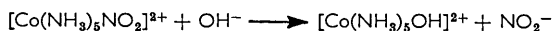


1076. *The Kinetics of the Reaction between Nitropentammine-cobalt(III) Perchlorate and the Hydroxide Ion.*

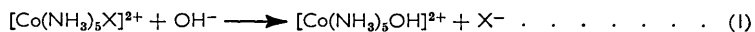
By G. C. LALOR and JUDITH LANG.

. The kinetics of the reaction



in aqueous solution have been studied in the temperature range 40—70° by following, spectrophotometrically, the rate of appearance of NO_2^- , and the disappearance of the complex ion at low ionic strengths. The bimolecular velocity constants vary with ionic strength in agreement with the Brönsted-Bjerrum theory for reactions with a charge product of -2. In common with similar reactions in the acidopentamminecobalt(III) series, the pre-exponential term of the Arrhenius equation is very high. The observed activation energies for the reactions of hydroxide ion with a series of substituted cobalt(III) complexes vary in such a way as to suggest that, in general, the ligand fields contribute to the total effect.

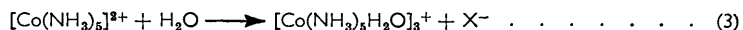
DESPITE numerous kinetic studies on the aquation of the cobalt pentammines, relatively little is known of the reactions of these complexes with the hydroxyl ion.



Brönsted and Livingstone¹ examined the bromo-complex, Adamson and Basolo² the chloro-complex, and Lalor and Moelwyn-Hughes³ the azido-complex. All these reactions show second-order kinetics and are characterised by high values of the pre-exponential terms, *A*, in equation (2).

$$k = A \exp(-E_A/RT) \dots \dots \dots (2)$$

In the reactions of the bromo- and azido-complexes the values of E_A for reaction (1) and for the corresponding aquation (3) are identical within experimental error. This does



not seem to be true for the chloro-complex where the value^{2,4} of the energies of activation for reaction (1) is less than that for reaction (3) by 5 kcal./mole.

EXPERIMENTAL

Preparation of $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{ClO}_4)_2$.—The nitrate salt, prepared by Basolo and Murman's method,⁵ was converted into the perchlorate by recrystallisations from sodium perchlorate-perchloric acid solutions. The perchlorate salt, after being washed successively at the pump with ice-cold water, ethanol, and ether, was dried at 50°.

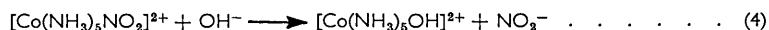
Analytical Methods Used for Complex.—(a) The purity of the complex ion was established by measuring the equivalent weight by passing a solution of the complex ion through a column of Dowex 50-X8 in the H^+ form and titrating the liberated acid with standard borax solution. (b) The content of nitro-group was measured after heating a known quantity of $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{ClO}_4)_2$ with excess of aqueous sodium hydroxide. The amount of nitrite ion formed was measured spectrophotometrically⁶ by diazotisation of sulphanilic acid, followed by coupling with 1-naphthylamine in a borax buffer. The yellow dye had λ_{max} 475 $\text{m}\mu$ (E_{max} 19,700 $\text{mole}^{-1} \text{cm}^2$) {Found: NO_2 , 11.9%; Equiv., 105.0. Calc. for $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{ClO}_4)_2$: NO_2 , 11.8%; Equiv., 104.5}.

¹ Brönsted and Livingstone, *J. Amer. Chem. Soc.*, 1927, **49**, 435.
² Adamson and Basolo, *Acta. Chem. Scand.*, 1955, **9**, 1261.
³ Lalor and Moelwyn-Hughes, *J.*, 1963, 1560.
⁴ Garrick, *Trans. Faraday Soc.*, 1937, **33**, 486; 1938, **34**, 1088.
⁵ Basolo and Murman, *Inorg. Synth.*, 1953, **4**, 174.
⁶ Staples, *Chem. and Ind.*, 1960, 1210.

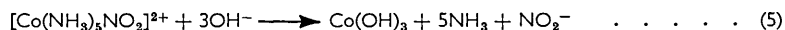
All measurements were made with a Beckman DU spectrophotometer with 1-cm. silica cells.

