294. *A Kinetic Study of the Azidopentamminecobaltic Ion in Water and in Basic and Acidic Solutions.*

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The kinetics of the reactions of the azidopentamminecobaltic ion in neutral, acidic, and basic solutions at various temperatures have been investigated spectrophotometrically.

The replacement of the azide by the hydroxyl ion is bimolecular, with velocity constants showing a normal primary electrolyte effect. The high value of the pre-exponential term in the Arrhenius equation is attributed to (i) the Coulombic attraction between the ions, (ii) the energy of the attacking ion in the field of the ligands flanking the octahedral facet which it approaches, and (iii) the distribution among classical oscillators of the non-electrostatic component of the activation energy. In octahedral, as distinct from tetrahedral, substitution effects (i) and (ii) are comparable.

In their effect on the temperature variation of the apparent energy of activation, factors (i) and (iii) act in opposite directions, and, taken jointly, can explain a fortuitous applicability of the two-constant equation of Arrhenius.

The spontaneous aquation is a pseudo-unimolecular reaction with the same energy of activation as for the bimolecular substitution.

Azidopentamminecobaltic nitrate reacts quantitatively with aqueous sodium hydroxide according to the reaction

$$[Co(NH_3)_5N_3]^{2+} + 3OH^- \longrightarrow Co(OH)_3 + 5NH_3 + N_3^-$$

but the instantaneous rate of reaction is proportional to the product of the concentrations of the complex ion and the hydroxyl ion, indicating that the rate-determining step is the bimolecular substitution

$$[Co(NH_3)_5N_3]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + N_3^- \qquad (1)$$

Experimental

Azidopentamminecobaltic nitrate was prepared from cobaltous nitrate, ammonium azide, and ammonia by aerial oxidation in aqueous solution. The product was recrystallised three times from dilute nitric acid [Found: NH_3, 27·3, 27·4; Co, 18·8; 19·1; N_3, 13·5%: equiv., 155·5, 155·2. Calc. for $Co(NH_3)_5N_3,2NO_3$: NH_3, 27·5; Co, 19·0; N_3, 13·55%; equiv., 155·1]. It contained $<0·5\%$ of ionic azide.

Absorption maxima were found at 5200 (ε 262) and 3020 Å (ε 7874). Adamson [1] gives 5200 Å but no value of ε. The extinction coefficients of other relevant solutes at 3020 Å are 11 $[Co(NH_3)_5,H_2O]$, 0·03 (Co^{2+}), 0·6 (N_3^-), and 7·07 (NO_3^-).

The stoicheiometric equation was established by the following analyses. Ammonia was estimated after distillation from alkaline solution, and titration against standard acid. The

[1] Adamson, *Discuss. Faraday Soc.*, **1960**, **29**. 163.

concentration of $Co(OH)_3$ was measured by the potassium iodide–thiosulphate method. To measure the concentration of azide ion,[2] a sample of reaction solution was treated with an excess of sodium nitrite, and the unused nitrite was determined by diazotisation of sulphanilic acid before coupling with α-naphthylamine and measurement of the optical density at 4750 Å.

The kinetic equation was established by showing that $d[N_3^-]/dt$, obtained by Staples's method,[2] was identical with $-d[Co(NH_3)_5N_3]^{2+}/dt$ obtained spectrophotometrically.

Reaction (1) is followed by relatively show changes leading to the precipitation of some cobaltic hydroxide. While the presence of this product during the main reaction does not affect its rate, it necessitates a slight modification of the extinction-coefficient method used to determine the concentration of the complex ion. The bimolecular substitution is accompanied by the pseudo-unimolecular aquation:

$$[Co(NH_3)_5N_3]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + N_3^- \qquad (2)$$

but the two simultaneous rates differ so widely that experimental conditions can be so chosen as to allow independent measurements of each. In acidic solutions, the rate of aquation is greater than in water, but the mechanism of the change as catalysed by acids is not yet established.

