196. *The Kinetics of Hydrogen Isotope Exchange Reactions. Part IX.*[*] *The Exchange between Cobalt(III) Ammines and Water.*

By H. Block and V. Gold.

The rate of the base-catalysed loss of deuterium from deuterated hexamminocobalt(III) and from deuterated oxalatotetramminocobalt(III) ions to water has been studied as a function of buffer composition, mainly in aqueous acetic acid–acetate buffers of constant ionic strength. Both reactions exhibit specific hydroxide-ion catalysis, in that the rates are proportional to hydroxide-ion concentration and the catalytic coefficient for the acetate ion is indistinguishable from zero. It is argued that the only acceptable mechanism for the exchange involves a rate-determining deuteron transfer from the complex ion to a base, and that the observation of specific catalysis is to be ascribed to a large value of the exponent in the Brønsted catalysis law. The reaction of the oxalatotetrammino-complex is about 20 times slower than that of the hexammine.

The acidity of aqueous solutions of hexamminocobalt(III) salts is discussed in relation to the exchange mechanism. It is concluded that the acidity cannot be due to a rapid proton-transfer equilibrium between the ammine and water, as is generally stated, but that it is due to association between hexamminocobalt(III) and hydroxide ions.

PREVIOUS Parts have dealt with acid-catalysed exchange reactions between solute and solvent species, and, in particular, the connection between the form of the catalysis and

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[*] Part VIII, *J.*, 1958, 3904.

the proton-transfer reactions involved in the mechanism. This approach has now been extended to two base-catalysed reactions, *viz.*, the exchange between the solvent (water) and deuterated hexamminocobalt(III) and oxalatotetramminocobalt(III) ions. The former ion [and also the trisethylenediaminecobalt(III) ion] exchange deuterium with the solvent water at a conveniently measurable rate over a certain range of pH values,[1] the rate increases with the pH value,[1] and all ammine hydrogen atoms are exchangeable.[1] The more quantitative conclusions drawn from the earlier work [1] are not so firmly established, as the experimental techniques then available made it expedient to use high concentrations of the ammines and ionic strengths as high as 0·4M. Such values are excessive for the detailed analysis of rate constants required for establishing the presence or absence of general base catalysis. This is particularly serious when, as here, triply charged ions are involved in the reaction.

In the work now reported the loss of deuterium from the partially deuterated ammine to an initially light aqueous buffer solution was followed by examination of the infrared spectra of the cobaltammine ions isolated by precipitation during the course of the reaction. The exchanging substrates were present (as chlorides) at an ionic strength not exceeding 0·02M, and groups of experiments were carried out at constant total ionic strengths up to 0·2M. The results can be analysed without ambiguity.

EXPERIMENTAL

Hexamminocobalt(III) chloride was prepared by oxidation of an ammoniacal solution of cobaltous and ammonium chloride with hydrogen peroxide in the presence of activated charcoal as catalyst.[2] Impurity in the form of aquopentamminocobalt(III) chloride was removed by Anderson, Briscoe, and Spoor's method.[1b] The pure hexammine was washed with water, alcohol, and ether and analysed for ammonia, cobalt(III), and chloride by standard volumetric methods [2] [Found: Cl^-, 40·1; NH_3, 37·5; Co^{3+}, 22·2. Calc. for $Co(NH_3)_6Cl_3$: Cl^-, 39·8; NH_3, 38·1; Co^{3+}, 22·1%].

Deuteration was effected by dissolving the salt in H_2O–D_2O mixtures of the required composition and keeping the solutions for one day at 25°. Complete isotopic equilibrium between solute and solvent is established within this time. The solutions thus obtained were used directly without prior separation of the heavy salt.

Chloroaquotetramminocobalt(III) chloride was prepared and purified according to the procedures described in Gmelin-Kraut's Handbuch.[3]

Oxalatotetramminocobalt(III) chloride was made by treatment of the previous salt with oxalic acid by the established procedure [4] (Found: Cl^-, 14·49; NH_3, 26·92. Calc. for $[Co(NH_3)_4C_2O_4]Cl$: Cl^-, 14·41; NH_3, 27·18%).

Deuteration was accomplished in two ways. Standard samples of the partially deuterated salt with known deuterium content were prepared by equilibrating the salt with D_2O–H_2O mixtures of known composition. Because of the low solubility of the complex, the deuterated samples used in the kinetic experiments were prepared by exchange of the more soluble precursor in the preparation [chloroaquotetramminocobalt(III) chloride] with D_2O–H_2O mixtures on a water-bath. The preparation of the oxalatotetrammine was then completed by treatment with oxalic acid as before. Because of the acidic conditions during this stage of the preparation and purification very little, if any, exchange would occur during these last steps.

