 (1953).

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

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

(9) N. V. Duffy and J. E. Earley, *J. Am. Chem. Soc.*, *89*, 272 (1967).

(10) A. I. Vogel, «Practical Organic Chemistry», Longmans, London, p. 182 (1966).

(11) Gmelin's, «Handbuch der Anorganischen Chemie», *64*, 109 (1938).

(12) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, *79*, 255 (1957).

desired pH and ionic strength. At intervals, the samples were either withdrawn with a pipette or extracted from the thermostat.

The volume of each sample was such as to contain not less than 50 mg of complex.

The samples were rapidly cooled in an ice bath and mixed with equal amounts of cold concentrated HBr. In a few seconds, a finely divided precipitate of $[Rh(NH_3)_5OH_2]Br_3$ was formed.* After stirring, the suspension was filtered off on a filtering crucible and the precipitate was washed several times with acetone,** air dried and kept in a vacuum dessicator, over SiO_2, for 12 hours.

When the enriched water was used for the runs, enriched HBr was also used as the precipitant. This way the enriched water could be recovered without any isotopic dilution.

The coordinated water of $[Rh(NH_3)_5OH_2]Br_3$ was liberated by heating the complex at 130°C and condensed in a sealing tube containing equal amounts (about 30 mg) of $Hg(CN)_2$ and $HgCl_2$.

The general procedure and the apparatus employed to convert the oxygen to CO_2 were those described in ref. 13 with a few changes. For instance, we have found that $HgCl_2$ was not necessary and, in fact, in most cases it was not used. This leads to a further simplification of the method since the treatment of the gaseous mixture with 5,6-benzoquinoline, necessary to remove HCl formed upon pyrolysis, could also be omitted.

The purified CO_2, transferred in a Urey tube, was then analyzed by means of a SP21F Italelettronica mass spectrometer.

The oxygen-18 atom fraction, α, of the original sample was then evaluated by the formula.

$$\alpha = \frac{1}{2R+1}$$

where R is the ratio between 44 and 46 mass intensities ($^{12}C^{16}O_2$ and $^{12}C^{16}O^{18}O$, respectively).

Exchange rate constants. General background on the kinetics of isotope exchange reactions is discussed in reff. 14 and 15.

For the reaction

$$[Rh(NH_3)_5{}^*OH_2]^{3+} + OH_2 \longrightarrow [Rh(NH_3)_5OH_2]^{3+} + {}^*OH_2 \qquad (1)$$

the plot of $-\ln|\alpha-\alpha_\infty|$ *vs.* time (α_∞ being the ^{18}O atom fraction at equilibrium) is expected to be linear with a slope, k_{obs}, related to the actual exchange rate constant, k_e, by the equation

$$k_{obs} = k_e \frac{f([complex])}{[complex]}$$

allowance being made for the large excess of solvent water, where f([complex]) is, in principle, any function of the complex ion concentration.

In carrying out the calculations it was assumed that α_∞ was coincident with the ^{18}O atom fraction of the pure solvent water. This value is known with accuracy, independent of experiment, when enriched complex and normal water were used ($\alpha_\infty = 2.00\times10^{-3}$). When the reverse experimental condition was chosen, the α_∞ value, determined through analysis, might be somewhat less accurate, leading to a corresponding uncertainty in the value of the constant. For this reason, most of the exchange runs were carried out starting from the enriched complex.

For the experiments in deuterium oxide (99.8% deuterium) it was first assumed that the oxygen-18 composition of the water were essentially the same as that of normal water. However, the presence of a definite curvature in the kinetic plots suggested that the assumption was not valid. As a matter of fact, the mass analysis of the deuterium oxide gave, for the oxygen, the isotopic composition reported in the sixth column of Table I.

Figure 1 shows a typical kinetic plot. The values of k_{obs}, obtained by least-squares analysis of the experimental points, are reported in Tables I and II together with the experimental conditions. The figures are accurate to ±3% when $\alpha_\infty = 2.00\times10^{-3}$. A somewhat lower degree of accuracy (±5%) is expected when enriched water is used.