Solutions of azidopentamminecobaltic nitrate in ion-free water were prepared by weight, and kept in a thermostat bath for measured times before the concentration of complex ion was determined from the optical density, ρ, towards light of wavelength 3020 Å. At low temperatures, reaction solutions were kept in stoppered vessels, and the 5-c.c. samples removed were quenched with 0·05 c.c. of 60% perchloric acid and centrifuged before their optical densities were determined in a Beckman D.U. spectrophotometer. At high temperatures, the solutions were kept either in sealed tubes or in vapour-free piston reactors of the type described by Farhat-Aziz and Moelwyn-Hughes.[3]

Results and Discussion

Kinetics of the Reaction between $[Co(NH_3)_5N_3]^{2+}$ *and* OH^-.—Convenient rates are found between 30° and 50° with solutions containing initially 2—200 mmoles/l. of sodium hydroxide and 0·05—0·10 mmole/l. of complex ion. The rate of decrease in the optical density always followed the first-order law,

$$k_1 = \frac{1}{t} \ln \left(\frac{\rho_0 - \rho_\infty}{\rho - \rho_\infty} \right) = \frac{1}{t} \ln \left(\frac{a}{a - x} \right), \qquad (3)$$

where t is the time in seconds, ρ is the optical density, and a is the initial concentration of complex ion. Typical plots are shown in Fig. 1.

The first-order constant, k_1, is proportional to the concentration, b, of hydroxyl ion, which, being greatly in excess, remains sensibly constant during each run. The bimolecular constant is consequently

$$k_2 = k_1/b = (1/bt) \ln [a/(a - x)]. \qquad (4)$$

Observed bimolecular constants are compared in Table 1 with those reproduced by the empirical equations representing their logarithms as a function of the square-root of the ionic strength, $\sqrt{j}$. The small concentrations of complex ion used make negligible contribution to the ionic strength. These equations are given in Table 2. Duplicate experiments showed that $\log_{10}k_2$ could generally be reproduced to within $\pm 0{\cdot}003$. The coefficients of $\sqrt{j}$ are correct to within $\pm 0{\cdot}047$ at the two lower temperatures and to within $\pm 0{\cdot}07$ at the highest temperature. The last column of Table 2 gives the limiting values of the gradients calculated according to the Brönsted–Bjerrum equation:

$$\frac{d \log_{10} k_2}{d\sqrt{j}} = \frac{z_A z_B \varepsilon^3}{2{\cdot}303(DkT)^{3/2}} \left(\frac{8\pi N_0}{1000} \right)^{1/2}, \qquad (5)$$

where z_A and z_B are the electrovalencies, ε is the protonic charge, D is the dielectric constant,

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[2] Staples, *Chem. and Ind.*, 1960, 1210.

[3] Farhat-Aziz and Moelwyn-Hughes, *J.*, 1959, 2635.

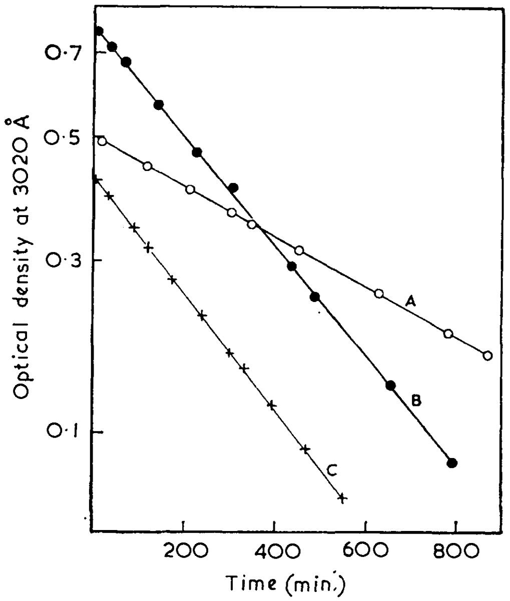

FIG. 1. Typical first-order plots for disappearance of $[Co(NH_3)_5N_3]^{2+}$ in aqueous NaOH.

(A) t = 40·0°; [NaOH] = 5·61 mmoles $l.^{-1}$.
(B) t = 30·0°; [NaOH] = 5·61 mmoles $l.^{-1}$.
(C) t = 50°; [NaOH] = 2·244 mmoles $l.^{-1}$.

TABLE 1.

Bimolecular velocity constants for the reaction $[Co(NH_3)_5N_3]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + N_3^-$ in aqueous solution.

Temp.	j (mmole $l.^{-1}$)	$4 + \log_{10} k_2$ ($l.$ mole^{-1} sec.$^{-1}$) obs.	calc.	Temp.	j (mmole $l.^{-1}$)	$4 + \log_{10} k_2$ ($l.$ mole^{-1} sec.$^{-1}$) obs.	calc.
30·0°	0	—	0·885	40·0°	0	—	1·631
	2·244	0·793	0·790		2·23	1·531	1·531
	19·0	0·628	0·629		5·58	1·476	1·476
	48·9	0·505	0·505		11·16	1·417	1·417
	104·1	0·378	0·382				
	188·6	0·288	0·286	50·0	0	—	2·365
					2·22	2·266	2·264
					5·56	2·208	2·208
					11·12	2·146	2·149

TABLE 2.