The chemical stability of hexamminocobalt(III) chloride and of oxalatotetramminocobalt(III) chloride under the conditions of the exchange experiments was confirmed by measuring the ultraviolet absorption spectra in aqueous buffer solutions covering the pH range studied and finding them to remain unchanged over a substantial period.

Conditions for Kinetic Experiments.—Reactions were carried out at 25°, phosphate and acetate buffers of known composition being used in ordinary water, with the addition of the requisite amount of potassium chloride to bring the total ionic strength of the solution (after addition of the complex salt) to a constant value for each group of experiments.

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[1] (*a*) Anderson, James, and Briscoe, *Nature*, 1937, **139**, 507; (*b*) Anderson, Briscoe, and Spoor, *J.*, 1943, 361.

[2] Palmer. " Experimental Inorganic Chemistry," Cambridge, 1954, p. 530.

[3] Gmelin-Kraut's " Handbuch der Anorganischen Chemie," 1909, Vol. V (i), p. 378.

[4] *Op. cit.*, p. 452.

Stoppered flasks containing the buffer solutions were immersed in the thermostat to attain the required temperature. The deuterated complex was then added in a suitable form, and the exchange allowed to proceed. Portions were removed at intervals and treated with precipitating reagent so as to throw down a suitable derivative for isotope assay. One of the samples was used for pH measurement of the reaction solution, a Cambridge pH meter with a glass electrode being used.

In the case of the hexamminocobalt(III) ion, the required amount of deuterated salt was added to the buffer as a solution (2 ml.) in the D_2O–H_2O solvent used for the preparative exchange, the total volume of the reaction mixture being made up to 100 ml. In this procedure the total concentration of deuterium in the system is sufficiently high for the ammine to contain a small but appreciable amount of deuterium at equilibrium, *i.e.*, at the completion of the kinetic exchange experiments. The isotope assay was performed on the hexamminocobalt(III) toluene-*p*-sulphonate, which was obtained by adding samples of the reaction solution to toluene-*p*-sulphonic acid (20%) in 0·5M-hydrochloric acid. Precipitation was accelerated by cooling (−10° to −30°) and vigorous stirring. It was verified that the presence of hydrochloric acid ensured the arrest of the exchange.

For the oxalatotetramminocobalt(III) ion, a weighed amount of the deuterated solid salt (chloride) was added to the reaction solution and quickly dissolved. For isotope assay the ion was precipitated as the naphthalene-2-sulphonate by the use of a saturated solution of naphthalene-2-sulphonic acid in 0·5M-hydrochloric acid.

Preparation of Standard Samples for Isotope Assay.—The two salts examined contain 18 and 12 equivalent hydrogen atoms respectively. A partially deuterated salt will therefore be a mixture of a number of species: the individual members of the mixture may differ not only in the number of deuterium atoms they contain (molecular isotopes), but also in their positions (isomers). The analytical method used is based on measurements of infrared absorption intensities. Since each member of the deuterated mixture will, in general, have a different absorption spectrum, different samples of identical deuterium content may have different absorption intensities at a given wavelength. In the exchange studies the mixtures of interest are those which have the equilibrium distribution of deuterium atoms, since the deuterated starting material for kinetic runs was prepared by equilibration and—if it may be assumed that secondary kinetic isotope effects are negligible—the deuterium loss is random. Standard samples for the construction of a calibration curve were accordingly prepared by individual equilibration of the ammines in D_2O–H_2O mixtures of different composition and subsequent precipitation of the appropriate sulphonates, and *not* by mixing light and heavy salts in known proportions, since such mixtures would contain a non-equilibrium distribution of deuterium. The precipitation was carried out by using a large volume (50—100 times the volume of the sample) of the solution of the sulphonic acid in light water. In this way, the water of crystallisation in the precipitate is essentially light and does not vary in composition from sample to sample. Occluded water could be removed from all samples, without accompanying exchange of the ammine hydrogen atoms, by washing the precipitate with dry acetone followed by rapid vacuum drying (see footnote to Table 1).

