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

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An ^{18}O study of the rate of water exchange of $[Ir(NH_3)_5OH_2]^{3+}$ in aqueous solution is presented. The rate constants are found to be independent of the hydrogen ion concentration in the range 0.01-0.5 M *and of the ionic strength ($0.96M \leqslant \mu \leqslant 3.0M$). The addition of large amounts of NaCl and NaBr slightly increases the rates. The activation enthalpy and entropy are 28.2 ± 0.2 Kcal/mole and $+3.0$ e.u. respectively. The mechanism is discussed on the basis of a comparison with the analogous Co^{III} and Rh^{III} complexes.*

Introduction

Water exchange studies are of great interest in elucidating the mechanism of the substitution reactions of metal complexes, since most of these reactions are carried out in water and usually lead to the formation of aquo species.

It has been suggested that the comparison between water exchange rate constants and anation rate constants of complex cations may give indications of the degree of bond formation between the metal and the entering anion.[1-3] From this point of view, different behaviour has been found for analogous complexes of different metals. Aquopentammine cobalt(III), for instance, exchanges its coordinated water with anionic ligands at a rate which is never higher than the water exchange, and which is frequently independent of the nature of the anion.[1,4] This fact has been interpreted as an indication of a dissociative interchange mechanism (I_d).

The analogous rhodium(III) complex, however, behaves differently since, as a rule, the substitution by anions of the cordinated H_2O becomes faster than the water exchange at a certain high value of anion concentration.[3,5]

Moreover, in a solvent exchange reaction it has been pointed out that the peculiar nature of both leaving and entering ligands makes it possible to obtain indications on its mechanism from activation data.[4,5] The above differences between aquopentammine complexes of Co^{III} and Rh^{III} are also shown in the activation parameters of the corresponding water exchange reactions; those concerning the rhodium complex are consistent with a significant metal-incoming water interaction in the activated state.[5]

Thus, it seemed interesting to extend both the water exchange and the anation studies to the $[Ir(NH_3)_5OH_2]^{3+}$ ion to look for the existence of a trend in the changing behaviour along the series of aquopentammine complexes of Co^{III}, Rh^{III}, and Ir^{III}.

This paper concerns the water exchange reaction of aquopentammine iridium(III) perchlorate.

The anation studies will be reported in a separate paper. Some data concerning both reactions have been reported in a brief communication.[6]

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.

The aquopentammine iridium(III) perchlorate was prepared by the reaction of chloropentammine iridium(III)[7] ion and sodium hydroxide, followed by precipitation with concentrated perchloric acid. The precipitated salt was purified by crystallization from water.

The oxygen-18 enriched complex was obtained either by hydrolysis of the chloro complex in enriched water containing sodium hydroxide or by exchanging the aquo complex with enriched water.

The purity of any aquo complex was checked by comparing the u.v. spectrum with that reported in the literature[7] and/or by determining its equivalent weight towards sodium hydroxide. Carefully weighed samples were titrated potentiometrically with standard NaOH, using a Radiometer 22 r pH-meter (glass electrode). The equivalent weight always agreed satisfactorily with the theoretical value.

From the titration curves it was also possible to determine the pK_a of the aquopentammine iridium(III) ion. At about 25°C the pK_a value was found to be 6 5, which is of the expected order when compared with those of the corresponding Co^{III} [8] and Rh^{III} [9] com-

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

[2] C.H. Langford and H.B Gray, «Ligand Substitution Processes», W.A. Benjamin, New York, p. 86 and 92, (1965).

[3] F. Monacelli, *Inorg. Chim. Acta*, *2*, 263 (1968).

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

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

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

[7] H.H. Schmidtke, *Inorg. Chem.*, *5*, 1682 (1966).

[8] R.C. Splinter, S.J. Harris, and R.S. Tobias, *Inorg. Chem.*, *7*, 897 (1968).

[9] A.J. Pöe, K. Shaw, and M.J. Wendt, *Inorg. Chim. Acta*, *1*, 371 (1967).

plexes. No attempt was made to control the ionic strength during the titrations but it can be estimated from the complex and added base concentrations to be about $10^{-2}\,M$.

