

Aquation and Base Hydrolysis of Nitratopenta-
amminerhodium(III) and -iridium(III) Complexes

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The acid and base hydrolysis of nitratopentaammine-rhodium(III) and iridium(III) cations have been studied kinetically. The observed rate constants were found to follow the equation $k_{obs} = k_{aq} + k_{OH} [OH^-]$. The activation parameters calculated at unit ionic strength ($NaClO_4$) are: (Rh), $\Delta H_{aq}^* = 23.3$ kcal/mole; $\Delta S_{aq}^* = -3$ e.u.; $\Delta H_{OH}^* = 27.5$ kcal/mole; $\Delta S_{OH}^* = 26$ e.u.; (Ir), $\Delta H_{aq}^* = 26.1$ kcal/mole, $\Delta S_{aq}^* = -4$ e.u.; $\Delta H_{OH}^* = 31.0$ kcal/mole; $\Delta S_{OH}^* = 19$ e.u.

Comparison with the analogous Co^{III} complex suggests for the aquation an essentially dissociative mechanism though some degree of associative character cannot be excluded. The addition of both $HClO_4$ and $NaClO_4$ up to 4 M decreases the aquation rates. This effect is explained in terms of decreased water activity.

The relatively high value of ΔS_{OH}^* suggests for the base hydrolysis of both complexes a mechanism via conjugate base with no clear distinction between S_N1CB and S_N2CB .

The activation entropy data are also discussed in relation to the standard entropy of the aqueous nitrate ion.

Introduction

The chemistry of octahedral complexes of 4d and 5d metal ions has recently received increasing attention in the attempt to gain further information about the substitution mechanism, by considering the effect of the nature of the central metal ion on the kinetic parameters.

Rhodium(III) and, to a lesser extent, iridium(III) complexes have been particularly studied because they may be compared with the analogous cobalt(III) compounds on which a considerable amount of work has been done.

In this paper kinetic data concerning the acid and base hydrolysis of the $[M(NH_3)_5NO_3]^{2+}$ ions, with $M = Rh$ and Ir , are reported and discussed.

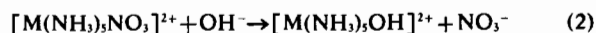
Experimental Section

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

Complexes. The preparation of nitratopentaammi-

neiridium(III) nitrate was previously reported^{1,2} while there are no reports on any nitratopentaamminerhodium(III) salt. Both complexes were prepared as perchlorate salts by essentially the same procedure. An amount of $[M(NH_3)_5OH_2](ClO_4)_3$, left from previous investigations,^{3,4} was dissolved in the minimum amount of water and converted to the nitrate salt by precipitation with concentrated nitric acid. The precipitate (yellowish $M = Rh$; white $M = Ir$) was kept at about 120°C for several hours until a constant weight was reached. The heated material proved to be much less soluble in water than the starting complex. A saturated solution of this material was treated with concentrated perchloric acid and a crystalline precipitate was obtained. This compound, readily soluble in water, was purified by repeated precipitations with concentrated $HClO_4$. The elemental analysis gave the following results: $M = Rh$, found: N, 19.16%; Cl, 16.24%. Calcd for $[Rh(NH_3)_5NO_3](ClO_4)_2$: N, 18.7%; Cl, 15.9%; $M = Ir$; found: N, 15.49%; Cl, 12.89%. Calcd for $[Ir(NH_3)_5NO_3](ClO_4)_2$: N, 15.6%; Cl, 13.2%. The spectrum of the iridium complex was found in agreement with the one reported in the literature.²

Kinetics. The reactions:



were followed by recording at intervals the optical densities of aqueous solutions of the complexes, at wavelengths where the variation of light absorption was suitably large (240-260 m μ). Either a Beckman DU 2 or DU spectrophotometer was used to follow the relatively slow reactions of the iridium complex and the aquation of the rhodium analogue. The fast base hydrolysis of the latter was followed with a Beckman DB recorder spectrophotometer, by using a two-section quartz cell where equal volumes (1.00 ml) of a neutral solution of the complex and of a sodium hydroxide-sodium perchlorate solution were allowed to equilibrate termally before mixing. The temperature was controlled to $\pm 0.15^\circ C$, at worst, by circulating water from a thermostat.

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(2) H.H. Schmidtke, *Inorg. Chem.*, **5**, 1682 (1966).

