# **586.** *The* $S_N$ *Mechanism in Inorganic Reactions. Part I. Hydroxide-ion Substitution in Halogenopentamminecobalt*(III) *Complexes*

By S. C. CHAN, K. Y. HUI, J. MILLER, and W. S. TSANG

The relative facility of replacement of halogens in inorganic nucleophilic substitution is compared with the patterns observed in organic compounds, which are strongly indicative of mechanism. In accordance with our views on this, substitutions of halogenopentamminecobalt(III) complexes with hydroxide ion in water are expected to follow the pattern of saturated aliphatic $S_N2$ reactions, *viz.*, $F < Cl < Br$ or I, and this is now confirmed experimentally. The kinetic results are discussed and an attempt is made to interpret them by analogy with aliphatic $S_N$ reactions in terms of electron affinities, bond dissociation, and solvation energies, and the corresponding changes in entropy.

INTERESTING and useful analogies may be drawn between nucleophilic substitution in organic and inorganic compounds, particularly when the relative ease of replacement of fluorine and other halogens is used to indicate the mechanism.

Bunnett and his co-workers [1,2] and Miller and his co-workers [3-6] have used this relationship to support the concept that aromatic $S_N2$ reactions proceed *via* a relatively stable intermediate complex. The latter commented [4,6] that any more facile replacement of fluorine results from its greater electronegativity which facilitates rate-determining bond formation between the reagent and carbon at the reactive centre, and not from bond strength factors. Factors leading to either high or low mobility of fluorine were discussed, with supporting theoretical computations.[6] In $S_N2$ reactions this relative mobility (relative to chlorine = 1 which has been called the group replacement factor or G.R.F.[7]) indicates whether significant bond breaking occurs in the rate-determining step, or not. In the former case, the G.R.F. of fluorine is consistently less than unity but, as discussed below, is not simply dependent on the bond strength. In the latter case, the G.R.F. is greater than unity due to the electronegativity effect.[4,6]

Interpretation (see below) is in terms of a one-step (saturated aliphatic type), or two-step (aromatic type) reaction proceeding *via* a relatively stable intermediate complex. In the latter certain conditions are necessary for the first transition state (bond-making step) to be rate-determining.

In inorganic $S_N2$ reactions we expect the occurrence of these aliphatic or aromatic type substitutions to depend on whether the lowest unfilled electronic energy level of the central atom is substantially above the highest filled one, or not, and thus on whether covalent bond formation by the entering nucleophile (ligand) can proceed without synchronous breaking of the bond to the replaceable group.

The present work deals with some reactions of cobalt(III) compounds where we expect the one-step substitution having a low G.R.F. for fluorine, similar to that found in $S_N2$ reactions of saturated aliphatic compounds.[4,8,9a]

[1] J. F. Bunnett and R. F. Zahler, *Chem. Rev.*, 1951, **49**, 297.

[2] J. F. Bunnett, E. W. Garbisch, and K. M. Pruitt, *J. Amer. Chem. Soc.*, 1957, **79**, 385.

[3] J. Miller, *Rev. Pure and Appl. Chem.* (*Australia*), 1951, **1**, 171.

[4] A. L. Beckwith, J. Miller, and G. D. Leahy, *J.*, 1952, 3552.

[5] B. A. Bolto and J. Miller, *Austral. J. Chem.*, 1956, **9**, 74 and 304.

[6] J. Miller, *J. Amer. Chem. Soc.*, 1963, **85**, 1628.

[7] B. A. Bolto, J. Miller, and V. A. Williams, *J.*, 1955, 2926.

[8] (*a*) E. D. Hughes, *Quart. Rev.*, 1952, **5**, 250; (*b*) C. K. Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 339.

[9] C. A. Bunton, " Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier, London, 1963, (*a*) p. 73, (*b*) p. 87.

## RESULTS AND DISCUSSION

The substrates used for the present investigation were the halogenopentamminecobalt(III) cations, here the choice of nucleophile and solvent is very limited. Water was used because the complex cobalt(III) cations were not sufficiently soluble in common organic solvents. However in dilute aqueous solutions, substitutions in halogenopentamminecobalt(III) complexes by most nucleophiles proceed *via* aquation with subsequent replacement of water from the aquo-intermediate,[10] *i.e.*,

$$[CoR_5X]^{n+} + H_2O \longrightarrow [CoR_5H_2O]^{(n+1)+} + X^-, \quad [CoR_5H_2O]^{(n+1)+} + Y^- \longrightarrow [CoR_5Y]^{n+} + H_2O$$