Let us now assume that the equilibrium constant for exchange is the same at every position in the ammine and that it is independent of the degree of deuteration of the ammine. This is equivalent to regarding a molecule RH_x with x equivalent exchangeable positions to be equivalent (for equilibrium considerations) to a system of x identical molecules rH each containing one exchangeable position. The equilibrium constant K_8 for exchange at one position

$$\mathrm{rH} + \mathrm{HOD} \rightleftharpoons \mathrm{rD} + \mathrm{H_2O};\quad K_8 = [\mathrm{rD}][\mathrm{H_2O}]/[\mathrm{rH}][\mathrm{HOD}] \quad . \quad . \quad . \quad (1)$$

may thus be considered independently of what has happened in the rest of the molecule.

The fractional abundance of deuterium in the ammine

$$F = \sum_{j=1}^{x} jC_j/xC \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(where C_j stands for the sum of the molar quantities of all species of formula $RH_{x-j}D_j$, and $C = \sum_{=0}^{x} C_j$) may then also be written as

$$F = [\mathrm{rD}]/([\mathrm{rD}] + [\mathrm{rH}]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

since, on our assumptions, the fractional abundance is the same at each position of the ammine. Combination of equations (1) and (3) then gives

$$F = K_8[\mathrm{HOD}]/([\mathrm{H_2O}] + K_8[\mathrm{HOD}]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For a solution made by mixing *a* moles of H_2O and *b* moles of D_2O, the molar amounts of H_2O and HOD (y) can be calculated in terms of the equilibrium constant for the disproportionation

$$\mathrm{H_2O} + \mathrm{D_2O} \rightleftharpoons 2\mathrm{HOD};\ K = [\mathrm{HOD}]^2/[\mathrm{H_2O}][\mathrm{D_2O}] \quad . \quad . \quad . \quad . \quad (5)$$

which may also be written

$$K = \frac{4y^2}{(2a - y + xCF)(2b - y - xCF)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

With a knowledge of the numerical values of K and K_8 it is then possible to solve equations (4) and (6) for F in terms of a and b. K has [5] the value 3·96 in the liquid phase at 25° and the equilibrium constant K_8 for the hexamminocobalt(III) ion, calculated from spectroscopic measurements [6] *via* partition functions, has the value 0·48. These values are very close to those obtained from a consideration of symmetry numbers alone (*viz.*, 4 and $\frac{1}{2}$, respectively). It is possible to use the round values to calculate the " statistical fractional abundance " (F') of the sample. This corresponds to an assumed random distribution of isotopes between water and salt. It is given quite simply by

$$F' = 2b/(2a + 2b + xC) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and is, in the present case, a good approximation to the true fractional abundance F. The value of K_8 for oxalatotetramminocobalt(III) ion is not known, since an accurate analysis of its infrared spectrum has not so far been achieved. The structural similarity of this ion to the hexammine and the close parallelism of their infrared spectra make it probable that K_8 would again lie in the range 0·45—0·55, and again the value $\frac{1}{2}$ leading to equation (7) was used. The kinetic measurements did not reveal any feature which caused us to suspect the adequacy of these assumptions.

Isotope Assay by Infrared Absorption Measurements.—" Nujol " mulls of approximately constant composition (7 mg. of ammine sulphonate with 0·2 ml. of " Nujol ") were prepared. The infrared absorptions in the relevant spectral regions (around 4 and 9·9 or 9·6 μ) were then recorded, a Grubb-Parsons S4 double-beam spectrophotometer being used under standardised conditions (slit width, scanning speed, and loop gain). The intensities of absorption maxima in the two regions are, respectively, sensitive and insensitive to the deuterium content, and the latter can thus be used as an internal standard to compensate for variations in concentration and thickness from sample to sample.[7] It was found for both salts that the function

$$G = \log\left(\frac{T_{\mathrm{D}}'}{T_{\mathrm{D}}}\right) \Big/ \log\left(\frac{T_{\mathrm{S}}'}{T_{\mathrm{S}}}\right)$$

(where T_{D} stands for the transmission at a peak sensitive to deuterium substitution (at 4·0 μ) and T_{S} for that of the deuterium-insensitive standard peak (at 9·9 μ for the hexammine toluene-*p*-sulphonate and at 9·6 μ for the oxalatotetrammine naphthalene-2-sulphonate, and T_{D}' and T_{S}' are respectively the transmissions at one of the absorption minima immediately adjacent to these bands) is a smooth single-valued function of F' for standard samples prepared as above. The calibration curves thus constructed were used to convert observed values of G of precipitated samples of the substrates of kinetic runs into F'. These analyses were generally carried out in duplicate for every point.