The usual type of thermostatic tanks were used with mercury-in-glass regulators and "electronic" relays. The temperature control was better than $\pm 0.02^\circ$. Temperatures were measured with a standard thermometer and are accurate to $\pm 0.03^\circ$.

Kinetic Procedure.—Solutions were prepared by dissolving the requisite amount of the complex ion in "ion-free" water containing standard carbonate-free sodium hydroxide. The sodium hydroxide solutions were allowed to equilibrate to the thermostat temperature before addition of the solid. At the lower temperatures well-stoppered volumetric flasks were used as reaction vessels; at higher temperatures a piston type vessel similar to one described by Farhat-Aziz and Moelwyn-Hughes⁷ was used.



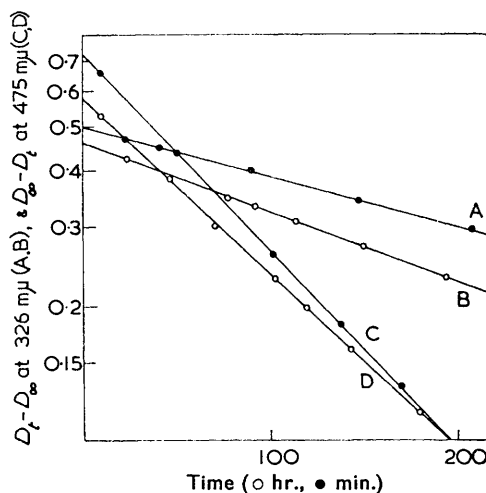
Reaction (4) is the first step in a sequence of reactions which add up stoichiometrically as follows:



The subsequent reactions lead to two complicating features: (a) $\text{Co}(\text{OH})_3$ is precipitated as the reaction proceeds, leading to a heterogeneous system; (b) hydroxide ion is being consumed in reactions other than (1). The presence of $\text{Co}(\text{OH})_3$ does not appear to affect the kinetics of

Fig. 1. Typical first-order plots for reaction.

- A, 60.23° , $[\text{NaOH}] = 16.64 \times 10^{-3}\text{M}$.
 B, 39.94° , $[\text{NaOH}] = 16.83 \times 10^{-3}\text{M}$.
 C, 70.21° , $[\text{NaOH}] = 5.61 \times 10^{-3}\text{M}$.
 D, 50.10° , $[\text{NaOH}] = 5.61 \times 10^{-3}\text{M}$.



reaction (4), and it can be removed by centrifugation before analysis. The kinetic consequences of the removal of OH^- by subsequent reactions can be rendered negligible by working with a large excess of hydroxide ion. Under these conditions reaction (4) is accurately of pseudo-first order. The rate of reaction is sensitive to variations in ionic strength, I , and this study was therefore carried out at low values of I . The results are extrapolated analytically to zero ionic strength.

The reaction was followed either by measurement of the optical density (D) of samples at $326 \text{ m}\mu$ after acidification or, below 10^{-4}M of complex ion, by measurement of $[\text{NO}_2^-]$. Experimental results were obtained in the temperature range $40\text{--}70^\circ$, with solutions containing initially between 0.05 and $0.50 \text{ mmole l}^{-1}$ of complex ion and from 2 to 25 mmole l^{-1} of hydroxide ion.

RESULTS

The analytical methods gave identical results, under the same experimental conditions, confirming that the process being studied is in fact correctly represented by equation (4). At each temperature first-order constants were obtained. Typical plots illustrating the rate of decrease in optical density of the complex ion and $D_\infty - D_t$ for the formation of NO_2^- are shown in Fig. 1. These first-order rate constants depend on the concentration, b , of hydroxide

⁷ Farhat-Aziz and Moelwyn-Hughes, *J.*, 1959, 2635.

ion, which remains effectively constant during the course of each run. The bimolecular constant, k_2 , is given by equation (6), where k_1 is the observed first-order constant, t the time in seconds, and a is the initial concentration of the complex ion. These second-order constants are functions of ionic strength, I , which, under the present conditions, is equal to the concentration of hydroxide ion. A summary of the observed second-order constants is given in Table 1, together with constants reproduced by the empirical equations which were found to represent $\log k_2$ as a function of I . The data at 70° are corrected for the relatively slow ($k = 9.7 \times 10^{-6} \text{ sec.}^{-1}$)⁸ first-order disappearance of the complex ion by simultaneous aequation

$$k_2 = k_1/b = \frac{2.303}{t} \log \left(\frac{D_0 - D_\infty}{D_t - D_\infty} \right) = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right) \quad \dots \quad (6)$$