Apart from the hydroxide ion, it is difficult to find another nucleophile which can compete successfully with water. Tobe [11] has explained this phenomenon in terms of the solvation of the complex ion. Even when the primary co-ordination of the central cobalt ion has been satisfied, a tightly bound and well-ordered primary solvent shell can still be formed as a result of hydrogen bonding and of interaction between solvent dipoles and unequally distributed charges on the surface. This solvent shell promotes aquation by keeping the reagent in a favourable position, but protects the complex against attack by an anionic or neutral reagent for which desolvation before reaction would be necessary. A hydroxide ion can, however, remove a proton from an adjacent, suitably oriented water molecule and form a new hydroxide ion which in its turn can repeat the process. This permits attack without physical penetration of the barrier. A report [12] that the cyanide ion, contrary to previous beliefs, is a good nucleophile towards cobalt(III) ammine complexes in aqueous solutions has been disproved by Chan and Tobe.[13]

The nucleophilic substitution of halogenopentamminecobalt(III) cations by hydroxide ion have been found to be of second order, first order with respect to each of the reactants, but the mechanism is controversial. Since our discussion is based on an $S_N2$ process, brief comments about the mechanism are desirable. Basolo and Pearson [14,15] suggested an $S_N1CB$ mechanism involving a pre-equilibrium in which the hydroxide ion removes a proton from one of the ammine nitrogens to form an amido conjugate base which then dissociates rapidly with the eventual formation of the hydroxo-product. The dissociation, although rapid, is rate-determining:

$$OH^- + [Co(NH_3)_4NH_3X]^{2+} \xrightleftharpoons{\text{fast}} [Co(NH_3)_4NH_2X]^+ + H_2O$$

$$[Co(NH_3)_4NH_2X]^+ \xrightarrow[\text{r.d.s.}]{} [Co(NH_3)_4NH_2]^{2+} + X^-$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_4NH_3,OH]^{2+}$$

However, Brown, Ingold, and Nyholm [16-20] prefer an $S_N2$ mechanism in which the hydroxide ion directly replaces X, as shown:

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

---

[10] F. Basolo, J. G. Bergmann, R. G. Pearson, and B. D. Stone, *J. Amer. Chem. Soc.*, 1954, **76**, 3079.

[11] M. L. Tobe, *Sci. Progr.*, 1960, **48**, 483.

[12] H. S. Nagarajaiah, A. G. Sharpe, and D. B. Wakefield, *Proc. Chem. Soc.*, 1959, 385.

[13] S. C. Chan and M. L. Tobe, *J.*, 1963, 966.

[14] F. Basolo and R. G. Pearson, " Mechanism of Inorganic Reactions," John Wiley and Sons, New York, 1958, p. 124.

[15] F. Basolo and R. G. Pearson, *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 25.

[16] D. D. Brown, C. K. Ingold, and R. S. Nyholm, *J.*, 1953, 2674.

[17] D. D. Brown and C. K. Ingold, *J.*, 1953, 2680.

[18] S. Asperger and C. K. Ingold, *J.*, 1956, 2862.

[19] C. K. Ingold, " Weizmann Memorial Lecture," 1958.

[20] C. K. Ingold, " Theoretical Organic Chemistry," Kekulé Symposium, Butterworths Scientific Publications, London, 1959, p. 98.

Although Pearson, Schmidtke, and Basolo [21] have some indirect evidence for a 5-co-ordinated reaction intermediate in dimethyl sulphoxide, it does not follow that the same situation exists in water. While the conjugate base may be sufficiently long-lived in non-hydroxylic solvents, it would be expected to take up a proton from the compact solvation shell in water as soon as it is formed and before it has time to dissociate *via* process $S_N1CB$.[22] Furthermore, attempts to detect the amido conjugate base spectroscopically in aqueous alkali have been unsuccessful [23] since the shifts to longer wavelengths, expected for the loss of a proton,[24] were not observed. On the other hand, Chan and Tobe [25] have obtained both kinetic and stereochemical evidence that neither the simple collision-activated bimolecular substitution nor the conjugate base mechanism occur, but that the mechanism of the substitution involves a bimolecular rearrangement between the solvation shell and the co-ordination shell, *i.e.*, deprotonation of the solvent shell and Grotthus chain transfer to the metal (see also ref. 26).

When the present work was near completion, it was suggested [27] that the isotopic fractionation factor, $A = ([^{16}O]/[^{18}O])_{product}/([^{16}O]/[^{18}O])_{solvent}$, could give information about the mechanism in the reaction of $[Co(NH_3)_5X]^+$ with hydroxide ions. The intermediate $[Co(NH_3)_4NH_2]^+$ in $S_N1CB$ reaction does not involve the departing group X, and $A$ should therefore be independent of the nature of X in reaction by this mechanism but it was assumed that this would not apply when mechanism $S_N2$ or $S_N2CB$ is operating. The results showed that $A$ was slightly greater than unity for X = Cl or Br, indicating mechanism $S_N1CB$, while the different value of $A$ when X = F was considered to result from $S_N2$ or $S_N2CB$ reaction. However the observations are also in accord with the bimolecular mechanism suggested by Chan and Tobe.[25] If we consider that the hydroxide ion is transmitted through and around the solvent shell by a Grotthus process and that it attacks the activated complex from the most suitable position, then isotopic fractionation should reflect the solvent shell. The amount of fractionation between the solvent shell and the solvent should not be large, and should only be affected by ligands whose solvation properties are rather specific,[28] such as powerfully hydrogen-bonding fluorine.