Kinetic Runs and Mass Analysis. The general procedure was that described in ref. 5 and was essentially that followed by Posey.[10]

The exchange experiments were carried out starting from the enriched complex dissolved in a medium of isotopically normal composition. All solutions were acidic ($[HClO_4] = 1 \times 10^{-2}\,M$) in order to suppress the acid dissociation of the aquo complex. The ionic strength was controlled by the addition of appropriate amounts of sodium (or lithium) perchlorate. A few runs were carried out in the presence of NaCl and NaBr.

The reaction:

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

was followed either by withdrawing the samples from a single solution kept at constant temperature in a thermostat, or by using several independently prepared samples. With either procedure the volume of the samples was such as to contain not less than 40 mg of aquo complex. When the exchange was carried out in the presence of sodium halides, part of the aquo complex was converted to the acido form. The volumes of the samples were calculated so as to contain at any time 40 mg of «unreacted» aquo complex. Each sample was mixed with an equal volume of concentrated HBr and rapidly cooled in an ice bath; this caused $[Ir(NH_3)_5OH_2]Br_3$ to precipitate. This solid was washed several times with acetone and ether and kept overnight in a vacuum dessicator over SiO_2. The coordinated water was liberated by heating the complex at 200°C for about 5 minutes then condensing it in a tube containing about 15 mg of $Hg(CN)_2$[12] which was then sealed. On pyrolysis at 400°C, CO_2 was obtained, and analysed by a mass spectrometer for the oxygen-18 content. Isotopic analyses were carried out with a SP21F Italelettronica mass spectrometer.

Exchange Rate Constants. For reaction (1), the plot of $-\lg(\alpha - \alpha_\infty)$ *vs.* time (α and α_∞ are the ^{18}O atom fraction at a given time and at equilibrium respectively) was found to be linear, as expected. The slope of the line, $k_{obs}/2.303$, was determined by a least-squares analysis of the experimental points. Occasionally, a few points showed a large deviation from linearity and *always* in the sense of a *lower* ^{18}O content. These deviations were attributed to contamination by atmospheric oxygen or by compounds containing isotopically normal oxygen. These points were not considered when computing the slopes. The infinite time atomic fraction, α_∞, was assumed to be equal to 2.04×10^{-3}, corresponding to that of natural water,[13] thus neglecting the contribution of the enriched complex to the equilibrium composition as well as any isotopic effect.

The values of k_{obs} are reported in Table I together with the reaction conditions. The uncertainties are probable errors.[14]

Results and Discussion

An inspection of Table I shows that the observed rate constant is not changed over a 50-fold variation of $[H^+]$ (exps. 7,8) nor is it sensitive to complex concentration (exps. 5,6,7). This is consistent with an exchange process involving only the aquo complex and an unknown number of solvent water molecules in the activated state, the constant k_{obs} thus being equal to the actual exchange rate constant.[15]

Moreover, the lack of influence of the ionic strength shown by exp. 10 is expected for an outer-inner sphere exchange of neutral ligands.

Only the addition of sodium chloride and bromide causes the rate to increase to a limited extent.

The Eyring plot (Figure 1) was found to be linear, with $\Delta H^* = 28.2 \pm 0.2$ kcal/mole and $\Delta S^* = +3.0$ e.u.

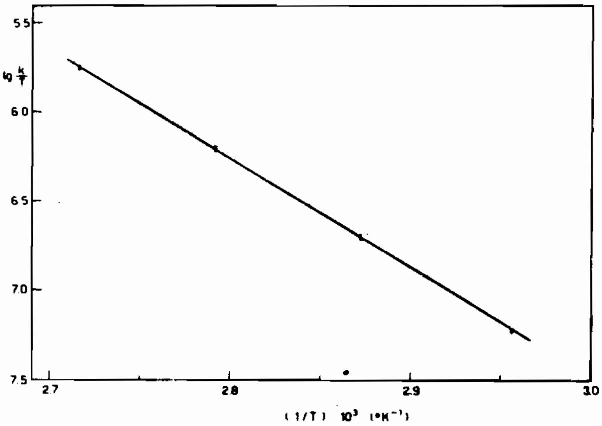

Figure 1. Eyring plot for the water exchange reaction of $[Ir(NH_3)_5OH_2]^{3+}$.