Table I. Exchange Reaction of $[Rh(NH_3)_5OH_2]^{3+}$ Ion

Exp.	T (°C)	$[complex]\times10^2$ (*M*)	$[HClO_4]\times10^2$ (*M*)	μ (*M*)	$\alpha_\infty\times10^2$	$k_{obs}\times10^5$ (sec^{-1})
1	20.3	5.0	1.0	0.31	1.51	0.54
2	30.0	7.0	1.0	0.43	1.51	2.20
3	40.0	1.8	1.0	0.12	0.200	7.7
4	40.0	9.5	1.0	0.53	1.53	7.7
5 [a]	40.0	7.0	1.0	0.52	0.200	7.5
6	40.0	7.0	5.0	0.47	0.200	7.6
7	40.0	7.0	10.0	0.52	0.200	7.6
8 [b]	40.0	7.0	1.0	0.43	0.43	8.0
9 [a]	50.0	5.0	1.0	0.50	0.200	24.4
10 [b]	60.0	7.0	1.0	0.43	0.43	88 (85) [c]

[a] Ionic strength adjusted with $NaClO_4$. [b] Runs in D_2O. [c] Extrapolated from data in H_2O.

(*) When NaCl was present in the reacting solution, $[Rh(NH_3)_5Cl]^{2+}$ was also in the precipitate as chloride and bromide salts.

(**) When the exchange was carried out in the presence of NaCl, methanol was used as the washing solvent. Sodium bromide, which is soluble in CH_3OH, could then be taken away if present in the precipitate.

(13) D. Rittenberg and L. Ponticorvo, *Int. J. Appl. Radiation Isot.*, *1*, 208 (1956).

(14) A. Frost and R. G. Pearson, «Kinetics and Mechanism», J. Wiley, New York, p. 192 (1961).

(15) H. A. C. McKay, *Nature* (London), *142*, 997 (1938).

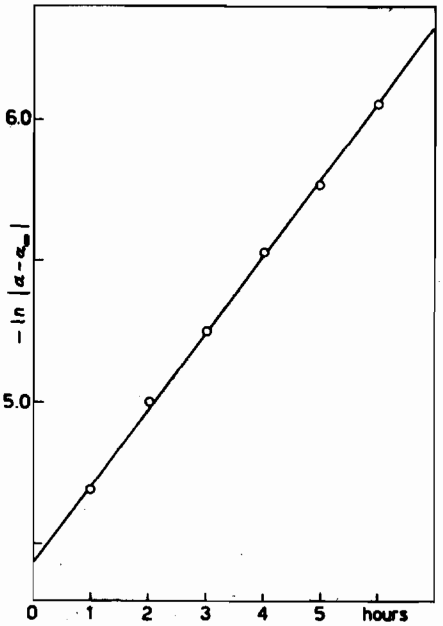

Figure 1. Rate of water exchange of $[Rh(NH_3)_5OH_2]^{3+}$ ion. Temperature 40°C.

The kinetic data reported herein are not conclusive as to the mechanism and their interest is mainly in view of a more extended analysis of the reactivity of the aquopentamminerhodium(III) ion.

One basis for discussion of this exchange reaction is with other related systems such as $[Cr(NH_3)_5OH_2]^{3+}$ and $[Co(NH_3)_5OH_2]^{3+}$ which have been studied.[7,9,18]

Kinetic data for the systems are presented in Table III; the order of exchange rates is Cr>Rh>Co.

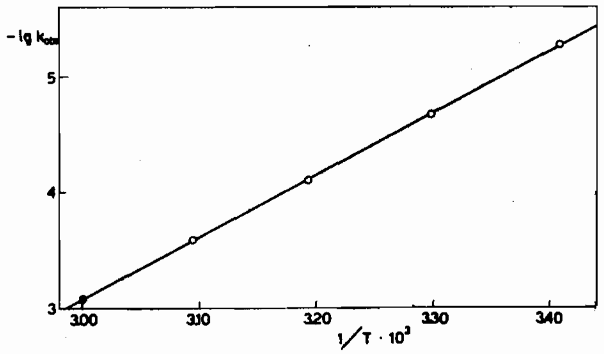

Figure 2. Temperature dependence of the exchange rate constants. Solvents: ○, H_2O ●, D_2O.