In substitution at carbon, it is generally accepted that the third electronic shell is not involved in displacement reactions, certainly not to the extent of permitting anything approaching a fully 5-covalent intermediate. Bond formation by the nucleophile is therefore synchronous with the departure of the displaced group in $S_N2$ reactions of saturated aliphatic compounds, with a single transition state involving a change from $sp^3$ to $sp^2p$ hybridisation.[9b] Changes consequent on bond breaking are thus involved in the rate-determining step, and fluorine is consistently found to be the most difficult to replace; typical G.R.F. values are $10^{-3}$, 1, 30—40, 80—100 for $S_N2$ reactions and about $10^{-5}$, 1, 25—60, 100—250 for $S_N1$ reactions.[8] Some actual results are compared with the present work in Table 1.

Aromatic carbon atoms are bonded directly to only three other atoms. Aromatic substitution can therefore proceed *via* an intermediate in which four atoms are bonded to the central carbon atom involving a change from $sp^2p$ to $sp^3$ hybridisation; [1-6] in some cases this intermediate can possess considerable stability.

For aromatic $S_N2$ reactions too the quite different G.R.F. values of the halogens are highly significant. Where the formation of the intermediate complex is rate-determining, bond breaking is not involved and the high electronegativity of fluorine, relative to the

---

[21] R. G. Pearson, H. H. Schmidtke, and F. Basolo, *J. Amer. Chem. Soc.*, 1960, **82**, 4434.

[22] S. C. Chan, Ph.D. Thesis, London, 1962.

[23] R. G. Pearson and F. Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 4878.

[24] A. A. Grinberg and G. P. Faerman, *Z. anorg. Chem.*, 1930, **193**, 193.

[25] S. C. Chan and M. L. Tobe, *J.*, 1962, 4351.

[26] S. C. Chan and F. Leh, " Proceedings of the VIIIth International Conference on Coordination Chemistry," Vienna, 1964, p. 298.

[27] M. Green and H. Taube, *Inorg. Chem.*, 1963, **2**, 948.

[28] Private discussion with Dr. M. L. Tobe and Professor Sir Christopher Ingold.

TABLE 1

Comparison of hydroxide substitutions of cobalt(III) and saturated aliphatic compounds

| | G.R.F.[a] (25°) | | | $E_{act}$ (Cl-compound = 0) | | |
|---|---|---|---|---|---|---|
| Group replaced | $Co(NH_3)_5Hal$ | MeHal | $OHC_2H_4Hal$[b] | $Co(NH_3)_5Hal$ | MeHal | $OHC_2H_4Hal$ |
| F .................. | 0·0087 | 0·096 | 0·0017 | −1·5 | −2·7 | −1·8 |
| Cl .................. | 1 | 1 | 1 | 0 | 0 | 0 |
| Br .............. | 4·16 | 22·4 | 53·7 | 0 | −1·3 | −1·4 |
| I .................. | 15·4 | 10·5 | 51·3 | +0·7 | −2·1 | −1·1 |

| | $\log_{10} B$ (Cl-compound = 0) | | |
|---|---|---|---|
| Group replaced | $Co(NH_3)_5Hal$ | MeHal | $OHC_2H_4Hal$ |
| F .................. | −3·2 | −3·0 | −4·1 |
| Cl .................. | 0 | 0 | 0 |
| Br .............. | +0·5 | +0·4 | +0·7 |
| I .................. | +1·7 | −0·5 | +0·9 |

[a] N. B. Chapman and J. L. Levy (*J.*, 1952, 1673) quote values of Br/F replacement ratios of 5000—7000 for the $S_N2$ reactions of some primary halides (Br/F ratios for the above three series are: 477; 233; 31600), but with $E_{act}$ values closely similar. The results of M. Conrad and C. Brückner (*Z. phys. Chem.*, 1889, **4**, 631) for reaction of propyl halides with $OEt^-$–EtOH give the G.R.F. of Cl, Br, and I as 1, 62, 131. The results of E. D. Hughes and U. G. Shapiro (*J.*, 1937, 1177) for *iso*propyl halides with $OEt^-$–EtOH give similar G.R.F. values 1, 36·6, 84·1. [b] Rate constants presumably refer, however, to an internal $S_N$ reaction by $-O^-$ and may be affected by differences in concentration of $-O^-$ relative to the alcohol.

other halogens, facilitates formation of the bond between the nucleophile and the carbon to which the fluorine is attached. This results in a difference of about 4 kcal. between the energies of activation of fluoro- and iodo-compound,[4,29] the entropy term being unaffected. For reaction of *p*-halogenonitrobenzenes with methoxide ions in methanol at 50° for example, G.R.F. values [29] are 312, 1, 0·845,* 0·361. Where the decomposition of the intermediate is rate-determining however, bond breaking is involved and the aliphatic pattern of G.R.F.'s is found.[6]

Miller [6] has given theoretical support for his suggestion that the bond-making step will be rate-determining for reactions in protic solvents with the nucleophilic atom in the first horizontal row of the Periodic Table (essentially nitrogen and oxygen).