Duplicate experiments showed that k_2 could usually be reproduced to within $\pm 2\%$. The equations which give $\log_{10} k_2$ as a function of ionic strength are reproduced in Table 2. The third column gives the dielectric constant of water calculated from the equation⁹ $d = d_0 \exp(-LT)$. The last column gives the limiting values of the gradients calculated according to the Brönsted-Bjerrum equation:

$$\frac{d \log_{10} k_2}{dI^{1/2}} = \frac{z_A z_B \epsilon^3}{2.303(dkT)^{3/2}} \left(\frac{8\pi N_0}{1,000} \right)^{1/2} \quad \dots \quad (7)$$

where z_A, z_B are the charges on reacting ions, ϵ is the protonic charge, d the dielectric constant, and T the absolute temperature. When the values of the various constants are inserted, and with $z_A z_B$ taken as -2 , equation (7) reduces to:

$$d \log_{10} k_2 / dI^{1/2} = - (7.295 \times 10^6) / (dT)^{3/2} \quad \dots \quad (8)$$

Constants of the Arrhenius Equation.—The plot of $\log_{10} k_2^\circ$ against $1/T$ is linear within experimental error, indicating that in this temperature range there is no perceptible variation of activation energy with respect to temperature. The accepted value of the activation energies was the mean of 6 calculated values. The temperature variation of k_2° can be reproduced to within 4% by equation (9).

$$k_2^\circ = 3.70 \times 10^{22} \exp(-38,000 \pm 950/RT) \quad \dots \quad (9)$$

TABLE 1.

Dependence of the rate constant of reaction (4) on ionic strength.

Temp. (°C)	[OH ⁻] = I (mmole l. ⁻¹)	5 + log ₁₀ k ₂		Temp. (°C)	[OH ⁻] = I (mmole l. ⁻¹)	5 + log ₁₀ k ₂	
		obs.	calc.			obs.	calc.
39.94	5.61	0.8850	0.8850	60.23	5.165	2.5228	2.5174
	11.21	0.8230	0.8208		5.860	2.5096	2.5082
	16.90	0.7700	0.7709		8.199	2.4800	2.4809
50.10	2.34	1.7640	1.7670	11.21	2.4516	2.4540	
	5.61	1.7130	1.7146	11.73	2.4440	2.4474	
	8.10	1.6800	1.6798	16.64	2.4091	2.4090	
	11.22	1.6467	1.6477	70.21	2.314	3.2700	3.2693
	11.73	1.6418	1.6412	5.860	3.2080	3.2093	
	16.90	1.5990	1.5969	11.71	3.1330	3.1325	

TABLE 2.

The variation of log₁₀ k₂ with ionic strength (I) at various temperatures (°C).

Temp.	log ₁₀ k ₂	Δ	Theor. limiting gradient
39.94	4.040 - 2.07 I ^{1/2}	73.1	2.108
50.10	4.873 - 2.19 I ^{1/2} + 0.50 I	69.7	2.156
60.23	3.666 - 2.25 I ^{1/2} + 1.28 I	66.5	2.208
70.21	2.379 - 2.32 I ^{1/2} + 1.30 I	63.5	2.173

⁸ Lalor, unpublished results.⁹ Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

The results obtained experimentally are compared with those calculated from this equation in Table 3.

TABLE 3.

A comparison of rate constants obtained experimentally and those calculated from equation (9).

T ($^{\circ}\text{K}$)	313.10	323.26	333.29	343.37
$\log_{10} k_2^{\circ}$ (obs.)	4.040	4.873	5.666	5.379
,, (calc.)	4.038	4.888	5.648	5.288

DISCUSSION

The kinetics of reactions (1) can be discussed from three points of view:

(a) *The Effect of Ionic Strength on the Reaction Rate.*—The present results closely resemble those previously obtained^{1,3} with other complex ions. The satisfactory agreement, over a range of temperature, between the observed values of $d \log_{10} k_2 / dT^{1/2}$ and those expected from the Brønsted-Bjerrum theory of ionic reactions with a charge product of -2 is considered support for regarding the rate-determining step as the bimolecular reaction of these complex ions with the hydroxide ion.