Table II. Effect of NaCl on the Exchange of $[Rh(NH_3)_5OH_2]^{3+}$ Ion

T (°C)	[complex]×10² (*M*)	[HClO₄]×10² (*M*)	[NaCl] (*M*)	$\alpha_\infty \times 10^3$	$k_{obs} \times 10^5$ (sec⁻¹)
50.0	3.8	1.0	0.55	0.200	25.4
65.0	—	—	0	—	132 [a]
65.0	20	1.0	2.0	0.200	154
65.0	20	1.0	4.0	0.200	162

[a] Extrapolated from the values at lower temperatures with no NaCl.

Results and Discussion

Exchange in acid solution. From the data of Table I the exchange appears to be first-order with respect to the complex, since a five-fold increase of its concentration (exps. 3 and 4) does not change the value of k_{obs}. Hence, from equation (2), k_{obs} becomes coincident with k_e. The exchange is neither sensitive to pH (exps. 5, 6 and 7), nor to the deuteration of either solvent or coordinated water (exps. 8 and 10).* The addition of large amounts of NaCl causes the rates to increase slightly, as reported in Table II.

The Arrhenius plot was found to be linear over a 40 degree range, as shown in Figure 2, with $\Delta H^* = 23.9 \pm 0.3$ kcal/mole and $\Delta S^* = -3$ e.u.

There is a general tendency to consider the reactions of inert octahedral complexes as mainly dissociative.[16,17] Nevertheless, the arguments on which the mechanistic hypotheses are base are not always completely convincing and, sometimes, different mechanisms are proposed for even the same reaction.

Table III. Kinetic Data for the Exchange Reaction of $[M(NH_3)_5OH_2]^{3+}$ Ions. Rate Constants at 25°C

M^{III}	$k_e \times 10^5$ (sec⁻¹)	ΔH^* (kcal/mole)	ΔS^* (e.u.)
Cr [a]	6 [a]	22 ±4	−4
Rh	1.07	23.9±0.3	−3
Co [b]	0.59	26.6±0.3	6.7

[a] Extrapolated from data of ref. 9. [b] Taken from ref. 7.

The water exchange of $[Co(NH_3)_5OH_2]^{3+}$ has been carefully studied by Hunt and Taube.[7] On the basis of the effect of pressure on the rate, it was suggested that the Co–OH₂ bond is first stretched to a critical distance before a water molecule from the outer solvation shell is able to interact with the metal. The activation entropy ($\Delta S^* = 6.7$ e.u.) is in agreement with a prominently dissociative mechanism, being close to the value expected[7] (7 e.u.) for a process where a coordinated water molecule becomes part of the solvent without a compensating loss of entropy by the entering ligand.

The water exchange of $[Cr(NH_3)_5OH_2]^{3+}$ is also believed to take pace by a process of extended metal-

---

(*) The observed small increase (< 5%) in the rates may be due to the uncertainty on the α_∞ value and cannot be taken into serious consideration.

(16) F. Basolo and R. G. Pearson, «Mechanism of Inorganic Reactions». J. Wiley, New York, p. 163 et foll. (1958).

(17) C. H. Langford and H. B. Gray, «Ligand Substitution Processes», W. A. Benjamin, New York, p. 90 et foll. (1965).

(18) A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, *20*, 825 (1952).

ligand bond breaking followed by a fast «collapse» of the solvation shell into the vacancy formed in the coordination sphere.[9]

However, if the same type of dissociation path would be assigned also to the exhcange reaction of $[Rh(NH_3)_5OH_2]^{3+}$ ion, the above reactivity sequence would not be explicable.

Owing to the greater loss of crystal field energy, a dissociative pattern should lead to a slower reaction and a higher activation enthalpy for the Rh^{III} complex compared to the analogous Cr^{III} and Co^{III} substrates.[19] This is particularly true for the water exchange reaction which does not bring about any change in the charge distribution and, hence, does not involve important energetic contributions by solvation in the activated state.

