Kinetic Studies on 4*d* and 5*d* Transition-metal Complexes. Part VII.[1] Kinetics of the Reactions of Chloro- and Bromo-penta-ammineiridium (III) Perchlorates with Sodium Hydroxide in Aqueous Solutions

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The kinetics of the reactions of $[Ir(NH_3)_5Cl]^{2+}$ and $[Ir(NH_3)_5Br]^{2+}$ with hydroxide ions are reported. Data were obtained in the temperature range 76—97 °C under conditions which allow extrapolation to zero ionic strength. The variation of the rate constants (units of $l\ mol^{-1}\ s^{-1}$) at zero ionic strength are reproduced by the equations: for $[Ir(NH_3)_5Cl]^{2+}$, $k^\circ_2 = 2{\cdot}262 \times 10^{17} \exp -(33{,}657 \pm 700)/RT$; and for $[Ir(NH_3)_5Br]^{2+}$, $k^\circ_2 = 1{\cdot}258 \times 10^{18} \exp -(35{,}153 \pm 800)/RT$. A good linear correlation exists between the entropies of activation of the reactions of a variety of acidopenta-ammine complexes and the entropies of hydration of the replaced ligands.

MANY kinetic studies have been reported on reactions of type (1), where $M = Cr^{III}$ and Co^{III} and X^- is a unidentate ligand. Part I [2] presented work on the halogenopenta-ammines of Rh^{III} and we reported [3] on reaction (1) for $[Ir(NH_3)_5I]^{2+}$. This paper presents similar work for $[Ir(NH_3)_5Cl]^{2+}$ and $[Ir(NH_3)_5Br]^{2+}$.

$$[M(NH_3)_5X]^{2+} + OH^- \longrightarrow [M(NH_3)_5OH]^{2+} + X^- \quad (1)$$

EXPERIMENTAL

All reagents were of analytical grade. Distilled water was passed down a column of Permutit Biodeminrolit ion-exchange resin before use. Carbonate-free sodium hydroxide was used.

Preparation and Analysis of Iridium Complexes.—Chloropenta-ammineiridium chloride was prepared by the method of Basolo and Hammaker.[4] Recrystallisation from aqueous perchloric acid gave $[Ir(NH_3)_5Cl](ClO_4)_2$. Bromopenta-ammineiridium bromide was prepared as follows: $[Ir(NH_3)_5Cl]Cl_2$ was converted into $[Ir(NH_3)_5OH]^{2+}$ by reaction with boiling sodium hydroxide solution. $[Ir(NH_3)_5H_2O]Br_3$ was then precipitated by acidification with hydrobromic acid. After drying the precipitate was converted into the bromo-bromide complex by heating at *ca.* 200 °C for 36 h, then recrystallised from aqueous perchloric acid to give the desired product.

Analytical Methods and Results.—Equivalent weights were determined by ion exchange with H^+ on a column of Dowex-50 W resin. For $[Ir(NH_3)_5Cl](ClO_4)_2$, the kinetics were followed by measuring the rate of release of chloride ion by the ferric alum–mercuric thiocyanate method.[5] For $[Ir(NH_3)_5Br]^{2+}$, bromide ion was measured spectrophotometrically at its absorption maximum at 204 nm (molar extinction coefficient = 6600) after removal of unchanged $[Ir(NH_3)_5Br]^{2+}$ on a carefully prepared Dowex-50 W column. A Zeiss PMQ II spectrophotometer was used throughout.

Kinetic Procedure.—The reactions were carried out in stoppered quartz flasks at 76—97 °C in the presence of a large excess (but still relatively low concentrations) of sodium hydroxide. Standard solutions of the base were prepared at 25 °C and allowed to equilibrate to temperature before a known weight of the solid complex was added. Aliquot portions were removed for study. Cooling to room temperature was sufficient to quench the reaction. Several concentrations of sodium hydroxide were used at each temperature to allow extrapolation of the results to zero ionic strength. Concentrations were corrected for the expansion of water from room temperature to the reaction temperature. The initial concentration of the complex ion was about 10^{-4}M. Temperature control was good to ±0·05 °C.