One of the calibration curves is given in Fig. 1. It passes through the origin and obeys a cubic law. The shape of the curve may be rationalised as follows: the absorptions at 4·0 μ are due to N–D stretching modes. These frequencies are slightly different for NH_2D, NHD_2, and ND_3 groupings, but are instrumentally not resolved. The intensity of absorption at a wavelength in this region will then be the sum of three different absorptions, each of which will

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[5] Kirshenbaum, " Physical Properties and Analysis of Heavy Water," McGraw-Hill, New York, 1951.

[6] Block, *Trans. Faraday Soc.*, in the press.

[7] Gold and Long, *J. Amer. Chem. Soc.*, 1953, **75**, 4543.

be proportional to the abundance of the grouping responsible. In the absence of isotope effects the fractional abundance of the grouping $NH_{3-n}D_n$ is given by the cubic expression $3!F^n(1 - F)^{3-n}/n!(3 - n)!$ and hence the sum of the three terms of this type, each multiplied by a different absorption coefficient, will produce a cubic dependence of the total absorption intensity on F.

FIG. 1. *Calibration curve for deuterium assay of hexamminocobalt*(III) *toluene*-p-*sulphonate.*

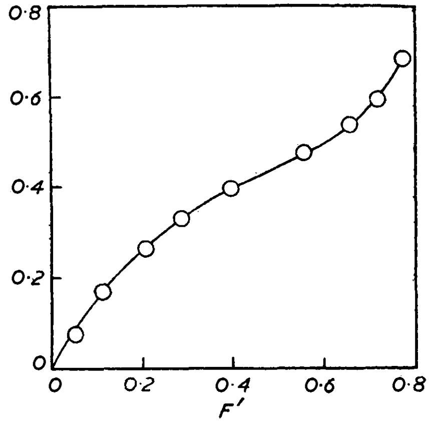
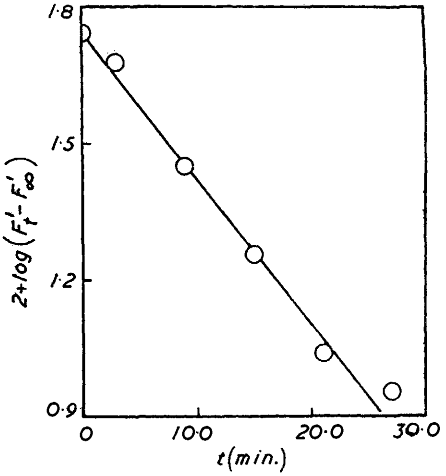


FIG. 2. *Specimen kinetic results* (Expt. 2*a*).



Results.—These are given in Tables 1—5.

TABLE 1. *Variation of the function* G *with* F′ *for hexamminocobalt*(III) *toluene*-p-*sulphonate.*

F'	G		Average G	F'	G		Average G
0·0543	0·074	0·077	0·076	0·3966	0·394	0·396	0·395
0·1127	0·166	0·173	0·170	0·5538	0·467	0·473	0·470
0·2081	0·256 0·263 0·270	0·258 0·267	0·263	0·6529	0·523	0·548	0·536
				0·7177	0·588 * 0·592 †	0·590 † 0·598 *	0·593
0·2858	0·328	0·336	0·332	0·7725	0·664	0·704	0·684

* Vacuum-dried immediately after acetone washing (normal procedure).
† Vacuum-dried after standing under acetone for 30 min.

TABLE 2. *Variation of the function* G *with* F′ *for oxalatotetramminocobalt*(III) *naphthalene-2-sulphonate.*

F'	G		Average G	F'	G		Average G	F'	G		Average G
0·1142	0·068	0·072	0·070	0·4277	0·223	0·225	0·224	0·6513	0·345	0·353	0·349
0·2252	0·133	0·145	0·139	0·4710	0·249	0·253	0·251	0·7603	0·412	0·431	0·422
0·3549	0·195	0·206	0·200								

TABLE 3. *Specimen kinetic results* (*Expt.* 2*a*)*: Deuterium loss from hexamminocobalt*(III) *ion to an acetate buffer.*

[AcOH] = 0·03898M; [KOAc] = 0·08M; [KCl] = 0; $[Co(NH_3)_6Cl_3]$ = 0·00333M.
Measured pH = 4·96. Total ionic strength = 0·10M.