We believe that $S_N2$ reactions of inorganic compounds will parallel the behaviour of saturated aliphatic or aromatic compounds depending on whether an electronic energy level of the central atom is sufficiently low or not to permit substitution *via* a relatively stable intermediate complex which contains an additional atom fully bonded to the central atom. Corresponding to this, one should observe G.R.F. values for the halogens such as have been described above.

The work presented in this Paper shows that in the bimolecular nucleophilic substitution of $[Co(NH_3)_5X]^{2+}$ by hydroxide ion (X = F, Cl, Br, and I), the G.R.F. pattern (F < Cl < Br < I) corresponds to that in saturated aliphatic compounds. Work is now in progress on $S_N2$ substitutions in platinum(II) complexes where the orbital situations are such that we expect to observe the aromatic pattern.

*Substitution by Hydroxide Ion in Fluoropentamminecobalt*(III) *Cation in Aqueous Solutions.* Fluoro-complexes of cobalt(III) have been known since 1907 [30,31] but few kinetic studies are available. Basolo and his co-workers have studied hydroxide substitution in difluorobis(ethylenediamine)cobalt(III) cations,[32] but their results are unsuitable for the

---

* Due to an arithmetical error this was given in the original Paper as 0·745.

[29] G. P. Briner, J. Miller, and (in part) M. Liveris and P. G. Lutz, *J.*, 1954, 1265.

[30] A. Hiendlmayr, " Beitrage zur Chemie der Chrom- und Kobalt-Ammoniake," Freising, 1907.

[31] H. Seibt, " Über Stereoisomer Difluoro- und Fluoroamminediäthylenediaminkobaltisalze," Zürich, 1913.

[32] F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 4883.

present purpose as the complexes investigated contain both orienting and displaceable fluorine ligands in the same molecule. For the present comparisons, the fluoropentamminecobalt(III) cation is more suitable, since the five ligands which are not replaced in the rate-determining step are identical.

The cation reacts quantitatively with aqueous sodium hydroxide according to the overall equation

$$[Co(NH_3)_5F]^{2+} + 3OH^- \longrightarrow Co(OH)_3 + 5NH_3 + F^-$$

but the reaction is of first order with respect to the complex ion and the hydroxide ion, indicating that the rate-determining step is the bimolecular substitution:

$$[Co(NH_3)_5F]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + F^-$$

Provided that the hydroxide ion is not in excess, destruction of the complex only sets in during the later stages of the reaction. The appropriate equilibrium constants [33,34] show that no complications are caused by the hydrolysis of the liberated fluoride ion:

$$F^- + H_2O \rightleftharpoons HF + OH^-, \quad 2F^- + H_2O \rightleftharpoons HF_2^- + OH^-$$

The complications caused by the background solvolysis have been shown to be slight.[34] The second-order rate constants, determined at different temperatures and ionic strengths, are collected in Table 2.

TABLE 2

Second-order rate constants ($k_2$) for the hydroxide substitution of fluoropentamminecobalt(III) nitrate in aqueous solutions

| Temp. | Initial $\mu$ * (mmole/l.) | $10^3k_2$ (l. mole$^{-1}$ sec.$^{-1}$) | Temp. | Initial $\mu$ * (mmole/l.) | $10^3k_2$ (l. mole$^{-1}$ sec.$^{-1}$) |
|---|---|---|---|---|---|
| 50·0° | 0 | (466) | 25·0° | 0 | (15·3) |
| 50·0 | 16·0 | 305 | 25·0 | 120 | 5·1 |
| 50·0 | 46·0 | 225 | 20·0 | 0 | (6·75) |
| 50·0 | 91·0 | 170 | 20·0 | 80·0 | 2·78 |
| 40·0 | 0 | (116) | 10·0 | 0 | (1·41) |
| 40·0 | 46·0 | 57·8 | 10·0 | 108 | 0·51 |
| 30·0 | 0 | (29·4) | 0·0 | 0 | (0·196) |
| 30·0 | 46·0 | 15·0 | 0·0 | 104 | 0·073 |
| 30·0 | 80·0 | 11·8 | | | |

Calculated values in parentheses

* Concentration of complex varied from 4·00 to 30·0 mmole/l. and of NaOH from 4·00 to 48·0 mmole/l.