(b) *The Magnitude of the Kinetic Parameters.*—All the reactions under consideration have unusually high pre-exponential terms and high energies of activation. This is true also of the reaction between the trisethylenediaminecobalt(III) ion and the hydroxide ion, for which Friend and Nunn¹⁰ find $k_2 = 6.5 \times 10^{19} \exp(-38,000/RT)$, but although this reaction has the same E_A value as reaction (4), the pre-exponential term is considerably lower, indicating the greater steric hindrance to be expected in the trisethylenediamine complex. A partial explanation of the high values of A_2 is provided by a consideration of contributions from internal degrees of freedom and electrostatic effects.³ The value of s , the number of internal modes of motion in the activated complex required to explain the high value of A_2 for $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$, is 13. Available data for reactions of this type are summarised in Table 4. From this it can be seen that there is no simple

TABLE 4.

A comparison of kinetic constants for related reactions $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+} + \text{OH}^-$.

Reference	X	k_2° at 25 $^{\circ}$ (l. mole $^{-1}$ sec. $^{-1}$)	A	E_A (cal./mole)	E	s
1	Br	7.5×10^0	1.96×10^{18}	23,760	25,250	6
2	Cl	8.45×10^{-1}	1.25×10^{21}	28,890	33,750	11
3	N_3	3.0×10^{-4}	6.27×10^{20}	33,180	37,600	10
This work	NO_2	4.2×10^{-6}	3.7×10^{22}	38,000	43,300	13
10	*	—	6.5×10^{19}	38,000	—	—

* Trisethylenediamine.

quantitative relation between A_2 and E_A (or E) for this series of reactions. If the first reaction is omitted, we may regard $\log_{10} A_2$ as 21.5 ± 0.7 , while E_A changes by about 9 kcal./mole. The Garrick mechanism¹¹ does not really contribute to an understanding of the high A_2 value.

(c) *Ligand-field Effects.*—Although ligand-field effects,^{12,13} due to lifting of the degeneracy of the central metal d orbitals under the perturbing influences of the surrounding ligands, are not large in comparison with heats of hydration of the gaseous

¹⁰ Friend and Nunn, *J.*, 1958, 4637.

¹¹ Garrick, *Nature*, 1937, 139, 507.

¹² Orgel, "Introduction to Transition Metal Chemistry," Methuen, London, 1960.

¹³ Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, 1962.

metal ion,¹⁴ they are comparable with the activation energies of reactions of complex ions in solution, and may play a role in the kinetics of reactions of transition-metal ions.^{15,16} If part of the energy of activation in reactions undergone by complex ions consists of the breaking or loosening of a ligand-central ion bond, activation energies in a series of complexes with the same central metal atom should be related to the ligand-field strengths of the ligands.

Consideration of the spectrochemical series^{17,18} is a logical starting point in an attempt to correlate the activation energies of the substitution reactions with the nature of the ligands being replaced. The longest-wavelength absorption peak in the visible region is generally a Laporte-forbidden spin-allowed transition which, for octahedral low-spin complexes, gives the value of Δ , the ligand-field splitting factor, after corrections for parameters of inter-electronic repulsion, which amount to at most 20%,¹⁹ are made. The pentamminecobalt(III) complexes do not of course have perfect octahedral symmetry and the extent of the distortion from octahedral symmetry will depend on how near the sixth ligand is to ammine in ligand-field strength. At this stage, however, these complications may be overlooked and a crude spectrochemical series can be obtained by considering ν_{\max} for the ligand-field bands of the complex ions. This method assumes an "average environment."¹⁹ The resulting series is given in Table 5 together with the values of λ_{\max} and ν_{\max} .

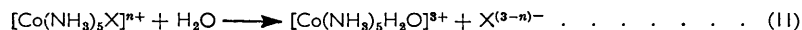
TABLE 5.

A spectrochemical series for $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$; $n = 2$, except for SO_4 ($n = 1$) and NH_3 ($n = 3$).