RESULTS AND DISCUSSION

The stoicheiometry of the reactions is accurately given by equation (1) and there is no evidence of release of ammonia from the complex ions even at somewhat higher concentrations of hydroxide ions than were used in the present study. Since the reactions were studied under pseudo-first-order conditions, rate constants, k_1, were obtained graphically from equation (2) where a is the initial concentration of complex ion and x the extent of change. The reactions are very slow but

$$k_1 = \frac{1}{t} \ln [a/(a - x)] \quad (2)$$

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[1] Part VI, C. S. Davis and G. C. Lalor, *J. Chem. Soc.* (*A*), 1970, 445.

[2] G. W. Bushnell, G. C. Lalor, and E. A. Moelwyn-Hughes, *J. Chem. Soc.* (*A*), 1966, 719.

[3] G. C. Lalor and T. Carrington, *J. Chem. Soc.* (*A*), 1969, 2509.

[4] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1962, **1**, 1.

[5] J. S. Swain, *Chem. and Ind.*, 1956, **20**, 418.

TABLE 1

Second-order rate constants for the reaction $[Ir(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [Ir(NH_3)_5OH]^{2+} + Cl^-$

T/°C	10^3[NaOH]/M	10^5k_2/l mol^{-1} s^{-1} Obs.	Calc.
76·95	0	—	22·75
	23·32	11·4	10·85
	35·01	9·75	9·91
	58·30	8·21	8·16
87·30	0	—	83·59
	19·12	48·9	48·36
	28·71	42·4	43·52
	38·24	40·7	40·00
	57·91	34·9	34·89
97·3	0	—	325·3
	16·11	186	185·9
	23·02	169	169·0
	27·59	160	160·2
	34·53	149	149·3

TABLE 2

Second-order rate constants for the reaction $[Ir(NH_3)_5Br]^{2+} + OH^- \longrightarrow [Ir(NH_3)_5OH]^{2+} + Br^-$

T/°C	10^3[NaOH]/M	10^5k_2/l mol^{-1} s^{-1} Obs.	Calc.
77·30	0	—	15·06
	30·31	5·80	5·81
	34·97	5·52	5·48
	41·96	5·18	5·05
	46·63	4·96	5·11
87·15	0	—	59·86
	30·13	23·4	23·0
	34·77	22·1	21·7
	41·71	19·8	20·0
	46·35	19·7	19·1
97·70	0	—	255·9
	29·91	97·9	97·1
	34·51	90·5	91·4
	46·0	80·5	80·2

TABLE 3

Kinetic data for reactions $[M(NH_3)_5X]^{2+} + OH^- \longrightarrow [M(NH_3)_5OH]^{2+} + X^-$ at zero ionic strength at 25 °C

Complex Ion	$k_2{}^0$/l mol^{-1} s^{-1}	A/s^{-1}	E_a/kcal mol^{-1}	$\Delta S^‡$/ cal mol^{-1} K^{-1}	Ref.
$[Cr(NH_3)_5Cl]^{2+}$	$6·71 \times 10^{-4}$	$2·5 \times 10^{16}$	26·7 ± 0·3	14·5	*a*
$[Cr(NH_3)_5Br]^{2+}$	$2·11 \times 10^{-3}$	$4·0 \times 10^{16}$	26·3 ± 0·3	15·4	*a*
$[Cr(NH_3)_5I]^{2+}$	$2·27 \times 10^{-2}$	$1·0 \times 10^{18}$	26·8 ± 0·3	21·8	*a*
$[Co(NH_3)_5F]^{2+}$	$1·34 \times 10^{-2}$	5×10^{17}	26·7	20·5	*b*
$[Co(NH_3)_5Cl]^{2+}$	1·63	$1·514 \times 10^{20}$	27·24	31·8	*c*
$[Co(NH_3)_5Br]^{2+}$	9·06	$1·596 \times 10^{21}$	27·62 ± 0·19	36·5	*d*
$[Co(NH_3)_5I]^{2+}$	17·3	$4·19 \times 10^{21}$	27·81 ± 0·25	38·4	*e*
$[Rh(NH_3)_5Cl]^{2+}$	$4·13 \times 10^{-4}$	$3·11 \times 10^{17}$	28·49 ± 0·33	19·5	2
$[Rh(NH_3)_5Br]^{2+}$	$3·52 \times 10^{-4}$	$8·71 \times 10^{18}$	30·55 ± 0·20	26·1	2
$[Rh(NH_3)_5I]^{2+}$	$3·74 \times 10^{-4}$	$8·91 \times 10^{19}$	32·85 ± 0·50	30·8	2
$[Ir(NH_3)_5Cl]^{2+}$	$4·83 \times 10^{-8}$	$2·262 \times 10^{17}$	33·77 ± 0·7	18·9	*f*
$[Ir(NH_3)_5Br]^{2+}$	$2·15 \times 10^{-8}$	$1·258 \times 10^{18}$	35·15 ± 0·8	22·3	*f*
$[Ir(NH_3)_5I]^{2+}$	$8·26 \times 10^{-9}$	$3·467 \times 10^{18}$	36·32 ± 0·63	24·3	3