Variation of $\log_{10} k_2$ ($l.$ mole^{-1} sec.$^{-1}$) with respect to $\sqrt{j}$ at various temperatures.

Temp.	$\log_{10} k_2$	Dielectric constant	Theor. limiting gradient
30·0°	$\bar{4}\cdot885 - 2\cdot074\sqrt{j} + 1\cdot60j$	76·5	−2·066
40·0	$\bar{3}\cdot631 - 2\cdot204\sqrt{j} + 1\cdot66j$	73·0	−2·108
50·0	$\bar{2}\cdot365 - 2\cdot230\sqrt{j} + 1\cdot68j$	69·9	−2·148

$\boldsymbol{k}$ is Boltzmann's constant, T is the absolute temperature, and $\boldsymbol{N}_0$ is the Avogadro number. Our results indicate that the rate-determining step is one between ions with an electrovalency product of −2, as in equation (1).

TABLE 3.

Bimolecular constants ($l.$ mole^{-1} sec.$^{-1}$) for reaction (1) at zero ionic strength.

Temp.	30·0°	40·0°	50·0°
$4 + \log_{10} k_2°$: obs.	0·885	1·631	2·365
by eqn. (6)	0·877	1·647	2·357

Table 3 shows that the bimolecular constants for reaction (1) at zero ionic strength can be summarised empirically as follows:

$$k°_2 = A_2 \exp(-E_A/\boldsymbol{R}T) = 6\cdot27 \times 10^{20} \exp[-(33{,}180 \pm 800)/\boldsymbol{R}T]. \qquad (6)$$

A_2, like k°_2, has the dimensions of volume mole^{-1} sec.$^{-1}$, and is therefore to be compared with some standard binary collision frequency, Z, such as that given, for example, by the kinetic theory in terms of the ionic radii r_A and r_B, and masses m_A and m_B:

$$Z\ (\text{l. mole}^{-1}\ \text{sec.}^{-1}) = \frac{N_0}{1000}(r_A + r_B)^2\left[8\pi \boldsymbol{k}T\left(\frac{1}{m_A} + \frac{1}{m_B}\right)\right]^{1/2}. \tag{7}$$

Recent work by Eigen and his collaborators[4] on rapid ionic reactions in solution has proved this expression to be correct in regard to order of magnitude. Comparison of A_2 with $\boldsymbol{k}T/\boldsymbol{h}$ is illogical, because the two terms have different dimensions. The numerical value of Z given by equation 7 is $\sim 2 \times 10^{11}$ l. mole^{-1} sec.$^{-1}$ for a variety of reactions. The ratio A_2/Z, referred to as P, is in this instance about 3×10^9, which is 30 times greater than any previously recorded value for ionic reactions. This large value of P must first be discussed.

The theory of the kinetics of ionic reactions in solution[5] starts with the assumption that the energy of activation, E, can be resolved into a non-electrostatic component, E_n, and an electrostatic component, E_e, the latter being given by Coulomb's law.* Then $E = E_n + E_e = E_n + z_A z_B \varepsilon^2/Dr$, where r is the separation of the charges in the activated complex, and P at infinite dilution becomes

$$P^{\circ} = \exp\left(-z_A z_B \varepsilon^2 L/D\boldsymbol{k}r\right), \tag{8}$$

where L is $-(\mathrm{d}\ln D/\mathrm{d}T)_P$. Applied to water at 25° ($D = 78{\cdot}53$ and $L = 4{\cdot}63 \times 10^{-3}$ deg.$^{-1}$), this gives

$$\log_{10} P^{\circ} = -4{\cdot}28 z_A z_B/\mathring{r}, \tag{9}$$

where $\mathring{r}$ is the critical interionic separation expressed in Å. On giving $\mathring{r}$ a typical value of 2·25 Å, the calculated value of P° becomes $5{\cdot}0 \times 10^5$ when $z_A z_B = -3$, and $2{\cdot}5 \times 10^{-8}$ when $z_A z_B = +4$. These agree with experiment as far as may be judged from data on the relatively few reactions which have been studied under the combined effects of temperature and ionic strength. When, however, equation (9) is applied to the present results, the critical interionic separation becomes 0·9 Å, which is unreasonably small.

Equation (8) is essential to an understanding of the regular trend of P° with reactions involving positive and negative electrovalency products, but it is an over-simplification, requiring at least two extensions.