Time (min.)	G		Average G	F_t'	$F_t' - F_\infty'$	$2 + \log(F_t' - F_\infty')$
0·00	0·480 0·472	0·475	0·476	0·562	0·551	1·741
3·00	0·447	0·434	0·440	0·487	0·476	1·678
9·00	0·330	0·343	0·336	0·292	0·281	1·449
15·00	0·250	0·253	0·251	0·190	0·179	1·253
21·00	0·172	0·184	0·178	0·120	0·109	1·037
27·00	0·144	0·137	0·140	0·091	0·080	0·953
∞	—	—	—	—	0·011 (calc.)	—

The first-order character of this reaction is illustrated by the rectilinear plot of Fig. 2. The rate constant, $k = \frac{1}{t}\ln\frac{F_0' - F_\infty'}{F_t' - F_\infty'}$, was evaluated from the slope of this graph.

TABLE 4. *Summary of kinetic results with hexamminocobalt*(III) *chloride.*

[Ammine] = 0·00333M.

Expt. No.	[AcOH]	[KOAc]	[KCl]	Total ionic strength	pH	$10^4\lambda$ (sec.$^{-1}$)
		(Molarities)				
1*a*	0·01949	0·04	0·04	0·10	4·85	8·96
1*b*	0·03802	0·04	0·04	0·10	4·66	4·88
1*c*	0·06338	0·04	0·04	0·10	4·45	3·14
1*d*	0·09969	0·04	0·04	0·10	4·31	2·33
2*a*	0·03898	0·08	0·00	0·10	4·96	11·82
2*b*	0·07604	0·08	0·00	0·10	4·71	6·21
2*c*	0·1268	0·08	0·00	0·10	4·49	3·84
3*a*	0·1313	0·18	0·00	0·20	4·66	7·03
3*b*	0·4179	0·18	0·00	0·20	4·28	2·43
3*c*	0·5544	0·18	0·00	0·20	4·23	2·06
	[KH_2PO_4]	[Na_2HPO_4]				
" Phosphate "	0·0567	0·00112	0·04	0·12	5·07	9·42

TABLE 5. *Summary of kinetic results with oxalatotetramminocobalt*(III) *chloride.*

[Ammine] = 0·01M; Total ionic strength = 0·20M throughout.

Expt. No.	[AcOH]	[KOAc]	[KCl]	pH	$10^4\lambda$ (sec.$^{-1}$)
	(Molarities)				
4*a*	0·01848	0·18	0·01	5·71	3·36
4*b*	0·02834	0·18	0·01	5·51	1·94
4*c*	0·04499	0·18	0·01	5·34	1·46
4*d*	0·05916	0·18	0·01	5·16	1·08
5*a*	0·001451	0·02	0·17	5·95	5·46
5*b*	0·003053	0·02	0·17	5·39	1·47
5*c*	0·006259	0·02	0·17	5·12	0·83

Discussion

The isotopic exchange of deuterium atoms bound to tetraco-ordinated nitrogen is expected to follow a dissociative mechanism [8] in which an N–D bond is severed before the attachment of the light isotope. Such a system is one in which the exchange under heterolytic conditions would involve in the rate-determining stage the removal of D^+ from its seat of attachment, *i.e.*, a type of reaction for which the detection of general base catalysis is possible. The experiments described in this paper were directed to the study of this possibility. Associative (or additive) and synchronous mechanisms would involve co-ordination to nitrogen of more than four groups and are therefore thought to be too improbable to merit further consideration. In the following treatment it has been assumed that all N–D bonds have the same reactivity, *i.e.*, that secondary isotope effects (which would make the rupture of each N–D bond dependent on the isotopic composition at other positions) are negligible. This assumption—which is implicit in all other work on the exchange of metal ammines—is justifiable only in the sense that secondary isotope effects are of no consequence when the kinetic comparisons apply to specimens of approximately the same initial fractional abundance and to runs covering approximately the same extent of reaction. The rate constants obtained will then in each case be a comparable mean of individual rate constants. The absolute magnitude of this kind of secondary isotope effect is at present unknown.

It will therefore be convenient to represent the exchange in terms of isolated, independent N–H bonds and again to consider the system to consist of a single type of hypothetical molecule with one exchangeable hydrogen atom. The deuterium loss from the solute will then be governed by the usual first-order rate law, $-\mathrm{d}F/\mathrm{d}t = \lambda(F - F_\infty)$.