*Substitution by Hydroxide Ion in Chloropentamminecobalt*(III) *Cation in Aqueous Solution.*—The hydroxide substitution in the chloropentamminecobalt(III) cation has been extensively studied by Adamson and Basolo,[35] and is repeated here only as far as is necessary for the extrapolation of rates to zero ionic strength and the calculation of Arrhenius parameters. The salts are not very soluble in water; the perchlorate which is among the most soluble was used in the kinetic studies. After allowances for differences in temperature and ionic strength, our results are in satisfactory agreement with those of Adamson and Basolo [35] which were therefore included in Table 3 and in the calculation of Arrhenius parameters at ionic strength.

*Substitution by Hydroxide Ion in Bromopentamminecobalt*(III) *Cation in Aqueous Solution.* The hydroxide substitution in the bromopentamminecobalt(III) cation has been studied

---

[33] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, 1962, p. 291.

[34] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd edn., Reinhold, New York, 1950, p. 485.

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

TABLE 3

Second-order rate constants ($k_2$) for the hydroxide substitution of chloropentamminecobalt(III) cation in aqueous solutions

| Temp. | Initial $\mu$ * (mmole/l.) | $10^2k_2$ (l. mole$^{-1}$ sec.$^{-1}$) | Temp. | Initial $\mu$ * (mmole/l.) | $10^2k_2$ (l. mole$^{-1}$ sec.$^{-1}$) |
|---|---|---|---|---|---|
| 20·0° | 0 | (58·9) | 18·0° | 0 | (44·5, 53·2) ‡ |
| 20·0 | 9·2 | 41·7 | 18·0 | 26·0 | 25·6 † |
| | | | 18·0 | 47·2 | 25·3 † |
| 20·0 | 16·0 | 37·7 | 11·0 | 0 | (15·6) |
| 20·0 | 51·9 | 26·8 | 11·0 | 47·2 | 7·5 † |
| 20·0 | 104·9 | 19·5 | 3·6 | 0 | (3·69) |
| 25·3 | 0 | (183) | 3·6 | 47·2 | 1·81 † |
| 25·3 | 47·2 | 86 † | 2·5 | 0 | (3·59) |
| 19·0 | 0 | (65·1) | 2·5 | 65·2 | 1·51 † |
| 19·0 | 56·0 | 29·0 † | | | |

Calculated values in parentheses

* Concentration of complex varied from 4·00 to 14·0 mmole/l., and of NaOH from 4·00 to 50·2 mmole/l. † Data from ref. 35 ‡ At 18°c, the data from ref. 35 showed virtually the same rate at two different ionic strengths. Consequently two different values of $k_2$ at $\mu = 0$ are obtained. Both are used in the calculation of the Arrhenius parameters by the method of least-squares.

colorimetrically by Bronsted and Livingston [36] at two temperatures. In order to determine the Arrhenius parameters for the reaction at zero ionic strength, we have extended the investigations to other temperatures and to varying ionic strength. The second-order rate constants determined by us (Table 4) are in satisfactory ageement with the reported data [36] at 25°, after allowance for the difference in temperature.

TABLE 4

Second-order rate constants ($k_2$) for the hydroxide substitution of bromopentamminecobalt(III) perchlorate and iodopentamminecobalt(III) perchlorate

| | | $10^2k_2$ (l. mole$^{-1}$ sec.$^{-1}$) | |
|---|---|---|---|
| Temp. | Initial $\mu$ * (mmole/l.) | Bromo-complex | Iodo-complex |
| 1·3° | (0) | (10·1) | (35·5) |
| 1·3 | 16·0 | 6·4 | 23·0 |
| 1·3 | 51·9 | 4·43 | 15·7 |
| 1·3 | 104·9 | 3·13 | 11·5 |
| 11·0 | (0) | (60·2) | (249) |
| 11·0 | 104·9 | 18·6 | 79·6 |
| 20·0 | (0) | (276) | (907) |
| 20·0 | 96·9 | 87 | 554 † |

Calculated values in parentheses

* Concentration of complex and NaOH varied from 2·00 to 4·00 mmole/l. † $\mu = 19·0$ mmole/l.

*Substitution by Hydroxide Ion in Iodopentamminecobalt*(III) *Cation in Aqueous Solutions*.—The hydroxide substitution in the iodopentamminecobalt(III) cation has been studied by Yalman [37] by a spectrophotometric method at an ionic strength of 1M. Comparison with our results is not really practicable because the simple linear relationship

$$\log_{10}k_2 = \log_{10}k_2^0 + 2Az_1z_2\mu^{\frac{1}{2}}$$

breaks down long before the high value of ionic strength previously employed is reached. Here the hydroxide substitution is considerably faster than both the background solvolysis and the destruction of the complex so that conditions may be so chosen that only the hydroxide substitution is observed.