In previous work,[5] the activation parameters for the water exchange reactions of aquopentammine cobalt(III) and rhodium(III) ions (see Table II) were compared. It was concluded that the second process has a more associative character. The argument was the lowering of both ΔS^* and ΔH^* on going from Co^{III} to Rh^{III}. Without a significant increase of the metal-incoming water interaction, the activation entropy should be nearly the same in both cases. In addition, since the crystal field loss and, presumably, the overall bond energies increase in the order Co < Rh,[a] ΔH^*

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

(11) F. Monacelli and T. Prosperi, unpublished results.

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

(13) «Chart of the Nuclides» General Electric, 5th Ed. 1956.

(14) H. Margenau and G.M. Murphy, «The Matematics of Physics and Chemistry», D. van Nostrand Co, New York, 2nd Ed. 1956, p. 519.

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

(16) F. Basolo and R.G. Pearson, «Mechanisms of Inorganic Reactions», 2nd Ed. (1967), John Wiley, N.Y., p. 169-70.

[a] There is no *direct* information on the absolute or even relative bond strengths for complexes of the type discussed here and the general idea that the order is $Ir^{III} > Rh^{III} > Co^{III}$, though reasonable in view of the order of effective charge and crystal field energy,[16] still needs an experimental confirmation. Far i.r. spectroscopy and X-ray structures should give useful indications and an explorative investigation in this direction has been undertaken in this laboratory.

Table I. Exchange rate constants at various temperatures and reaction conditions.

Exp.	T (°C)	complex concentration (mg/ml)	$[HClO_4]$x10^2 (M)	$[X^-]$ (M)	μ[a] (M)	k_{obs}x10^4 (sec^{-1})
1	65.2	20	1.0	—	0.96	0.199±0.003
2	65.1	20	1.0	—	0.96	0.199±0.003
3	75.0	21	1.0	—	0.96	0.714±0.011
4	75.0	21	1.0	—	0.96	0.677±0.018
5	85.0	4	1.0	—	0.96	2.26±0.06
6	85.0	10	1.0	—	0.96	2.18±0.03
7	85.0	20	1.0	—	0.96	2.17±0.02
8	85.0	20	50	—	0.96	2.28±0.04
9	85.0	18	1.0	—	0.64 [b, c]	2.57
10	85.0	3.3	1.0	—	3.0 [c]	2.16
11	85.0	19	1.0	2.0(Cl^-)	2.5	2.65±0.06
12	85.0	21	1.0	3.0(Cl^-)	3.2	2.56±0.08
13	85.0	24	1.0	2.0(Br^-)	2.7	2.83±0.15
14	95.0	20	1.0	—	0.96	6.37±0.15
15	95.0	20	1.0	—	0.96	6.63±0.17
16	95.0	22	1.0	—	0.96	6.66±0.07

[a] Ionic strength controlled by addition of $NaClO_4$ unless otherwise indicated. [b] Ionic strength controlled with $LiClO_4$. [c] Runs with only 3 points.

should also increase unless a change to a more associative pattern occurs.

Table II. Activation parameters for the exchange reaction of $[M(NH_3)_5OH_2]^{3+}$ cations (M= Co, Rh, Ir).

M	$k_{25°C}$ 10^5 (sec^{-1})	ΔH* (Kcal/mole)	ΔS* (e.u.)	Ref.
Co	0,59	26.6±0.3	+6.7	4
Rh	1.07	24.1±0.3[a]	—0.65[a]	5
Ir	0.0065	28.2±0.2	+3.0	—

[a] Data calculated by H.L. Bott and A.J. Pöe (19).