The absence of any perceptible exchange in acidic solutions allows us to omit from further consideration the participation of hydrogen-ion catalysis or a water-catalysed reaction and makes it unlikely that acetic acid molecules effect catalysis. If general base

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[8] Gold and Satchell, *Quart. Rev.*, 1955, **9**, 51.

catalysis operates, the velocity constant in acetic acid–acetate buffers will be composed of two additive terms corresponding to catalysis by the two bases present in solution:

$$\lambda = k_{OH^-}[OH^-]f_{OH^-}f_C/f_{X_1} + k_{OAc^-}[OAc^-]f_{OAc^-}f_C/f_{X_2} \quad . \quad . \quad . \quad (8)$$

where f_C is the activity coefficient of the complex ion and f_{X_1} and f_{X_2} those for the two transition states. Because of the known effect [9] of hexamminocobalt(III) chloride on pH, the concentration of hydroxide was not computed from the buffer composition. For every run the pH value of the solution was measured. The hydroxide-ion concentration is related to pH through the equations [10]

$$pH = -\log f_{\pm}[H^+]; \quad K_w = [H^+][OH^-]f_{H^+}f_{OH^-}$$

On the assumption that at the ionic strength used

$$f_{H^+} = f_{OH^-} = f_{\pm}$$

equation (8) becomes

$$\lambda = k_{OH^-}K_w\frac{f_C}{f_{X_1}} \times 10^{-pH} + k_{OAc^-}[OAc^-]\frac{f_{OAc^-}f_C}{f_{X_2}}$$

FIG. 3. pH *dependence of exchange velocity for hexamminocobalt*(III) *chloride.*

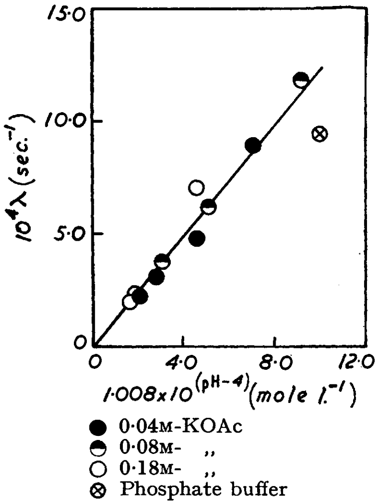
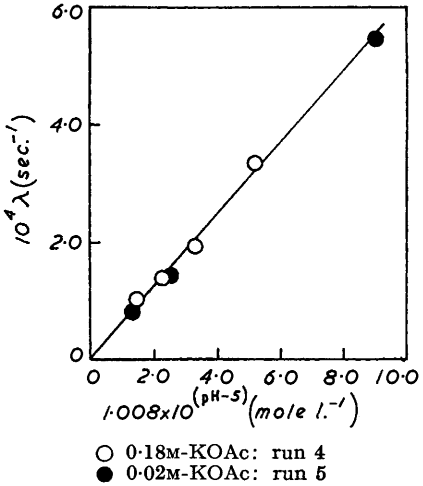


FIG. 4. pH *dependence of exchange velocity for oxalatotetramminocobalt*(III) *chloride.*



For a series of experiments at constant acetate-ion concentration, and constant and low ionic strength

$$\lambda = k'_{OH^-}K_w \times 10^{-pH} + k'_{OAc^-}[OAc^-]$$

i.e., the experimental rate constant should be a linear function of 10^{-pH} with an intercept corresponding to the numerical value of the second term. The graphs in Figs. 3 and 4 show that the intercept is indistinguishable from zero in both cases, *i.e.*, catalysis neither by acetate ion nor by water is detected. The results are summarised in Table 6.

TABLE 6. *Summary of catalytic coefficients.*

	k'_{OH^-} (sec.$^{-1}$ mole^{-1} l.)	k'_{OAc^-} (sec.$^{-1}$ mole^{-1} l.)	Maximum value of k'_{OAc^-}/k'_{OH^-}
$Co(NH_3)_6^{3+}$	$(1{\cdot}21 \pm 0{\cdot}10) \times 10^6$	$<6 \times 10^{-4}$	5×10^{-10}
$Co(NH_3)_4C_2O_4^+$	$(6{\cdot}3_4 \pm 0{\cdot}3) \times 10^4$	$<6 \times 10^{-5}$	10^{-9}

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[9] Cobb and Anderson, *Trans. Faraday Soc.*, 1944, **40**, 145.
[10] British Standard 1647: 1950.

For the results for the hexamminocobalt(III) ion the experimental points are scattered quite widely about the best straight line. The groups of points for the different series of experiments seem to show some separate trends, though none of them indicates a tendency to a finite intercept. The effect is barely outside the limits of experimental error, but it might be caused by salt effects which are expected to be considerably more important with this triply charged ion than for the univalent oxalatotetramminocobalt(III) ion.