(1) The non-electrostatic component of the energy of activation may be distributed among a number, s, of classical oscillators. That this is true for numerous reactions in solution is no longer in doubt. An approximate theoretical expression for the bimolecular velocity constant then takes the form:

$$k^{\circ}_2 = Z\exp\left(-E/\boldsymbol{k}T\right)\cdot\frac{(E/\boldsymbol{k}T)^{s-1}}{(s-1)!}\cdot\exp\left(-z_A z_B \varepsilon^2/Dr\boldsymbol{k}T\right). \tag{10}$$

Quantitative applications of this equation depend largely on whether Z is or is not dependent on temperature. In reactions controlled by diffusion, Z varies inversely as the viscosity. When activating collisions are of the shuttling type, involving solvent molecules, Z is proportional to the viscosity. In the absence of proof either way, we shall

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* The terms E, E_m, E_e, and E_A henceforth refer to molecular, rather than molar, energies except when specifically given in calories per mole.

[4] Eigen and de Maeyer, *Naturwiss.*, 1955, **44**, 413; *Discuss. Faraday Soc.*, 1954, **17**, 194; Internationales Kolloquim über schnelle Reaktionen in Lösungen, Max-Planck-Gesellschaft zur Förderung der Wissenschaften, 1959.

[5] Christiansen, *Z. phys. Chem.*, 1924, **113**, 35; Moelwyn-Hughes, *Proc. Roy. Soc.*, 1936, *A*, **155**, 308; 1936, *A*, **157**, 667.

assume that Z is given correctly by equation (7) and is therefore effectively independent of temperature. The apparent, or observed, energy of activation then becomes

$$E_A = \boldsymbol{k}T^2(\mathrm{d}\ln k^\circ_2/\mathrm{d}T) = E - (s-1)\boldsymbol{k}T + z_Az_B\varepsilon^2(1 - LT)/Dr. \qquad (11)$$

By eliminating E from equations (10) and (11), and comparing the result with equation (6), we find:

$$P^\circ = \frac{\exp(-z_Az_B\varepsilon^2L/Dr\boldsymbol{k})}{\exp(s-1)\,.\,(s-1)!}\left[\frac{E_A}{\boldsymbol{k}T} + (s-1) - \frac{z_Az_B\varepsilon^2}{Dr\boldsymbol{k}T}(1-LT)\right]^{s-1} \qquad (12)$$

In the present reaction, $E_A/\boldsymbol{R}T$ at 25° is 53·3, $z_Az_B = -2$, and, with $r = 3$ Å, the term $z_Az_B\varepsilon^2(1 - LT)/Dr\boldsymbol{k}T$ becomes $+1{\cdot}807$. To account for the observed value of P°, it is necessary to take s as 10, a value not uncommon for reactions in water, as shown by the temperature variation of the apparent energy of activation in the decomposition of trihalogenoacetic acids[6] and the mutarotation of sugars.[7] It may therefore be concluded that, with reasonable values of r and s, equation (10) is capable of accommodating the main features of reaction (1), without, of course, offering any interpretation of the magnitude of the activation energy, which, corrected according to equation (11), becomes 37,600 cal. mole^{-1}. The justification for using the macroscopic value of D is provided by the verification of equation (5) and by recent evidence on the dissociation constants of electrolytes in various media.[8]

The temperature coefficient of the apparent energy of activation, according to equation (11) is

$$\mathrm{d}E_A/\mathrm{d}T = -\boldsymbol{k}[(s-1) + (z_Az_B\varepsilon^2L^2T)/Dr\boldsymbol{k}]. \qquad (13)$$

When, as here, z_Az_B is negative, the effect of distributing the energy among coupled oscillators and the electrostatic effect act in opposite directions. In fact, with the values of s and r found necessary here, the two terms cancel exactly. The two-constant equation of Arrhenius (equation 6) can thus hold strictly but fortuitously.

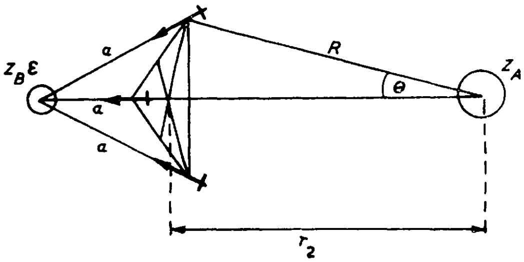

FIG. 2. Electrostatic interaction between an ion and one face of a 6-co-ordinated octahedral complex ion.

(2) Electrostatic contributions to the energy of activation other than that due to the interaction of the ions are to be included. The electric field due to the dipoles of the polar molecules or anions situated at the apices of the octahedron surrounding the central ion directs the approach of the attacking ion towards the centre of a facet and is responsible for an energy which, as we shall see, is comparable in magnitude to the coulombic contribution.