[a] M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Amer. Chem. Soc.*, 1961, **83**, 2453. [b] S. C. Chan, K. Y. Hui, J. Miller, and W. S. Tsang, *J. Chem. Soc.*, 1965, 3207. [c] G. W. Bushnell and G. C. Lalor, *J. Inorg. Nuclear Chem.*, 1969, **30**, 219. [d] M. B. Davies and G. C. Lalor, *J. Inorg. Nuclear Chem.*, 1969, **31**, 799. [e] M. B. Davies and G. C. Lalor, *J. Inorg. Nuclear Chem.*, 1959, **31**, 2189. [f] This work.

were all followed for more than one half-life. Replicate determinations of k_1 gave values which usually agreed to better than ±3%.

The second-order rate constants are given by $k_2 = k_1/b$, where $b = [OH^-]_0$ is effectively constant throughout each run. The values of k_2 were fitted to equation (3) for the Brönsted–Bjerrum primary salt effect by use of the method of least squares. The resulting

$$\log k_2 = \log k_2{}^\circ + AI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) \qquad (3)$$

equations using $Q = I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ are: for $[Ir(NH_3)_5Cl]^{2+}$: at 76·95 °C, $\log k_2 = \bar{4}·3569 - 2·2899Q$; at 87·30 °C, $\log k_2 = \bar{4}·9222 - 1·9688Q$; at 97·30 °C, $\log k_2 = \bar{3}·5123 - 2·4878Q$. For $[Ir(NH_3)_5Br]^{2+}$: at 77·30 °C: $\log k_2 = \bar{4}·1778 - 2·7885Q$; at 87·15 °C, $\log k_2 = \bar{4}·7772$ $2·7674Q$; at 97·70 °C, $\log k_2 = \bar{3}·4080 - 2·8528Q$. The estimated error in the $k^\circ{}_2$ term is, in the worst case, 5%. This is for the last entry in Table 2. Rate constants obtained from these equations are compared with the observed ones in Tables 1 and 2.

Equations (4) and (5) are the Arrhenius equations for the reactions of the chloro- and bromo-complexes respectively under zero ionic-strength conditions. These equations reproduce the rate constants to better than ±4%. The limits are the estimated errors in the activation energies.

$$k_2{}^\circ/\text{l mol}^{-1}\,\text{s}^{-1} = 2·262 \times 10^{17} \exp - (33{,}657 \pm 700)/RT \qquad (4)$$

$$k_2{}^\circ/\text{l mol}^{-1}\,\text{s}^{-1} = 1·258 \times 10^{18} \exp - (35{,}153 \pm 800)/RT \qquad (5)$$

The present work gives the kinetic data required to complete the series of reactions of type (1) for Cr^{III}, Co^{III}, Rh^{III}, and Ir^{III} with X = Cl, Br, and I. The available kinetic data for reaction (1) are summarised in Table 3.