---

[36] J. N. Bronsted and R. Livingston, *J. Amer. Chem. Soc.*, 1927, **49**, 435.

[37] R. G. Yalman, *Inorg. Chem.*, 1962, **1**, 16.

The liberated iodide ion has been shown to complicate the reaction according to the scheme:[37]

$$[Co^{III}(NH_3)_5I]^{2+} + I^- \longrightarrow [Co^{II}(NH_3)_5I]^+ + I, \quad 2I \rightleftharpoons I_2,$$

$$[Co^{II}(NH_3)_5I]^+ + 6H_2O \longrightarrow [Co^{II}(H_2O)_6]^{2+} + 5NH_3 + I^-$$

However, this redox reaction depends on the concentration of the iodide ion in solution and it was found that when the complex was supplied as the perchlorate (one of the more soluble salts), the solution contains virtually no free iodine during the first half-life of the hydroxide substitution. The second-order rate constants are collected in Table 4. For this complex the high rate of reaction brings us to the limit of the sampling technique employed and, consequently, the data reported for the higher temperatures are the least reliable.

*Discussion.*—The results reported in Tables 2—4 are treated in a similar manner to that described by Bolto and Miller.[5] For each of the complexes, rates were determined at not less than three ionic strengths at one temperature. At other temperatures, rates were determined at one ionic strength only. The plots of $\log_{10}k_2$ against $\mu^{\frac{1}{2}}$ are all straight lines from which the intercepts on the $\log_{10}k_2$ axis give the rate constants at zero ionic strength ($k_2^0$) for the particular temperatures; the gradients are always less than the theoretical values (cf. ref. 5). The experimental slope is then rewritten as $C/(DT)^{\frac{3}{2}}$ where $C$ is a temperature-independent term and $D$ is the dielectric constant of the solvent at absolute temperature $T$. Using the interpolated values of $D$ for water,[38] it was possible to calculate against $1/T$ $k_2^0$ at all experimental temperatures for each complex. The "best" straight line, $\log_{10}k_2^0$ gave the activation energies and $\log_{10}B$. The relevant data are shown in Table 5. The errors in Arrhenius parameters do not exceed about 2%, except for the chloro-compound where the results of two independent groups are combined; even there the error is only 3%.

TABLE 5

Rates and Arrhenius parameters for the hydroxide substitution of halogenopentamminecobalt(III) cations in water at 25° and zero ionic strength

$k_2^0 = B \exp (E_{act}/RT)$ (at $\mu = 0$)

| Displaced group | $k_2^0$ (25°) (l. mole$^{-1}$ sec.$^{-1}$) | $E_{act}$ (kcal. mole$^{-1}$) | $\log_{10}B$ | G.R.F. (25°) |
|---|---|---|---|---|
| F ........................ | 0·0130 | 26·7 | 17·7 | 0·0087 |
| Cl ........................ | 1·49 | 28·2 | 20·9 | 1 |
| Br ...................... | 6·20 | 28·2 | 21·4 | 4·16 |
| I ........................ | 22·9 | 28·9 | 22·6 | 15·4 |

It can be seen from Table 5 that the rates of hydroxide substitution of halogen in halogenopentamminecobalt(III) complexes follow the order F < Cl < Br < I, the pattern for $S_N2$ reactions of saturated aliphatic compounds. Although $E_{act}$ is least for the fluoro-compound, this is more than counterbalanced by the small value of $\log_{10}B$. This suggests that factors consequent on the partial rupture of the metal–halogen bonds control the order of reactivities, and that the pattern of the bond dissociation energies (B.D.E.) is very similar to that of carbon–halogen bonds. Information on this is scanty, but it is noteworthy that the average bond energy of the Co–Cl in $CoCl_3$ [39] is only slightly less than that of C–Cl bonds in carbon tetrachloride [40-42] and that the heats of dissociation of manganese and nickel halides [43] are found to be in the order F > Cl > Br > I and Cl > Br > I, respectively.

---

[38] P. S. Albright and L. J. Gosting, *J. Amer. Chem. Soc.*, 1946, **68**, 1063.

[39] T. L. Allen, *J. Chem. Phys.*, 1957, **26**, 1644.

[40] M. Bodenstein, P. Gunther, and F. Hofmeister, *Z. angew. Chem.*, 1926, **39**, 875.

[41] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," New York, 1936.

[42] U.S. National Bureau of Standards, "Selected Values of Thermodynamic Properties," Washington, 1952.

[43] E. M. Bulewicz, L. F. Phillips, and T. M. Sugden, *Trans. Faraday Soc.*, 1961, **57**, 921.