	I *†	Br	Cl *	N ₃	SO ₄ †	NO ₃ †	H ₂ O †	NCS **†	NH ₃ **‡	NO ₂
λ_{\max} . (m μ)...	585	545	530	518	513	502	498	500	475	458
ν_{\max} . (cm. ⁻¹)	17,094	18,349	18,868	19,305	19,493	19,920	20,080	20,000	21,053	21,934

* From Adamson and Sporer, *J. Inorg. Nuclear Chem.*, 1958, **8**, 214. All other λ_{\max} values were measured during this work. † Base substitution not yet studied. ‡ Kinetic parameters are not yet available for aquation or base substitution.

It might be expected that E_A should increase smoothly, and perhaps linearly, with ν_{\max} for a given series of complex ions, if the mechanism of substitution is common to all the ions. Furthermore, if equation (11) and reaction (1) both involve the breaking



of the Co-X bond as the critical step, the slopes of plots of E_A against ν_{\max} for both series of reactions should be similar. The data for the few base substitutions that have been studied are shown in Fig. 2, in which the observed activation energies, E_A , are plotted against ν_{\max} .

Correction of E_A to give E by means of equation (12), where s is the number of internal degrees of freedom which contribute to the activation energy, R is the gas constant, r the distance of closest approach of the oppositely charged ions in the activated complex ($\sim 3 \text{ \AA}$), and the other terms have been defined in connection with equation (7), does not

$$E_A = E - (s - 1)RT + \frac{z_A z_B e^2}{dr} (1 - LT) \dots \dots \dots (12)$$

¹⁴ Orgel, *J.*, 1952, 4756.

¹⁵ Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958.

¹⁶ Pearson, *J. Chem. Educ.*, 1961, **58**, 164; *J. Phys. Chem.*, 1959, **63**, 321.

¹⁷ Fajans, *Naturwiss.*, 1922, **11**, 655.

¹⁸ Tschuida, *Bull. Chem. Soc. Japan*, 1938, **13**, 388, 436, and 471.

¹⁹ Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962.

alter the trend of the results. We note that, with the exception of the nitro-complex, E_A does in fact appear to be related to the position of the ligand in the spectrochemical series above. The anomalous position of the nitro-compound may be due to π -bonding, which probably plays a role in this instance,²⁰ and is known not to in the others. The more extensive data available on the aquations²¹ are shown in Fig. 3.

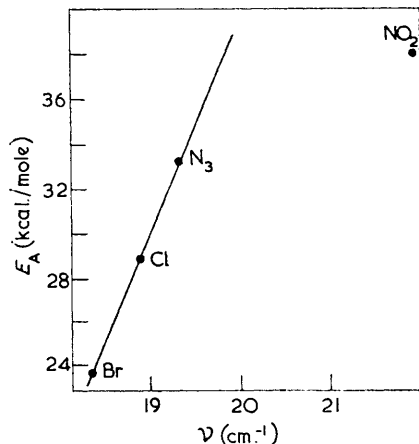


FIG. 2. Ligand-field effects on the apparent energies of activation of the reactions with OH^- .

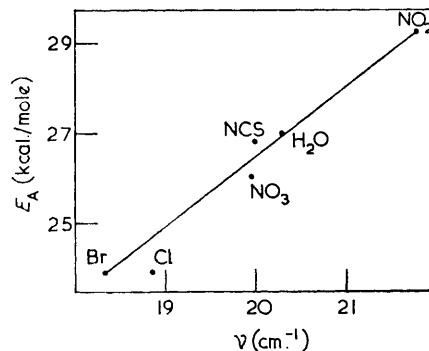


FIG. 3. Relationship between the apparent energy of activation in aquation and ν_{max} of the first ligand-field band for Co(III) complexes.

With the exception of the azido-complex ($E_A = 33$ kcal./mole) and the sulphato-complex ($E_A = 19$ kcal./mole) it is seen that the activation energy for the aquations increases linearly with the strength of the ligand field.

We thank Dr. E. A. Moelwyn-Hughes for valuable discussions and Dr. L. E. Orgel, F.R.S., for helpful comments on the manuscript. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

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²⁰ Staples and Tobe, *J.*, 1960, 4812.

²¹ See, *e.g.*, the compilation by Stranks in "Modern Co-ordination Chemistry," eds. Lewis and Wilkins, Interscience, New York, 1960.