In Fig. 2 an ion (charge $z_A\varepsilon$) is shown at a perpendicular distance r_2 from one of the facets of a regular octahedron. If the length of the dipoles is small compared with the internuclear distance, the energy of interaction between the approaching ion and the three dipoles at the corners of the facet is approximately

$$u = 3z_A\varepsilon\mu\sin\phi\cos\theta/DR^2,$$

where μ is the dipole moment of the ligand, ϕ is the angle subtended between the polar

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[6] Johnson and Moelwyn-Hughes, *Proc. Roy. Soc.*, 1940, *A*, **175**, 118.
[7] Kendrew and Moelwyn-Hughes, *Proc. Roy. Soc.*, 1940, *A*, **176**, 352.
[8] Inami, Bodenseh, and Ramsey, *J. Amer. Chem. Soc.*, 1961, **83**, 4745.

axis and the plane of the facet, R is the distance between the centre of the ion (charge $z_A\varepsilon$) and each dipole, and θ is the angle of inclination of the line of centres to the normal. From the properties of the regular octahedron, we have

$$\sin\phi = (2/3)^{1/2}, \text{ and } R^2 = r_2^2 + (2/3)a^2,$$

a being the distance between the centre of the complex ion and the corners of the octahedron. It follows that

$$u = \sqrt{3}\,.\,z_A\varepsilon\mu/\{Dr_2^2[1 + \tfrac{2}{3}(a/r_2)^2]^{3/2}\}. \tag{14}$$

When the two ions are at the same distance $(a/\sqrt{3})$ from the facet,

$$u = \sqrt{2}\,.\,z_A\varepsilon\mu/Da^2. \tag{15}$$

The ratio of the ion–dipole interaction to the Coulombic interaction in this configuration is

$$\frac{u(\text{ion–dipole})}{u(\text{ion–ion})} = \frac{2(2/3)^{1/2}\mu}{z_B\varepsilon a}, \tag{16}$$

which, even with the gas values of μ for such ligands as ammonia and water, is of the order of magnitude unity. It is, however, the higher dipole moment possessed by the ligand in the presence of the central field that should be employed, and a value of $\sin\phi$ nearer unity than $1/\sqrt{3}$.

The more general expression for the energy of activation of reactions of the kind now considered is clearly, after omission of a small factor,

$$E = E_n + \frac{z_A z_B \varepsilon^2}{Dr_1} + \frac{\sqrt{6}\,.\,z_A\varepsilon\mu}{Dr_2^2}\left[1 + \frac{2}{3}\left(\frac{a}{r_2}\right)^{-2}\right]^{-3/2} \tag{17}$$

where r_1 is the critical distance between the central ion and the attacking ion, and r_2 the critical distance of the latter from the facet. They are related as follows:

$$r_2 = r_1 - a/\sqrt{3}. \tag{18}$$

The theoretical expression for P° now becomes

$$\ln P^\circ = -\left(\frac{z_A z_B \varepsilon^2}{Dr_1} + \frac{\sqrt{6}\cdot z_A\varepsilon\mu}{Dr_2^2}\right)\frac{L}{\boldsymbol{k}}. \tag{19}$$

The omission of the second term in this equation provides an explanation for the fact that the critical interionic distance calculated from equation (8) is much more reasonable in the reaction $CH_2Br{\cdot}CO_2^- + S_2O_3^{2-} \longrightarrow [O_3S_2{\cdot}CH_2{\cdot}CO_2]^{2-} + Br^-$ than in the reaction $[Cr(H_2O)_6]^{3+} + CNS^- \longrightarrow [Cr(H_2O)_5CNS]^{2+} + H_2O$. The values originally found were, respectively, 3·63 and 1·56 Å. Precise values of a and P° make it possible to determine the distances r_1 and r_2 and thus to gain some insight into the configuration of the reactive complex, whether octahedral or tetrahedral.

