

447. The Aquation of Fluoropentamminecobalt(III) Cation in Neutral and in Acidic Solutions.

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The rate constants for the aquation of the $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ cation have been measured in neutral and in acidic solutions containing varying amounts of nitric acid. The results are consistent with the expression

$$k_{\text{obs}} = k_1 + k_2[\text{H}^+]$$

where k_1 and k_2 are constants at constant temperature. In this reaction, two different mechanisms, *viz.*, $S_{\text{N}}2$ and $S_{\text{P}}2$, take place simultaneously, to extents depending on the acidity of the medium. In the $S_{\text{N}}2$ process, the outgoing fluorine ligand is pushed away from the central atom by the incoming nucleophile (water), while in the $S_{\text{P}}2$ process, the outgoing ligand is pulled away from the central atom by an electrophilic reagent, the hydrogen ion, probably with the help of the incoming water. The kinetics have been studied over a range of temperatures and the Arrhenius parameters for both the $S_{\text{N}}2$ and the $S_{\text{P}}2$ components determined. At a hydrogen-ion concentration of 0.1N, the contribution from the $S_{\text{N}}2$ component is slight. The lower activation energy for the $S_{\text{N}}2$ reaction is believed to be due, in part at least, to hydrogen-bonding between the incoming and the outgoing ligands.

THE role of the chlorine and bromine ligands acting either as orienting or as replaced groups in substitution reactions of octahedral cobalt(III) complexes has been thoroughly investigated.¹ However, the behaviour of the fluorine ligand has not been well studied. Basolo *et al.* have prepared some fluorobis(ethylenediamine)cobalt(III) complexes² and measured the rates of hydrolysis and racemisation of the difluorobis(ethylenediamine)-cobalt(III) cation.³ Their kinetic results are, however, unsuitable for our present purpose as the complex investigated contained both the orienting and the replaced ligands in the same molecule. It is desirable to study these two behaviours of the fluorine ligand separately and the work presented in this Paper is concerned with the ligand acting as a replaced group in octahedral aquation. Investigations of the fluorine ligand acting as an orienting group are now in progress.

Aquation of Fluoropentamminecobalt(III) Cation in Neutral Solution.—The fluoropentamminecobalt(III) complex used for the kinetic studies was in the form of the nitrate and the reaction was followed by measuring the increase of free fluoride-ion concentration in the solution by titration⁴ with thorium nitrate solution using a 0.1% aqueous solution of sodium alizarinsulphonate as indicator, the anionic fluoride being previously separated from the complex cation by means of a cation-exchange resin column. Basolo *et al.*³ had observed that adsorption of the difluorobis(ethylenediamine)cobalt(III) complexes on the cation-exchange resin induced the release of co-ordinated fluorine. We observed the same result with the fluoropentamminecobalt(III) complex when Amberlite IR 120(H⁺) was used. However, if the resin was first converted into the Na⁺ form by passing a solution of sodium chloride through the column, adsorption of the complex cation could then take place without inducing the release of co-ordinated fluorine and this procedure was finally adopted. Such observations were understandable in terms of the acid-catalysed release

¹ (a) Ingold, Nyholm, and Tobe, *J.*, 1956, 1691; (b) Nyholm and Tobe, *J.*, 1956, 1707; (c) Asperger and Ingold, *J.*, 1956, 2862; (d) Tobe, *J.*, 1959, 3776; (e) Baldwin and Tobe, *J.*, 1960, 4275; (f) Staples and Tobe, *J.*, 1960, 4803; (g) Baldwin, Chan, and Tobe, *J.*, 1961, 4637; (h) Chan and Tobe, *J.*, 1962, 4531; (i) Chan and Tobe, *J.*, 1963, 514; (j) Chan and Tobe, *J.*, 1963, 5700; (k) Chan, *J.*, 1963, 5137; (l) Tobe, *Sci. Progress*, 1960, **48**, 485; (m) Ingold, Nyholm, and Tobe, *Nature*, 1960, **187**, 477.