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

The reacting solutions were generally made by mixing the proper volumes of stock solutions of NaClO_4 , HClO_4 or NaOH and adding a weighed amount of solid complex. The latter was always the minor component of the mixture, its concentration being lower than $1 \times 10^{-3} M$.

When analyzed according to a first-order scheme, the optical data yielded strictly linear plots over more than 2 half-lives. Both aquation and base hydrolysis were complete under the conditions chosen since the equilibrium spectra were found equivalent to those of the aquo and the hydroxo species, allowance being made for the absorption due to the free nitrate ion.

Results

The rate constants, k_{aq} , measured for reaction (1) at the ionic strength $\mu = 1.0 M$ are reported in Table I. The corresponding Arrhenius plots were found to be linear for both complexes and the calculated activation parameter appear in Table II together with

Table I. Aquation rate constants of $[\text{M}(\text{NH}_3)_5\text{NO}_3]^{2+}$ ions. Ionic strength $1.0 M$ (NaClO_4), hydrogen ion concentration $0.01 M$.

M = Rh		M = Ir	
T (°C)	$k_{\text{aq}} \times 10^4$ (sec ⁻¹)	T (°C)	$k_{\text{aq}} \times 10^5$ (sec ⁻¹)
41.4	1.05	60.2	0.82 ₅
41.4	1.05	60.2	0.83 ₂
51.3	3.3 ₅	70.2	2.57
51.2	3.3 ₅	70.2	2.56
63.1	12.3	70.0	2.63
		85.1	13.3
		85.1	13.5

Table II. Aquation of $[\text{M}(\text{NH}_3)_5\text{NO}_3]^{2+}$ complex ions. Activation parameters and rate constants at 25°C. Uncertainties are probable errors.

M	$k_{\text{aq}} \times 10^7$ (sec ⁻¹)	ΔH_{aq}^* (kcal/mole)	ΔS_{aq}^* (e.u.)	Ref.
Co	240	24.3	2	5
Rh	123	23.3 ± 0.2	-3	present work
Ir	0.685	26.1 ± 0.2	-4	present work

Table III. Aquation rate constants of $[\text{M}(\text{NH}_3)_5\text{NO}_3]^{2+}$ ions in the presence of variable concentrations of sodium perchlorate and perchloric acid. M = Rh, T = 63.0°C; M = Ir, T = 85.0°C.

M = Rh			M = Ir		
$[\text{NaClO}_4]$ (M)	$[\text{MClO}_4]$ (M)	$k_{\text{aq}} \times 10^5$ (sec ⁻¹)	$[\text{NaClO}_4]$ (M)	$[\text{HClO}_4]$ (M)	$k_{\text{aq}} \times 10^4$ (sec ⁻¹)
0.10	0.01	1.40	1.0	0.01	1.34
1.00	0.01	1.23	2.0	0.01	1.18
2.02	0.01	1.03	3.0	0.01	1.01
3.0	0.01	0.83 ₅	4.0	0.01	0.86 ₀
4.0	0.01	0.71 ₃	—	0.10	1.52
4.0	0.01	0.72 ₀	—	0.50	1.37
—	0.10	1.39	—	1.0	1.26
—	1.0	1.15	—	1.0	1.27
—	1.93	0.88 ₀	—	2.0	0.99 ₀
—	3.00	0.66 ₉	—	3.0	0.78 ₀
—	3.86	0.52 ₀	—	4.0	0.61 ₀

other data, relevant for the following discussion.

Table III shows the effect of the addition of sodium perchlorate and perchloric acid on the rate of aquation of both nitratocomplexes. In all cases the rates are lowered and perchloric acid is more effective in this sense than sodium perchlorate.

The rate of base hydrolysis (2) was found to increase with sodium hydroxide concentration. When the observed rate constants are plotted against the hydroxide concentration, at constant ionic strength, a linear plot is obtained for both metal complexes with a definite intercept very close to the value of k_{aq} at the same temperature and ionic medium conditions.

The kinetic data in basic solution were, then, analysed according to the equation:

$$k_{\text{obs}} = k_{\text{aq}} + k_{\text{OH}}[\text{OH}^-]$$

and the results are given in Table IV. From the value of k_{OH} at different temperatures the corresponding activation parameters have been calculated and are reported in Table V.