Kinetics of the Disappearance of the Azidopentamminecobaltic Ion in Neutral and Acid Solutions: the Spontaneous Aquation.—All the experiments carried out in the acid solution show that the logarithm of the optical density decreases linearly with respect to time. Some instances are shown in Fig. 3. The rate of conversion of the complex ion is thus a first-order process. The first-order constant, k_1, however, increases with the concentration of hydrogen ion, though not linearly. As in the catalytic decomposition of diazoacetic ester,[9] the first-order constant, k_1, at any temperature can be reproduced in terms of the concentration, c_H, of hydrogen ion by the equation:

$$k_1 = k_1^\circ + bc_H + dc_H^2, \tag{20}$$

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[9] Moelwyn-Hughes and Johnson *Trans. Faraday Soc.*, 1941, **37**, 1; Albery and Bell, *ibid.*, 1961, **57**, 1942.

where k_1^0, b, and d are constants. Values of k_1, with the limits of reproducibility, are summarised in column 3 of Table 4, and compared with those reproduced by the empirical equations:

$$\text{At } 69{\cdot}6°\text{:}\quad 10^6\, k_1\ (\text{sec.}^{-1}) = 3{\cdot}617 + 4{\cdot}29c_H + 77{\cdot}4c_H^2$$

$$\text{At } 79{\cdot}6°\text{:}\quad ,, \quad = 14{\cdot}13 + 29{\cdot}2c_H + 148c_H^2$$

$$\text{At } 89{\cdot}6°\text{:}\quad ,, \quad = 55{\cdot}4 + 136c_H + 201c_H^2$$

where c_H is the concentration of hydrogen ions in moles/l.

The constants $k_1°$ of equation (20) referring to the spontaneous aquation

$$[Co(NH_3)_5N_3]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + N_3^- \qquad (21)$$

can be summarised, with an accuracy of ±4%, by the empirical equation

$$k\ (\text{sec.}^{-1}) = A \exp(-E_A/\mathbf{R}T) = 1{\cdot}14 \times 10^{16} \exp(-33{,}730 \pm 1000)/\mathbf{R}T. \qquad (22)$$

That $k_1°$ is independent of ionic strength is evident from the results obtained at 69·6° with solutions containing a fixed concentration (14·0 mmoles/l.) of perchloric acid and varying concentrations (50, 125, and 150 mmoles/l.) of sodium perchlorate. We found $10^6k_1°$ to be, respectively, 3·58, 3·66, and 3·65. The same value of $k_1°$ was found by using hydrochloric, nitric, and sulphuric acid.

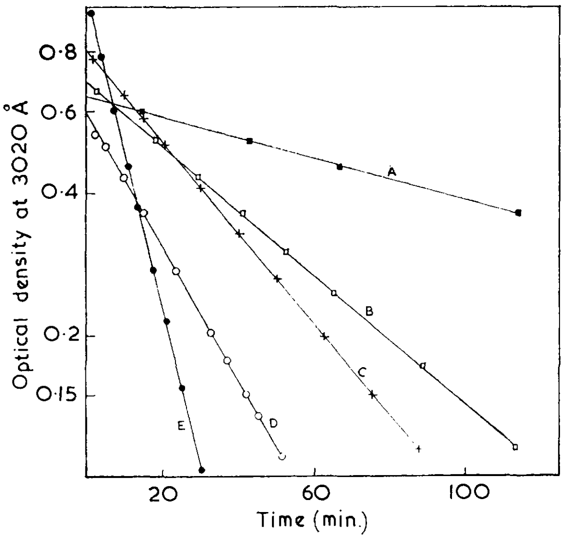

FIG. 3. Typical first-order plots of disappearance of $[Co(NH_3)_5N_3]^{2+}$ in acid solution.

(A) $t = 59{\cdot}7°$, $[H^+] = 105{\cdot}9$ mmoles $l.^{-1}$; (B) $t = 69{\cdot}57°$, $[H^+] = 70{\cdot}6$ mmoles $l.^{-1}$; (C) and (D) $t = 89{\cdot}57°$, $[H]^+ = 42$ (C) and 174·0 (D) mmoles $l.^{-1}$; (E) $t = 79{\cdot}57°$, $[H]^+ = 141{\cdot}2$ mmoles $l.^{-1}$.

TABLE 4.

First-order constants for the rate of disappearance of $[Co(NH_3)_5N_3]^{2+}$ in neutral and acidic aqueous solutions.