² Matoush and Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 3972.

³ Basolo, Matoush, and Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 4883.

⁴ Willard and Winter, *Ind. Eng. Chem. Analyt.*, 1933, **5**, 7.

of co-ordinated fluorine to be described below. It is worth mentioning that Staples⁵ also observed similar acid-catalysed release of co-ordinated azido-ligand. The observed first-order rate constants were obtained from the semi-logarithmic plots of $\log_{10}(V_{\infty} - V_t)$ against time, where V_t is the titre of thorium nitrate consumed when the reaction is stopped at time t . In view of the long half-life of the reaction, V_{∞} was calculated from the weight of sample taken. The semi-logarithmic plots remained linear until after about 40–50% reaction and these initial slopes were used to calculate the first-order rate constants for the aquation. Titration of the reaction mixture with thorium nitrate after ten half-lives indicated that the aquation was reversible and that equilibrium was reached at about 85–90% completion of reaction depending on the temperature of the medium and the initial concentration of the complex. The observed first-order rate constants determined in this way at different temperatures are collected in Table 1. They have the following temperature dependence:

$$k_1 = 7.4 \times 10^7 \exp(-21,300/RT) \text{ sec.}^{-1}$$

TABLE 1.

First-order rate constants for the aquation of fluoropentamminecobalt(III) cation in neutral aqueous solutions at various temperatures.

Temp. (°c)	Initial [complex] (mmole/l.)	$10^7 k_1$ (sec. ⁻¹)	Temp. (°c)	Initial [complex] (mmole/l.)	$10^7 k_1$ (sec. ⁻¹)	Temp. (°c)	Initial [complex] (mmole/l.)	$10^7 k_1$ (sec. ⁻¹)
25.0	4.01	0.84	35.0	4.04	2.40	45.0	4.04	7.6
"	5.07	0.88	"	5.01	2.42	"	5.04	7.4
"	6.05	0.86	"	6.05	2.52	"	6.01	7.3
"	7.01	0.90	"	7.01	2.45	"	7.03	7.5

Aquation of Fluoropentamminecobalt(III) Cation in Acidic Solutions.—In the presence of acid, the aquation of fluoropentamminecobalt(III) cation proceeded much faster and the observed first-order rate constants depended on the concentration of acid added. The complex was supplied as the nitrate, and nitric acid was used to supply the hydrogen ions. The ionic strength of the reaction medium was adjusted to an initial value of 0.112M by the addition of calculated amounts of potassium nitrate. As the aquation proceeds the ionic strength increases, but the effect is negligible compared with the experimental error, since the ionic strength of the reaction medium calculated for the complete replacement of co-ordinated fluorine is only 0.124M. The kinetics were studied by following the increase of free fluoride-ion concentration in the solution titrimetrically. As before, the anionic fluoride was separated from the complex cation by means of a cation exchange resin in the Na⁺ form and was determined by the thorium nitrate method.⁴ The reaction was found to be virtually complete after 10 half-lives and spectrophotometric analysis of the reaction mixture after completion of reaction indicated that the product was the aquopentamminecobalt(III) cation. The observed first-order rate constants were obtained from the semi-logarithmic plots of $\log_{10}(V_{\infty} - V_t)$ against time, where V_t and V_{∞} are the titres of thorium nitrate consumed when the reaction is stopped at time t and after ten half-lives, respectively. The observed first-order rate constants of the reaction in solutions containing varying amounts of nitric acid at different temperatures are collected in Table 2. At constant temperature, the plots of the observed first-order rate constants against hydrogen-ion concentration were straight lines passing virtually through the origin, given by the following expressions:

$$k = 1.07 \times 10^{-4} [\text{H}^+] \text{ sec.}^{-1} \text{ at } 25.0^\circ$$

$$k = 5.2 \times 10^{-4} [\text{H}^+] \text{ sec.}^{-1} \text{ at } 35.0^\circ$$

$$k = 2.5 \times 10^{-3} [\text{H}^+] \text{ sec.}^{-1} \text{ at } 45.0^\circ.$$

⁵ Staples, Ph.D. Thesis, London, 1960.