The apparent absence of an intercept in Figs. **3** and **4** leads to the conclusion that only catalysis by hydroxide ions is operative in both reactions. The last column in Table **6** lists the maximum values which experimental uncertainties allow for the ratio $k_{\mathrm{OAc}^-}/k_{\mathrm{OH}^-}$. These values may be compared with the value of $\sim 5 \times 10^{-7}$ found for the corresponding ratio for the decomposition of nitramide,[11] where the exponent in the Brønsted catalysis law is 0·83. The absence of general catalysis can for most systems be taken to mean either that the Brønsted exponent lies close to unity—which results in experimentally inaccessible general base catalysis [12]—or that substrate and bases are involved in a rapid proton-transfer pre-equilibrium. Attention being restricted to dissociative mechanisms, the essential steps of the base-catalysed exchange are

$$\mathrm{XNH_2D}^{Z+} + \mathrm{B}_i^- \xrightarrow{k_i} \mathrm{XNH_2}^{(Z-1)+} + \mathrm{B}_i\mathrm{D} \quad . \; . \; . \; . \; . \quad (9)$$

$$\mathrm{XNH_2}^{(Z-1)+} + \mathrm{H_2O} \xrightarrow{\mathit{Fast}} \mathrm{XNH_3}^{Z+} + \mathrm{OH}^- \quad . \; . \; . \; . \; . \quad (10)$$

$$\mathrm{B}_i\mathrm{D} + \mathrm{OH}^- \overset{\mathit{Fast}}{\rightleftharpoons} \mathrm{B}_i^- + \mathrm{DOH}$$

where $\mathrm{XNH_2D}^{Z+}$ stands for the heavy hexamminocobalt(III) or oxalatotetramminocobalt(III) ion and B_i^- for the catalysing base. This mechanism implies general base catalysis and requires that [8]

$$\lambda = \sum k_i[\mathrm{B}_i^-]$$

To be compatible with our results the Brønsted exponent must then have a value near unity. The first step may or may not be composite in nature, involving first an association. For the case of hydroxide-ion catalysis this composite first step could be

$$\mathrm{XNH_2D}^{Z+} + \mathrm{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{XNH_2D{\cdot\cdot}OH}^{(Z-1)+} \quad . \; . \; . \; . \quad (11)$$

$$\mathrm{XNH_2D{\cdot\cdot}OH}^{(Z-1)+} \xrightarrow{k_2} \mathrm{XNH_2}^{(Z-1)+} + \mathrm{DOH}$$

With the condition that $k_{-1} \gg k_1$ (which is essential to accord with the finding that the reaction is of first order with respect to hydroxide ions, and which is a reasonable one for the present system as estimated by the degree of ion association predicted from the Bjerrum model [13]), the rate constant λ is now given by $\lambda = k_1k_2[\mathrm{OH}^-]/(k_{-1} + k_2)$. If $k_{-1} \ll k_2$ the occurrence of prior association has no experimentally detectable effect on the kinetic equation. If $k_2 \ll k_{-1}$, $\lambda = K_{\mathrm{A}}k_2[\mathrm{OH}^-]$, where $K_{\mathrm{A}}(\equiv k_1/k_{-1})$ is the association constant for the reaction

$$\mathrm{XNH_2D}^{Z+} + \mathrm{OH}^- \rightleftharpoons [\mathrm{XNH_2D}^{Z+}{\cdot\cdot}\mathrm{OH}^-]^{(Z-1)+}$$

The determination of kinetic orders cannot provide any evidence concerning the rôle of this association in the reaction. That ionic association is important for these complexes (in the thermodynamic sense) is indicated, not only by calculations based on the Bjerrum theory, but also by the acidity of the salt solutions (as discussed below) and by the infrared spectra of the crystalline hexamminocobalt(III) chloride and iodide.[6] These measurements

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[11] Brønsted and Pedersen, *Z. phys. Chem.*, 1923, **108**, 185.

[12] Brønsted and Wynne-Jones, *Trans. Faraday Soc.*, 1929, **25**, 59.

[13] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955, Chapter 14.

show that there is much stronger bonding to chloride ions than to iodide ions. The difference is large for a crystal-field effect, and points to some form of stronger bonding, such as a " hydrogen bond." Also, the infrared spectrum does not show greater detail when the specimens are cooled to −183°, a temperature at which rotation of the ammonia ligands would be expected to be frozen. This suggests that the ligands are not in free rotation at room temperature either, but that some rotation-hindering bonding occurs. It is expected that the hydroxide ion would bond even more readily than the chloride ion.