Temp.	$HClO_4$ (mmoles $l.^{-1}$)	10^6k_1 (sec.$^{-1}$) obs.	calc.	Temp.	$HClO_4$ (mmoles $l.^{-1}$)	10^6k_1 (sec.$^{-1}$) obs.	calc.
69·6°	0	—	3·617	89·6°	0	—	55·4
	35·38	3·865 ± 0·015	3·869		14·05	56·8 ± 0·3	57·3
	70·60	4·305 ± 0·025	4·305		19·40	57·4 ± 0·6	58·1
	141·2	5·765 ± 0·036	5·765		57·70	64·7 —	63·9
					145·5	79·7 ± 0·6	79·2
79·6	0	—	14·13		197·0	90·4 ± 0·3	90·0
	15·0	14·63 ± 0·03	14·60				
	50·0	16·00 ± 0·22	15·96				
	100·0	18·57 ± 0·30	18·53				
	150·0	21·80 ± 0·30	21·84				
	200·0	25·85 ± 0·25	25·89				

If the rate-determining step is the breaking of a weak bond in an activated structure wherein an energy E is distributed among s classical oscillators, it is legitimate to compare the data with the theoretical expression for a unimolecular constant obtained by combining the equations of Herzfeld[10] and Berthoud:[11]

$$k_1^\circ = \frac{\boldsymbol{k}T}{\boldsymbol{h}} \cdot \exp(-E/\boldsymbol{R}T) \cdot \frac{(E/\boldsymbol{R}T)^{s-1}}{(s-1)!}, \tag{23}$$

where $\boldsymbol{h}$ is Planck's constant. The apparent energy of activation is now

$$E_A = \boldsymbol{k}T^2(\mathrm{d}\ln k_1^\circ/\mathrm{d}T) = E - (s-2)\boldsymbol{k}T. \tag{24}$$

The minimum value of s found by comparing equations (22) and (23) is 4, which enables us to write equation (23) as follows:

$$k_1^\circ = \left(\frac{E}{6\boldsymbol{h}}\right)\left(\frac{E}{\boldsymbol{k}T}\right)^2 \cdot \exp(-E/\boldsymbol{k}T). \tag{25}$$

The actual value of s is probably higher.

Comparison with Data for Similar Reactions.—Except in the magnitude of the various velocity constants, the present results closely resemble these of Brönsted and Livingston[12] on the reactions of bromopentamminecobaltic ion in neutral and alkaline solutions. Most of their rates were measured at 25°, but a few experiments at 15° enabled them to give the values of k_{25}/k_{15} for the aquation as 4·06, and for the hydroxyl-ion reaction at ionic strength 0·0025 as 4·00 ± 0·09. The apparent energies of activation for the two reactions are, as they note, the same. We find the same result with the azidopentamminecobaltic ion, though, at 25°, our bimolecular constant is 10^7 lower than theirs. The apparent energy of activation at zero ionic strength can be found from the equation[13]

$$E_A{}^j = E_A{}^\circ + 800 z_A z_B \sqrt{j}, \tag{26}$$

which gives the correction in cal. mole^{-1} at 25°.

From the pseudo-unimolecular constants found by Garrick[14] for the aquation of the chloropentamminecobaltic ion at 2·5° intervals between 20° and 30°, three of the four values found for the energy of activation lie within the limits 23,880 ± 150 cal. mole^{-1}. His value of k_1 at 25° is 40% lower than that measured conductometrically by Lamb and Marden[15] but is accepted here as being the better datum. The bimolecular reaction between this complex ion and the hydroxyl ion has been investigated by Adamson and Basolo,[16] whose results at an ionic strength of 0·0473 indicate that E_A is 28,800 ± 400 cal. mole^{-1}. This value and that of their k_2 at 25° have been adjusted, by means of equations (26) and (5), respectively, to zero ionic strength, though their data, contrary to those of Garrick on the rate of attack of this complex ion by nitrate and sulphate ions, show no apparent primary salt effect.

Our results are compared with those of the earlier workers in Table 5, where the bimolecular constants are given in l. mole^{-1} sec.$^{-1}$, and the pseudo-unimolecular constants in sec.$^{-1}$. The pre-exponential terms of the Arrhenius equations are given, respectively, in the same units. The corrected energies of activation have been obtained by using equations (11) and (24).

High values of A characterise the reactions of the three complex ions with hydroxyl ion. The same is true of the bimolecular reaction between the trisethylenediaminecobalt(III)

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[10] Herzfeld, *Ann. Phys.*, 1919, **59**, 635.

[11] Berthoud, *J. Chim. phys.*, 1914, **12**, 564.

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ion and the hydroxyl ion for which Friend and Nunn[17] find $k_2 = 6{\cdot}5 \times 10^{19} \exp(-38{,}000/\boldsymbol{R}T)$. These four reactions have an average value of $\log_{10} A_2 = 20{\cdot}0$, though the velocities differ by a factor of 10^9. Equations (12) and (19) provide at least partial explanations of this fact.

TABLE 5.

Comparison of kinetic constants for three pairs of related reactions.