In octahedral cobalt(III) complexes the bonding orbitals used are the $3d^24s4p^3$ hybrid orbitals in which the two $3d$ orbitals are of the $d_\gamma$ type. The three $3d_\epsilon$ orbitals which may be considered as non-bonding (or $\pi$-bonding in the presence of ligands capable of accepting electrons) are also completely filled. The next available energy level, the $4d$ level, is too high in energy[44] to permit its participation to form a fully-bonded 7-co-ordinated intermediate. Instead the octahedral $d^2sp^3$ orbitals are modified to either (i) $dsp^3$ with a $d$ orbital shared between the incoming and the outgoing groups, or (ii) $d^2sp^2$ with a $p$ orbital shared between the incoming and the outgoing groups. Of the two possibilities, we prefer (i) which is now discussed in greater detail. If the $d_{z^2}$ orbital is shared, the resulting fully-bonded portion of the intermediate will have $d_{x^2-y^2}sp^3$ hybridisation which can be viewed as a combination of $d_{x^2-y^2}sp^2$ (giving four square planar bonds) and $p_z$ (giving the apical bond); *i.e.*, a square pyramidal structure results (Figure 1). If, on the other hand, the $d_{x^2-y^2}$ orbital is shared, the resulting fully-bonded portion of the intermediate will have $d_{z^2}sp^3$ hybridisation which can be viewed as a combination of $sp^2$ (giving three trigonal planar bonds) and $d_{z^2}p_z$ (giving two linear axial bonds); *i.e.*, a trigonal bipyramidal structure results (Figure 2). In the reaction of halogenopentamminecobalt(III) complexes, it is impossible to tell which of the two $d$ orbitals is shared as the five remaining ligands (*i.e.*, $NH_3$) are identical, but we prefer a shared $d_{x^2-y^2}$ orbital with its greater separation of entering and replaced group. Asperger and Ingold[18] have postulated two possible transition states for bimolecular nucleophilic substitutions in octahedral cobalt(III) complexes, one for direct replacement and the other for edge-displacement. Our present considerations can be easily reconciled with their views as the structures postulated by us are similar, if not identical, to theirs.

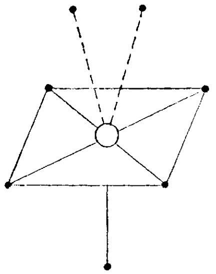


FIGURE 1. $d_{x^2-y^2}sp^3$ + shared $d_{z^2}$

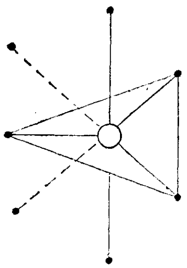


FIGURE 2. $d_{z^2}sp^3$ + shared $d_{x^2-y^2}$

The structure in Figure 1 could also be derived from a $d^2sp^2$ combination with a shared $p_z$ orbital but that depicted in Figure 2 would then be difficult to visualise

The present results show that the G.R.F.'s of the halogens are similar to those in $S_N2$ reactions of saturated aliphatic compounds (Table 1) but quite unlike those in aromatic $S_N2$ reactions (see above). A further similarity is that the order of G.R.F.'s depends on opposing effects of activation energy ($E_{act}$) and entropy ($\log_{10}B$) with the latter predominating for the difference between F and Cl. The value of $E_{act}$ would favour the rate order F > Cl (and the very limited data for aliphatic reactions suggest Cl < Br and I) but it is clear that there is no simple relationship with the B.D.E.

There is almost no information available to permit predictions for cobalt(III) and an attempt is made to draw analogies from the similar pattern of aliphatic $S_N2$ reactions. Even for the latter there are very few kinetic data which include fluoro-compounds, particularly values of the Arrhenius parameters (Table 1).

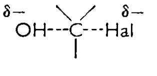
Table 1 shows clearly that the order of the rates is F < Cl < Br and I for the reactions of cobalt(III) and saturated aliphatic compounds. The pattern of the Arrhenius parameters is less precise but the order is F < Cl, Br, and I for both $E_{act}$ and $\log_{10}B$ ($S_{act}$), and

---

[44] C. A. Coulson, " Valence," Oxford University Press, London, 1953, p. 35.

especially marked for $\log_{10}B$. It is in complete contrast to aromatic $S_N2$ reactions where $\log_{10}B$ is approximately constant and $E_{act}$ varies in the order F < Cl < Br < I.