TABLE 2.

Observed first-order rate constants for the aquation of fluoropentamminecobalt(III) cation in aqueous solutions containing varying amounts of nitric acid at different temperatures.

Ionic strength of reaction medium = 0.112M.							
Temp. (°C)	Initial [complex] (mmole/l.)	Added [H ⁺] (mole/l.)	10 ⁵ k (sec. ⁻¹)	Temp. (°C)	Initial [complex] (mmole/l.)	Added [H ⁺] (mole/l.)	10 ⁵ k (sec. ⁻¹)
25.0	4.00	0.02	0.19	35.0	4.03	0.02	0.9
"	"	0.04	0.44	"	"	0.04	2.1
"	"	0.06	0.64	"	"	0.06	3.1
"	"	0.08	0.84	"	"	0.08	4.2
"	"	0.10	1.10	"	"	0.10	5.3
				45.0	4.07	0.02	4.7
				"	"	0.04	10.0
				"	"	0.06	15.1
				"	"	0.08	20.3
				"	"	0.10	25.5

The slopes of these plots, corresponding to the second-order rate constants k_2 for the bimolecular electrophilic substitution of fluoropentamminecobalt(III) cation by water, have the following temperature dependence:

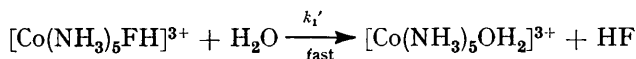
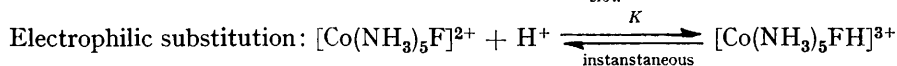
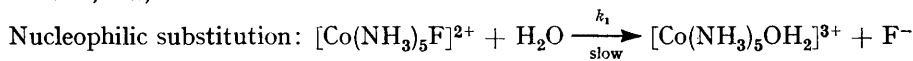
$$k_2 = 1.3 \times 10^{18} \exp(-30,200/RT) \text{ l. sec.}^{-1} \text{ mole}^{-1}.$$

DISCUSSION

The foregoing data on the aquation of fluoropentamminecobalt(III) cation may be summarised by the expression:

$$k_{\text{obs}} = k_1 + k_2[\text{H}^+]$$

which is consistent with the idea that the reaction takes place by a combination of two mechanisms, *viz.*,



The observed rate of aquation is given by

$$\text{Rate} = k_1 [\text{fluoro-complex}] + k_1' [\text{protonated fluoro-complex}].$$

$$\text{Since } K = [\text{protonated fluoro-complex}]/[\text{fluoro-complex}][\text{H}^+]$$

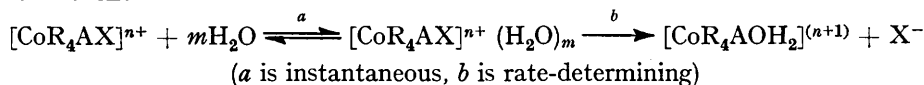
the rate expression becomes

$$\begin{aligned} \text{Rate} &= k_1 [\text{fluoro-complex}] + k_1' K [\text{fluoro-complex}][\text{H}^+] \\ &= (k_1 + k_1' K [\text{H}^+]) [\text{fluoro-complex}]. \end{aligned}$$

Thus k_2 , the slope of the linear plot of k_{obs} against $[\text{H}^+]$, is identical to $k_1'K$. In nucleophilic aquation, the outgoing fluorine ligand is pushed away from the cobalt atom by the incoming nucleophile (water), while in the electrophilic process, the outgoing fluorine is pulled away from the cobalt atom by the electrophilic hydrogen ion. The possibility of help from a nucleophile in carrying the process to completion is not excluded by the observation that an electrophilic reagent is involved.