Conclusions

Aquation. The activation parameters for the aquation reaction of nitratopentaamminerhodium(III) and -iridium(III) are similar and close to the ones of the corresponding cobalt(III) species. This fact suggests a substitution mechanism which is essentially the same for all three complexes and, hence, predominantly dissociative.⁵ It is, however, interesting to note that ΔS_{aq}^* decreases on going from the lighter to the heavier metal, thus confirming a tendency already observed within structurally related complexes of these metal ions.^{4,6,9} This tendency might be indicative of an increasing associative character of the mechanism,

Table IV. Pseudo first-order rate constants for the base hydrolysis of $[M(NH_3)_5NO_3]^{2+}$ ions at varying OH^- concentration and constant ionic strength (1.0 M NaClO₄). Uncertainties are half-dispersions.

T (°C)	NaOH × 10 ² (M)	k _{obs} × 10 ³ (sec ⁻¹)	k _{OH} (sec ⁻¹ M ⁻¹)	T (°C)	NaOH × 10 ² (M)	k _{obs} × 10 ³ (sec ⁻¹)	k _{OH} (sec ⁻¹ M ⁻¹)
M = Rh							
42.1	0.00	0.11 ^a	—	33.0	4.00	2.61	0.0652
42.2	3.00	7.10	0.233	33.1	3.00	1.98	0.0646
42.0	2.50	6.22	0.244	33.0	2.00	1.38	0.0670
42.0	2.00	4.85	0.237				Ave. 0.0656 ± 0.0012
42.0	1.50	3.80	0.246	20.2	0.00	0.007 ^a	—
42.1	1.00	2.47	0.236	20.2	20.0	1.68	0.00837
42.1	1.00	2.52	0.241	20.1	15.0	1.27	0.00842
42.1	1.00	2.44	0.233	20.1	10.0	0.88	0.00873
		Ave.	0.239 ± 0.007	20.3	5.0	0.44	0.00866
33.0	0.00	0.04 ^a	—				Ave. 0.00855 ± 0.00019
M = Ir							
70.1	0.00	0.26 ^a	—	60.1	0.30	1.72	0.0546
70.1	0.60	12.8	0.209	60.0	0.22	1.30	0.0554
70.1	0.50	11.0	0.215	60.1	0.10	0.64	0.0558
70.1	0.40	9.10	0.221				Ave. 0.0557 ± 0.0010
70.1	0.30	7.00	0.225	50.0	0.00	0.023 ^a	—
70.0	0.22	5.24	0.226	50.0	0.80	0.997	0.0122
70.1	0.10	2.74	0.248 ^b	50.0	0.60	0.750	0.0121
		Ave.	0.219 ± 0.008	50.0	0.40	0.521	0.0125
60.1	0.00	0.08 ^a	—	50.0	0.25	0.351	0.0131
60.1	0.60	3.47	0.0565	50.0	0.10	0.138	0.0115
60.1	0.50	2.84	0.0552				Ave. 0.0123 ± 0.0007
60.1	0.40	2.34	0.0565				

^a Calculated background aquation rate constants. ^b Not included in the average.

Table V. Base hydrolysis of $[M(NH_3)_5NO_3]^{2+}$ complex ions. Activation parameters and rate constants at 25°C. Uncertainties are probable errors.

M	k _{OH} (sec ⁻¹ M ⁻¹)	ΔH _{OH} [‡] (kcal/mole)	ΔS _{OH} [‡] (e.u.)	Ref.
Co	15	28.1	43	18
Co	12	28.8	43	17
Rh	1.8 × 10 ⁻²	27.5 ± 0.3	26	present work
Ir	1.9 × 10 ⁻⁶	31.0 ± 0.2	19	present work

as in the case of water acting as leaving group.⁸ However, it should be remembered that, when the leaving group is an anion, solvation effects make it more difficult the interpretation of the activation entropy.

Effect of perchlorates on the aquation rate. It is known that the addition of electrolytes containing anions other than perchlorate generally increases the rate of aquation of complex cations as a consequence of ion-pair formation.^{10,12}

On the contrary, there are several reports showing that perchlorates decrease the aquation rates.^{9,13} This retardation effect is also shown by both nitratopentaamminerhodium(III) and iridium(III) cations (see Table III) and may be explained in terms of reduced

water activity. In agreement with this interpretation, perchloric acid, which is more effective than sodium perchlorate in decreasing the water activity,¹⁴ shows also the larger kinetic effect. Unfortunately, the lack of water activity data at the conditions used for the kinetic experiments does allow us to test this hypotheses on a quantitative basis.