The activation energies for reactions (6) correlated

$$[M(NH_3)_5I]^{2+} + OH^- \longrightarrow [M(NH_3)_5OH]^{2+} + I^- \qquad (6)$$

well[3] with Jorgensen's g factor[6] for various M^{III}. Figure 1 shows the observed activation energies for the reactions being discussed plotted against g. The plot

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[6] C. K. Jörgensen, 'Absorption Spectra and Chemical Bonding,' Pergamon, Oxford, 1962.

for the iodo-complexes has been discussed[3] and the present data do not add much to the earlier conclusions. An obvious difficulty is that in these series a variation of 2 or 3 kcal mol^{-1} in the activation energy is significant, yet if the conjugate base mechanism is assumed, ΔH for reaction (7) is included in the E_A values; only if ΔH does not change much from metal to metal would a quantitative comparison of activation energies with g be valid. This may be so for the iodo-complexes, but further development would require knowledge of the thermodynamics of ionization to give the conjugate bases.

The variation of reaction rate with the nature of the halogeno-ligand is of interest. In the chromium and cobalt series there are remarkable increases in rates in going from X = F to X = I. The effect is most marked with Co^{III} where A increases by a factor of nearly 10^4. The results for Rh^{III} and Ir^{III} series differ somewhat from those of the 3*d* metals. For the former the rates are very low and the order with respect to the halogeno-ligand is reversed compared with that for the 3*d* complexes. Also activation energies play a more prominent role. A common feature, however, is the increase of A with atomic number of the halogeno-ligand. A summary of these observations, with average values, is in Table 4.

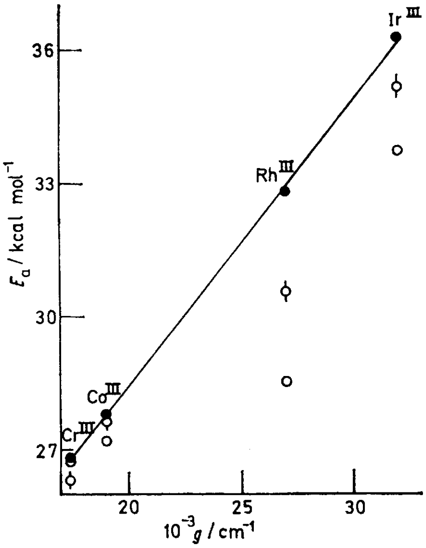

FIGURE 1 The activation energies of the reactions of halogeno-penta-ammine complexes with hydroxide ion (●, iodo-; ϕ, bromo-; ○, chloro-) as a function of Jorgensen's *g*-factor

The relative effects leading to inversion of the expected rate order I > Br > Cl in the Rh^{III} and Ir^{III} complexes are readily understood when the value of A required to keep the rates at the value for the first member, despite the observed increase in activation energy, is calculated. To have k_2 constant at the value observed for $[Co(NH_3)_5F]^{2+}$, A should increase by factors of 2·48, 4·71, and 6·52 times the value observed for $[Co(NH_3)_5F]^{2+}$ in going from X = Cl to X = I. The observed values are 303, 3192, and 8380. For the Rh^{III} series, the rates at 25 °C would remain unchanged relative to $[Rh(NH_3)_5Cl]^{2+}$ if the A values increased by factors of 32·4 and 1580, instead of 27 and 282 as observed. For Ir^{III} the values are 21 and 90 instead of the observed 5·6 and 15·4.

TABLE 4

Average values of activation parameters for the reactions of halogenopenta-ammines with OH$^-$. The quantities in parentheses give the range between the highest and the lowest values of E_A and $\Delta S^‡$ in each series

M^{III}	Cr	Co	Rh	Ir
E_a/kcal mol^{-1}	26·6(0·8)	27·3(1·1)	30·6(4·4)	30·6(2·7)
$\Delta S^‡$/cal mol^{-1} K^{-1}	17·2(7·3)	31·6(8·9)	25·5(11·3)	21·8(5·4)

The mechanism currently favoured for the cobalt-ammines is (7)—(9), which has been thoroughly dis-

$$[Co(NH_3)_5X]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2X]^+ + H_2O \ (K) \quad (7)$$

$$[Co(NH_3)_4NH_2X]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4NH_2]^{2+} + X^- \ (k_8) \quad (8)$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+} \quad (9)$$