The nucleophilic aquation of complexes of the type $[\text{CoR}_4\text{AX}]^{n+}$, where R represents a monodentate ammino-ligand (*e.g.*, NH_3) or half of a bidentate ammino-ligand (*e.g.*, ethylenediamine), A represents an orienting ligand, and X represents a replaceable ligand which

may be Cl, Br, or NO₃, has been confirmed in the past to take place by a duality of mechanisms¹ in which the reaction occurs between a complex ion and its aqueous solvation shell:^{11,m}



When the orienting group A possesses electropositive electron-displacement effects, the rate-determining step in the above scheme will involve a slow heterolysis of X to give a non-symmetric intermediate "cobaltium" ion which then reacts very rapidly with the aqueous solvent shell, *i.e.*, an S_N1 mechanism is involved. When, however, the orienting group A possesses electronegative electron displacement effects such as the NH₃ ligand used in the present investigation, the rate-determining step will involve a single synchronised act in which a water molecule from the solvent shell attacks and X leaves the complex simultaneously, *i.e.*, an S_N2 mechanism is involved. Adamson and Basolo⁶ studied the deuterium isotope effect upon the rate of bimolecular aquation of the chloro- and bromo-pentamminecobalt(III) cations and concluded that the transition state corresponds to that expected for a bimolecular attack adjacent to the outgoing group, the reaction being assisted by hydrogen-bonding between the outgoing ligand, the incoming water, and a *cis*-ammonia ligand. Asperger and Ingold,^{1c} however, preferred a different transition state in which the water, by virtue of the electronegativity of the oxygen, makes use of one of the empty 4*d* orbitals of the cobalt atom to establish its attack, the incoming water and the outgoing halogen being each bound by a 3*d*4*d* hybrid orbital. Tobe^{1d} then examined the Arrhenius parameters for the aquation of the complex ion, *trans*-[Co(en)₂NH₃X]²⁺, where X = Cl, Br, or NO₃, and agreed with the mechanism of Asperger and Ingold, but his data also indicated that when hydrogen-bonding is possible, the activation energy of the process will be lowered. The first-order rate constants for the nucleophilic aquation of [Co(NH₃)₅X]²⁺ cations are now collected in Table 3, together with the appropriate Arrhenius parameters. It can be seen that along the series F, Cl, Br, NO₃, the rate of nucleophilic aquation increases indicating that the strength of the Co-X bond is in the order F > Cl > Br > NO₃. The activation energy also increases along the series, thus supporting Tobe's^{1d} postulation that the breakage of the Co-X bond has not proceeded far in the transition state and that the stereospecific hydrogen-bonding between the incoming water and the outgoing ligand in the order F > Cl > Br > NO₃, lowers the activation energy. The data therefore suggests that the nucleophilic reaction of the fluoropentamminecobalt(III) ion with the aqueous solvation shell is also bimolecular. The

TABLE 3.

First-order rate constants and Arrhenius parameters for the bimolecular nucleophilic aquation of [Co(NH₃)₅X]²⁺ cations in aqueous solutions.

X	k_1 at 25° (sec. ⁻¹)	E (kcal./mole)	log ₁₀ B
F	8.7 × 10 ⁻⁸	21.3	7.9
Cl*	1.7 × 10 ⁻⁶	23.7	11.5
Br*	6.3 × 10 ⁻⁶	24.0	12.4
NO ₃ †	2.7 × 10 ⁻⁵	26.0	14.4

* Data from ref. 7. † Data from ref. 8.

relatively large tendency of the fluorine ligand to form a hydrogen bond is due to the high value of its electronegativity and the relative weakness with which the nitrate-group forms a hydrogen bond has been explained by Tobe^{1d} as being due to the fact that the

⁶ Adamson and Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261.