Base hydrolysis. There is now a substantial agreement on the fundamental aspect of the mechanism of base hydrolysis when the substrate is a complex containing acidic protons.^{15,16} The high value of the activation entropy observed in such reactions is one of the main arguments in favour of a conjugate base mechanism whose slow step may be, however, either unimolecular (S_N1 CB) or bimolecular (S_N2 CB).

Present data on nitratopentaamminerhodium(III) and -iridium(III) ions are consistent with the conjugate base mechanism but it may be noted that the activa-

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(15) F. Basolo and R.G. Pearson, « Mechanisms of Inorganic Reactions », 2nd Ed., John Wiley, New York, 1967 p. 177 and foll.

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tion entropies are considerably lower than the value found for the analogous cobalt(III) complex.^{17,18} As suggested in a similar case,⁹ this situation might indicate for the heavier metals a S_N2 CB mechanism. However, a safe choice cannot be made on the basis of the present data.

Entropy correlations. It has been shown that when the activation entropies, ΔS^\ddagger , for the acid-independent aquation of a series of $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$ complexes

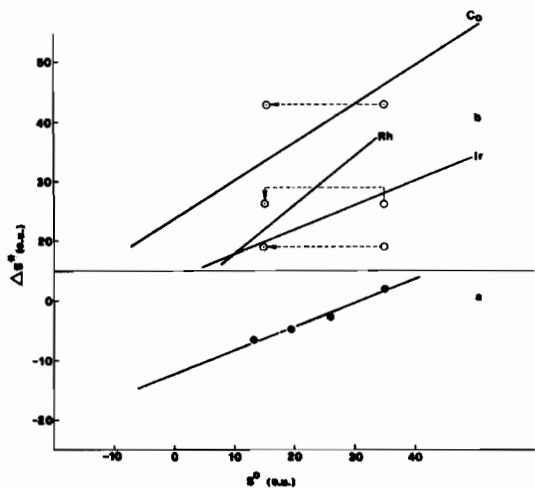


Figure 1. Entropy correlations for $[\text{M}(\text{NH}_3)_5\text{X}]^{2+}$ complexes. a) Aquation of $[\text{Rh}(\text{NH}_3)_5\text{X}]^{2+}$ ions. Values for $\text{X} = \text{Cl}^-$, Br^- and I^- are taken from ref. 21. b) Base hydrolysis of $[\text{M}(\text{NH}_3)_5\text{X}]^{2+}$ complexes. The lines are taken from ref. 20. The points refer to the nitratocomplexes of the three metals shown. The arrows show the shift of the points upon correction for the rotational entropy¹⁹.

are plotted against the standard entropy, S° , of the aqueous X^- ions, a linear correlation is obtained, provided that S° for a polyatomic anion, like nitrate, is corrected by subtracting the contribution due to the rotational term.¹⁹ Figure 1a shows the relation between ΔS^\ddagger and S° for the aquation reaction of some $[\text{Rh}(\text{NH}_3)_5\text{X}]^{2+}$ ions. In this case, nitrate ion fits the relationship when the value $S^\circ = 35$ e.u. is used, that is, when free rotation is fully considered. The slope of the straight line is about 0.4, a value not dissimilar from that observed for the aquation of $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$ ions (0.53).¹⁹

The data on the aquation of $[\text{Ir}(\text{NH}_3)_5\text{X}]^{2+}$ complexes are too scant, and very likely, not accurate enough to allow for this type of analysis.

Linear entropy correlations have been found also for the base hydrolysis of the acidopentaamine complexes of Co^{III} , Rh^{III} and Ir^{III} .²⁰ When nitrate complexes are included, it seems that the extent of free rotation gained by the nitrate ion in the activated state changes with the coordinating metal.

In fact, while a reasonable fit is obtained for the cobalt complex, if the entropy S° is *not* corrected for rotation, the rhodium(III) and the iridium(III) complexes fall near the corresponding line when the standard entropy of the aqueous NO_3^- ion is corrected by subtracting the estimated¹⁹ rotational fraction (see Figure 1b).

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