The reaction scheme involving association may explain the high value of the Brønsted exponent which is required to account for the lack of catalysis by species other than OH^-, although there is at present insufficient information about the values of Brønsted exponents to say if such a special explanation is required. In the product $K_A k_2$ it is possible that the value k_2 would differ from base to base in a manner compatible with a lower Brønsted exponent, but that the catalysis by hydroxide ions could nevertheless swamp the catalysis by other bases because its high hydrogen-bonding power causes its value of K_A greatly to exceed that for other bases.

The observation of specific hydroxide catalysis cannot be explained by the simplest model for other cases of specific catalysis, *viz.*, the occurrence of a rapid proton-transfer pre-equilibrium followed by the slow step. In the present case this would be equivalent to assuming that reaction (9) and its reversal are rapid compared with reaction (10). Such a scheme is meaningless since the reversal of equation (9) can involve not only the heavy acid B_iD but also B_iH and, since $[B_iH] \gg [B_iD]$, this implies that the exchange velocity is governed by step (9). In other words, reaction (9) cannot be involved as a pre-equilibrium: it must be the rate-controlling step, as we have stated before. A statement by Anderson, Briscoe, and Spoor[1b] to the effect that such a mechanism is possible and that the implied rapidity of the proton transfer from $Co(NH_3)_6^{3+}$ to the base water accounts for the acidity of the solutions of this ion is therefore misleading, despite the fact that it has been widely quoted and accepted.[14]

In fact, the acidity of the hexamminocobalt(III) ion is a direct consequence of the ionic association which we have discussed before. An association equilibrium (11) would cause an aqueous solution to have an acidic reaction. The equilibrium constant K_D for the dissociation

$$[Co(NH_3)_6OH]^{2+} \rightleftharpoons Co(NH_3)_6^{3+} + OH^-$$

has[15] the value 0·0138 mole l.$^{-1}$. Combining this with the value $1{\cdot}008 \times 10^{-14}$ for the ionic product of water, we obtain the acid ionisation constant for $Co(NH_3)_6^{3+}$ *via* the equilibrium

$$Co(NH_3)_6^{3+} + H_2O \rightleftharpoons [Co(NH_3)_6OH]^{2+} + H^+$$

as
$$K = \frac{[[Co(NH_3)_6OH]^{2+}][H^+]}{[Co(NH_3)_6^{3+}]} = \frac{K_w}{K_D} \approx 7 \times 10^{-11} \text{ mole l.}^{-1}$$

This value is compatible with direct pH measurements and potentiometric titrations of aqueous solutions of hexamminocobalt(III) chloride, which we have carried out to verify this point.

On this view, the hexamminocobalt(III) ion is an acid, not by virtue of its ability to act as a proton donor, but by virtue of its affinity for hydroxide ions. It is important to recognise this distinction—which is similar to that which leads to the existence of separate acidity functions[16] H_0 and J_0—if incorrect applications of Brønsted's views on the definition of acids and bases are to be avoided. The phenomenon appears to be particularly important to the consideration of acid–base catalysis by complex ions. This has hitherto

[14] Basolo in Bailar (ed.), " Chemistry of Coordination Compounds," Reinhold, New York, 1956, p. 426; Sidgwick, " Chemical Elements and their Compounds," O.U.P., London, 1950, Vol. II, p. 1399; Stranks and Wilkins, *Chem. Rev.*, 1957, **57**, 743.

[15] Caton and Prue, *J.*, 1956, 671.

[16] Gold and Hawes, *J.*, 1951, 2102.

always been based on the implicit assumption of their behaviour as Brønsted acid–base systems, but this may clearly not always be correct.

The twenty-fold difference in reactivity between the hexamminocobalt(III) and the oxalatotetramminocobalt(III) ions is surprisingly small if one argues that the main difference between the ions is one of total electric charge. However, the situation is not so straightforward. The charge on the hexammine is distributed mainly among the ligand molecules[17] and hence the maximum charge on any ammonia group will be $+\frac{1}{2}\mathbf{e}$. In the oxalatotetrammine the comparable charge will lie in the range $+\frac{1}{4}\mathbf{e}$ to $+\frac{3}{4}\mathbf{e}$, depending on the extent of ionic character which the oxalate group retains in the complex, the upper limit being applicable if the oxalate group is completely ionic and the lower one if it is totally covalent. The exchange rate would seem to indicate that the value is in fact slightly less than $+\frac{1}{2}\mathbf{e}$.

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[17] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 2nd edn., 1940, Chap. III.