The present study shows that the activation entropy of the water exchange of the aquopentammine iridium(III) cation lies between those of the cobalt(III) and rhodium(III) analogues, whereas the activation enthalpy is higher than the others (see Table II). Thus, the activation parameters for the reaction of the iridium complex do not follow the trend expected from the results obtained with the cobalt and rhodium complexes.

By extending the above argument to the system under study, this fact could indicate a decrease of associative character with respect to the exchange reaction of $[Rh(NH_3)_5OH_2]^{3+}$. However, present findings do not preclude an appreciable degree of bond-making in the transition state for the iridium complex compared with the cobalt one, since ΔS* is still significantly lower for the former.

The activation enthalpy, which is about 4 Kcal/mole higher than that for the rhodium complex, suggests however that the exothermic contribution from the partial formation of the iridium-incoming water bond does not compensate for the larger energy required to stretch the iridium-outgoing water bond. This is not unexpected since the CFSE loss is larger for $[Ir(NH_3)_5OH_2]^{3+}$ than for $[Rh(NH_3)_5OH_2]^{3+}$ and, presumably, the overall metal-water bond energies are in the same order.[b]

Preliminary data on the anation by Cl^-, Br^-, and N_3^- seem to confirm the tendency of the $[Ir(NH_3)_5OH_2]^{3+}$ ion to react by an associative pattern, since at a certain high anion concentration these reactions become faster than the concomitant water exchange,[10,11] this behaviour being very close to that found for the rhodium complex.[3] Of course this fact alone does not preclude a dissociative mechanism if a relatively strong labilization of the metal-oxygen bond induced by the anion is assumed and the latter can compete successfully with water for the intermediate. However, it should be remembered that the aquopentammine cobalt(III) cation, which tends to associate with anions even more strongly, does not show such an effect.

The sensitivity of the exchange reaction to the presence of anions should be discussed. The available data are admittedly insufficient to draw a satisfactory picture of this effect but, from Table I (exps. 10, 11, 12, 13) it appears that anions like Cl^- and Br^- increase the exchange rate to a detectable extent while ClO_4^- ions seem to be ineffective. Similar behavior was shown by $[Rh(NH_3)_5OH_2]^{3+}$.[5] The most common explanation of the accelerating effect produced by *anions* on the replacement reactions of complex *cations* is given in terms of ion pairing.[17] If this is the case, the lack of a detectable effect when ClO_4^- ions are used suggests that the latter species has a limited tendency to form ion-pairs, at least with $[Ir(NH_3)_5OH_2]^{3+}$, in agreement with the anation results obtained on this substrate.[6] An extensive investigation on the effect of anions on the water-exchange rates of aquopentammine metal(III) complexes has been undertaken. Finally, it is interesting to note that the exchange rate constants of the aquopentammine cobalt(III), rhodium(III), and iridium(III), at 25°C, are in the ratio 90: 170: 1, which is not far from that found for the aquation of the corresponding trifluoroacetato complexes.[18] The acid-catalyzed aqua-

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[b] See footnote [a].

(17) F. Basolo and R.G. Pearson, «Mechanisms of Inorganic Reactions», 2nd Ed. (1967), John Wiley, N Y., p. 178 and refs. therein.

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

(19) H.L. Bott and A.J. Pöe, *J. Chem. Soc.* (*A*), 1745 (1969).

tion of acetato and pivalato complexes follow a similar pattern. A carbon-oxygen cleavage was suggested in order to account for the influence of the metal which was expected to be much larger in the case of a metal-oxygen bond breaking. The results concerning the water exchange of the corresponding aquo complexes demonstrate that the above reactivity ratio does not preclude the metal-donor atom fission. In fact, Andrade, *et al.*,[20] have recently pointed out that the slowest reacting carboxylatopentammine iridium(III) systems place an upper limit on the rate of the C–O cleavage aquation path, so that the metal-oxygen bond breaking appears to be more likely and consistent with the ^{18}O exchange data reported by the above authors.

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(20) C. Andrade, R B. Jordan, and H. Taube, *Inorg. Chem.*, 9, 711 (1970).