⁷ Adamson and Wilkins, *J. Amer. Chem. Soc.*, 1954, **76**, 3379.

⁸ Bronsted, *Z. phys. Chem.*, 1926, **122**, 383.

two terminal oxygen atoms of the ligand have already taken advantage of the favourable position for hydrogen-bonding with adjacent amino-ligands.

As to the S_{B2} component in the aquation of the fluoropentamminecobalt(III) cation, the activation energy is relatively high (30.2 kcal./mole) and so is the rate of aquation (1.07×10^{-4} sec.⁻¹ at 25.0° and unit hydrogen-ion concentration). This is easily understandable since the S_{B2} aquation may be looked upon as a nucleophilic aquation in which the replaced group is -FH instead of -F. The Co-F bond is expected to be weakened as a result of hydrogen-bonding to form Co-FH, thus explaining the relatively high rate. The comparatively high activation energy can be understood provided that a reasonable suggestion can be made to account for the weakness with which the protonated fluorine ligand -FH, must be assumed to form a hydrogen bond with the incoming water. One possible suggestion is that the fluorine atom in the departing -FH ligand, being already hydrogen-bonded to a proton, can only form a very weak hydrogen bond with the attacking water, if at all.

EXPERIMENTAL

Preparation.—Fluoropentamminecobalt(III) nitrate was prepared by the method of Basolo and Murmann⁹ from carbonatopentamminecobalt(III) nitrate. The crystals were purified by dissolution in the minimum amount of water at 45°, filtration and addition of solid ammonium nitrate to the filtrate {Found: Co, 20.4; NH₃, 29.5; F, 6.8. Calc. for [Co(NH₃)₅F](NO₃)₂: Co, 20.5; NH₃, 29.7; F, 6.6%}.

Analytical Procedures.—(a) *Cobalt.* An appropriate amount of the Co(III) complex was converted quantitatively into a solution of Co(II) sulphate¹⁰ which was then estimated iodometrically by the method of Laitinen and Burdett.¹¹

(b) *Ammonia.* The ammonia in the complex was analysed by the method of Horan and Eppig,¹² involving heating the sample in excess of alkali and distilling the ammonia into excess of standard acid. Arsenic(III) oxide is added to prevent oxidation of the ammonia by the cobalt(III). The excess of acid is then determined by titration with standard alkali.

(c) *Fluorine.* A suitable weighed amount of the complex was warmed with excess of sodium hydroxide solution in a water-bath until no more ammonia was evolved. The solution was filtered, and the filtrate and washings were neutralised with chloroacetic acid and titrated with standard thorium nitrate, sodium alizarinsulphonate being used as indicator.

Kinetics.—The reaction solutions were made up by dissolving a weighed amount of the complex in the appropriate solvent previously brought to the temperature of the reaction. Samples were withdrawn from time to time and passed through a cation-exchange resin (Amberlite IR 120; Na⁺ form), and the ionic fluoride content in the effluent was estimated by the thorium nitrate method. The resin column was surrounded by ice-water to reduce aquation of the complex adsorbed on the resin. Furthermore, the resin was flushed continually with water between separations.

Thermostats were of the conventional design, the temperature being kept constant to 0.05° with a Jumo-Shandon contact thermometer and a Jumo mercury vertical relay Type GKT 15-0. Spectrophotometric measurements were made by using 4-cm. silica cells and a Unicam S.P. 500 spectrophotometer.

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⁹ Basolo and Murmann, *Inorg. Synth.*, 1953, **4**, 171.

¹⁰ Chan, Ph.D. Thesis, London, 1962.

¹¹ Laitinen and Burdett, *Analyt. Chem.*, 1951, **23**, 1268.

¹² Horan and Eppig, *J. Amer. Chem. Soc.*, 1949, **71**, 581.