				E_A	E	
Ref.	Reaction	k at 25°	A	(cal. mole^{-1})		s
12	$[Co(NH_3)_5Br]^{2+} + OH^-$	$7{\cdot}5 \times 10^0$	$1{\cdot}96 \times 10^{18}$	23,760	25,250	6
16	$[Co(NH_3)_5Cl]^{2+} + OH^-$	$8{\cdot}45 \times 10^{-1}$	$1{\cdot}25 \times 10^{21}$	28,890 ± 400	33,750	11
This work	$[Co(NH_3)_5N_3]^{2+} + OH^-$	$3{\cdot}0 \times 10^{-4}$	$6{\cdot}27 \times 10^{20}$	33,180 ± 800	37,600	10
12	$[Co(NH_3)_5Br]^{2+} + H_2O$	$6{\cdot}5 \times 10^{-6}$	$2{\cdot}53 \times 10^{12}$	23,900	23,300	1
14	$[Co(NH_3)_5Cl]^{2+} + H_2O$	$1{\cdot}67 \times 10^{-6}$	$5{\cdot}41 \times 10^{11}$	23,880 ± 150	23,280	1
This work	$[Co(NH_3)_5N_3]^{2+} + H_2O$	$2{\cdot}1 \times 10^{-9}$	$1{\cdot}14 \times 10^{16}$	33,730 ± 1000	35,130	4

The bromopentamminecobaltic ion reacts with hydroxyl ion about 9 times, and undergoes aquation about 4 times, as fast as the corresponding chloro-ion. These ratios are not very different from the ratios k_{Br}/k_{Cl} of the bimolecular constants governing the reactions $CH_3X + OH^- \longrightarrow CH_3{\cdot}OH + X^-$, which is 22, or from the ratio of their rates of hydrolysis, which is 16. Replacement of a chlorine atom by a bromine atom in $[Co(NH_3)_5X]^{2+}$ has thus a similar effect to the corresponding replacement in CH_3X. The two sets of data suggest a contrast as well as a comparison. Thus, for example, k_2 (bimolecular substitution at the saturated carbon atom)/k_1 (pseudo-unimolecular hydrolysis) is about 3×10^2 l. mole^{-1} whereas k_2 (bimolecular substitution at the saturated cobaltic ion)/k_1 (pseudo-unimolecular aquation) is about 3×10^5. Moreover, E_A (pseudo-unimolecular hydrolysis) — E_A (bimolecular substitution) is about 6000 cal. mole^{-1} for the methyl halides,[18] whereas E_A (pseudo-unimolecular aquation) — E_A (bimolecular substitution) is zero for two of the pairs considered here and negative for the other pair. These facts, and the magnitude of the constants A, suggest that aquation is a kinetically simpler process than hydrolysis, as could be expected from the fact that the water molecule retains its identity in the former case[19] and loses it in the latter. The fragmentary data on the aquation reactions cited in Table 5 are, however, insufficient to warrant any sound generalisation. On the other hand, the kinetic constants for the substitution reactions are fairly reliable, and indicate that octahedral substitution is more complicated than, though similar in nature to, tetrahedral substitution.

A mechanism of these substitution reactions proposed by Garrick[20] consists of the rapid establishment of an equilibrium

$$[Co(NH_3)_5X]^{2+} + OH^- \underset{k_1}{\overset{k_2}{\rightleftharpoons}} [Co(NH_3)_4NH_2X]^+ + H_2O$$

followed by the rate-determining step

$$[Co(NH_3)_4NH_2X]^+ + H_2O \xrightarrow{k_3} [Co(NH_3)_5OH]^{2+} + X^-,$$

and the rapid reaction

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{k_4} [Co(NH_3)_5OH]^{2+}.$$

The observed second-order constant can be interpreted as the product of the pseudo-unimolecular hydrolysis constant, k_3, and an equilibrium constant (k_2/k_1). In principle,

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[17] Friend and Nunn, *J.*, 1958, 1567.

[18] Heppolette and Robertson, *Proc. Roy. Soc.*, 1959, *A*, **252**, 273; Glew and Moelwyn-Hughes, *ibid.*, 1952, *A*, **211**, 254; Moelwyn-Hughes, *ibid.*, 1938, *A*, **164**, 295; 1949, *A*, **196**, 540; 1953, *A*, **220**, 386.

[19] See Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1960, Lewis and Wilkins, "Modern Coordination Chemistry," Interscience Publ., Inc., New York, 1960.

[20] Garrick, *Nature*, 1937, **139**, 507.

such a mechanism can account for the large A_2 term found. As far, however, as a quantitative estimate can be made from the pK_A values of the complexes concerned, the effect in these instances would be to allow a much lower A_2 value than is found.

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