For the aquopentamminerhodium(III) ion a mechanism where both bond-making and bond-breaking are of comparable importance appears to better explain the experimental evidence.

There are other observations in agreement with this hypothesis. The suggested figure[7] for the entropy difference between free and bonded water may somewhat change by changing the metal,[20] however, its sign and magnitude should be indicative of mechanism. Hence, a decrease of ΔS^* towards a negative value, going from $[Co(NH_3)_5OH_2]^{3+}$ to $[Rh(NH_3)_5OH_2]^{3+}$ is in agreement with a mechanism involving, for the latter complex, a more pronounced participation of a solvent molecule in the transition state. The ΔS^* value (−4 e.u.) reported for the proposed dissociative exchange of $[Cr(NH_3)_5OH_2]^{3+}$ ion[9] would apparently weaken the above argument, but, owing to the large uncertainty on the ΔH^* value of this reaction (±4 kcal/mole), ΔS^* may actually range from −17 to +9 e.u.

The presence of large amounts of NaCl has only a small effect on the rate of water exchange. From data concerning similar systems,[8,21] it may be inferred that at high $[Cl^-]$ the complex and the chloride ion should be largely associated, but this does not seem to affect significantly the rate.

This observation is particularly important in view of our preliminary results on the Cl^- anation of $[Rh(NH_3)_5OH_2]^{3+}$, which indicate that, at higher values of $[Cl^-]$, this reaction becomes faster than the concomitant water exchange.

An investigation of this reaction is progress and will be the subject of a separate paper. If confirmed, significant nucleophilic participation of Cl^- in the anation reaction would provide further evidence for the displacement character of the substitution reactions on some rhodium(III) systems, in agreement with the conclusions of other authors.[2,3,22]

Exchange in basic solutions. Taking advantage of the stability of pentamminerhodium(III) complexes at high pH values, some experiments on the exchange of $[Rh(NH_3)_5OH]^{2+}$ in basic solutions have been carried out and the results are summarized in Table IV. Even under drastic conditions, no appreciable exchange was observed. Assuming that a 10% decrease in the enrichement of the hydroxo complex could be detected, the half-life of the reaction

$$[Rh(NH_3)_5{}^*OH]^{2+} + OH^- \rightleftharpoons [Rh(NH_3)_5OH]^{2+} + {}^*OH^-$$

may be estimated as greater than 150 hours at 60°C. Unfortunately, there are no data in the literature about analogous systems, which could allow us to establish a comparison. The value $t^{1/2} = 1.4 \times 10^3$ hours obtained at 25°C for $[Co(NH_3)_5OH]^{2+}$ in a slightly basic medium[7] should be considered as a rough figure. It confirms, however, that also for the Co^{III} complex OH^- is a poor leaving group, possibly in connection with its high basicity.

Table IV. Exchange Experiments on $[Rh(NH_3)_5OH]^{2+}$ in Basic Aqueous Solutions[a,b]

T (°C)	$[OH^-]$ (*M*)	$\alpha \times 100$ (after reaction)	Time of reaction (hours)
40.0	0.1	1.19	2
		1.15	2
		1.21	4
		1.18	4
		1.20	6
60.0	0.1	1.19	4
		1.21	24

[a] The complex was always $4.0 \times 10^{-2} M$. [b] $\alpha_\infty \times 100 = 0.200$.

Acknowledgment. The authors are gratefully indebted to Prof. J. O. Edwards for helpful discussions and critically reading of the manuscript.

---

(19) R. G. Pearson, *J. Chem. Ed.*, *38*, 164 (1961).
(20) W. M. Latimer and W. J. Jolly, *J. Am. Chem. Soc.*, *75*, 1548 (1953).
(21) V. A. Fedorov, V. E. Mironov and F. Ya. Kul'ba, *Zhur. Neorg. Khim.*, *7*, 2524 (1962).
(22) W. Robb and M. M. Steyn, *Inorg. Chem.*, *6*, 616 (1967).