cussed.[7] The rate-determining step (8) is a unimolecular change with an expected pre-exponential term of *ca.* 10^{13} s^{-1}. The observed values, which exceed this by many powers of 10, can be accommodated: the observed rate constant is k_8K and the standard entropy change $\Delta S°$ for reaction (8) is included in the observed pre-exponential factor. Values of $\Delta S°$ of *ca.* 36 cal mole^{-1} K^{-1}, which are possible,[8] are required. As $\Delta S°$ should not depend too much on the nature of X, the major source of variation in the pre-exponential term in a series is reaction (8), and in the S_N1 limiting case $\Delta S^‡$ might correlate with the entropy of hydration of X$^-$. This plot is given in Figure 2. Data for uni-negative ligands other than X$^-$ = halogeno-ions are included where possible.[9] Since most data are available for Co^{III} this plot is particularly interesting. The ions NO_2^-, NCS$^-$, and N_3^- would be expected to possess rotational entropy which may or may not also exist in the activated state. It seems that there is a substantial rotational contribution in the case of X = NO_2, less in the NCS and NO_3 complexes, and very little in the azido-complex. It is difficult to assess the magnitude of the rotational entropy even for a linear molecule in solution. A figure of 15 cal mol^{-1} K^{-1} for N_3^- seems

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[7] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 2nd edn., 1967.

[8] A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261.

[9] G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1963, 1560; G. C. Lalor and J. Lang, *J. Chem. Soc.*, 1963, 5620; D. L. Gay and G. C. Lalor, *J. Chem. Soc.* (*A*), 1966, 1179; A. J. Cunningham, D. A. House, and H. J. K. Powell, *J. Inorg. Nuclear Chem.*, 1971, **33**, 572.

a little high, but not impossible. The relationship between N_3^- and the others is similar in the Rh^{III} series indicating an ' excess rotational contribution,' in this case, of 13 cal mol^{-1} K^{-1}.

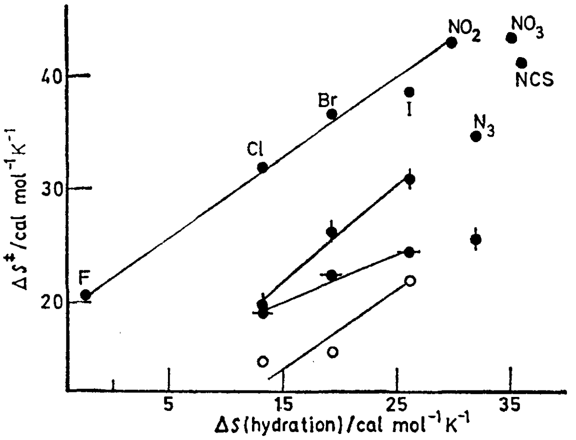

FIGURE 2 Relationships between the entropies of activation of reactions $[M(NH_3)_5X]^{2+} + OH^- \longrightarrow [M(NH_3)_5OH]^{2+} + X^-$ and the entropy of solvation of X^- (○, Cr; ●, Co; ⏀, Rh; ●, Ir). Data for Co^{III} complexes, except when X is a halogeno-ion, from ref. 9. Data for $[Rh(NH_3)_5N_3]^{2+}$ from C. S. Davis and G. C. Lalor, *J. Chem. Soc.* (*A*), 1968, 2328

The data for iridium(III), though limited, give a fairly good line, but the points for Cr^{III} are rather scattered. On the whole, however, it appears that the relationships between $\Delta S^‡$ and S° are not fortuitous and the values of the slopes, *viz.*, 0·7, 0·8, 0·8, and 0·6 for Cr, Co, Rh, and Ir, respectively, support the view that the X ligand is weakly bound in the transition state for those reactions.

A similar comparison between $\Delta H^‡$ and H° shows that (*a*) the values of $\Delta H^‡$ for Cr^{III} show no significant change with X, (*b*) Co^{III} halogeno-complexes show slight changes only, although complexes with X = NO_2, NCS, and N_3 exhibit rather different behaviour, (*c*) $[Rh(NH_3)_5N_3]^{2+}$ is similar to $[Co(NH_3)_5N_3]^{2+}$, (*d*) $\Delta H^‡$ values for the Rh^{III} and Ir^{III} complexes increase linearly with $H^\circ_{X^-}$. The increases in activation energies for reaction (1), therefore, correlate more closely with the heat of solvation of the displaced ion than with the presumed order of bond strengths.

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