Application of Miller's procedure [6,45] to the heats of reaction of Me Hal + $OH^- \longrightarrow$ Me OH + $Hal^-$ gives relative values —2·5, 0 (for Cl), —0·5, +1·5. Since the single transition state involves a partial change corresponding to this reaction, the similarity of this sequence to that of $E_{act}$ patterns in Table 1 is significant. Qualitatively we can, however, consider the situation further, bearing in mind that (i) the same bond is being formed (C–OH) in all four reactions; (ii) the electronegativity factor considered in aromatic substitution [6] should similarly facilitate bond formation by $OH^-$ here (F > Cl > Br > I); (iii) partial bond rupture opposes the effect of (ii) and tends to reverse the order; (iv) the electron affinity is greater for Cl than for the other halogens but the differences in affinity are considerably less than those of B.D.E. and the heat of hydration and appear to be a minor factor only. The major factor seems to be solvation of the charged transition state shown inset which we expect to decrease with polarity in the usual order, so that the transition state of the fluoro-compound is the most solvated. As a result, the entropy of activation (in the $\log_{10}B$ term) will have the least value for the fluoro-compound because of the increased ordering of solvent molecules and because its transition state ion is the smallest.[46a] Since the B.D.E. component opposes the reduction in $E_{act}$ due to both electronegativity [6] and increased solvation, it is not surprising that the entropy factor is left to control the rate (and G.R.F.). This discussion must be regarded as speculative though it is in general agreement with that of Moelwyn-Hughes [47] who considers solvation as the key factor.



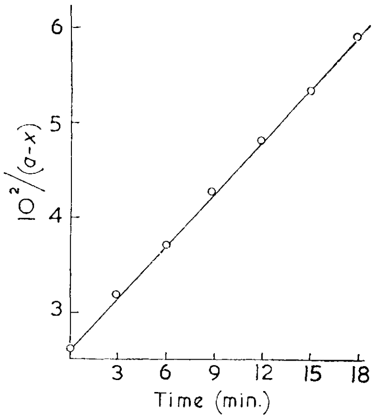


FIGURE 3. Typical second order plot for the base hydrolysis of the $[Co(NH_3)_5F]^{2+}$ cation at 50°

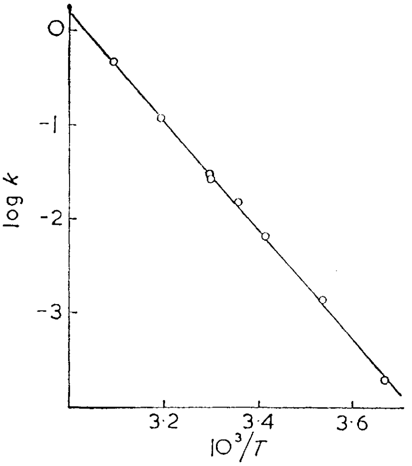


FIGURE 4. Arrhenius plot of the base hydrolysis of the $[Co(NH_3)_5F]^{2+}$ cation

The correspondence of the G.R.F.'s in the organic and inorganic series is surprisingly close in both order and magnitude, and thus supports our suggestion that the latter substitutions too are typical $S_N2$ processes with concurrent bond formation and fission, as described above. The main difference is the smoother order in the Co(III) series than in the two aliphatic series for which full data are available. It would be unwise to speculate

---

[45] J. Miller, Proceedings of the International Symposium of Organic Reaction Mechanisms, Cork, 1964, in the press.

[46] A. A. Frost and R. G. Pearson, " Kinetics and Mechanism," 2nd edn., Wiley, New York, 1961, (*a*) p. 133; (*b*) p. 143.

[47] D. N. Glew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1952, **211**A, 254.

too much on this, and experimental work on other systems is clearly required. The absolute values of the Arrhenius parameters differ substantially not only because of differences in absolute values of B.D.E., but also because the inorganic reactions occur between a singly charged anion and a doubly charged cation whereas the organic reactions either occur between a singly charged ion and a dipolar molecule, or involve an internal process. The former should thus show [46b] the largest $\log_{10}B$, as observed; $E_{\text{act}}$ is always a few kcal. greater in the cobalt series.

It is noteworthy that the *order* of replacement in saturated aliphatic $S_N1$ reactions is the same in the $S_N2$ reactions but that there is a substantially greater spread, Ingold [8b] quoted a G.R.F. of $10^{-5}$ for fluorine, and a G.R.F. as low as $10^{-6}$ has been recorded resulting from an *increase* of $E_{\text{act}}$ from 12·5 to 22·6 kcal., while $\log_{10}B$ also *increases* slightly.[48] The energy of bond breaking is then clearly the major influence and the very limited data suggest that the relative ease of replacement depends mainly on the values of B.D.E. We would expect a similar result in inorganic $S_N1$ reactions and our kinetic data are thus in themselves evidence not only for an $S_N2$ mechanism but also against the mechanism $S_N1CB$.

It is also noteworthy that the very marked differences between the relative reactivities of the halogens in bimolecular nucleophilic substitutions of aliphatic and aromatic compounds are minimally reflected in differences of $E_{\text{act}}$. In all the series so far studied the value for the fluoro-compound is less than for the chloro-compound, and the low reactivity for fluorine is associated with small values of the entropy term ($\log_{10}B$). Where the reactivity of fluorine is large the values of $\log_{10}B$ seem to be about normal for the class of reaction.

We expect the aromatic type of substitution to occur, for example, in platinum(II) complexes which are square planar. In these complexes, the bonding orbitals are of the type $5d_{x^2-y^2}6s6p_x6p_y$. The next unfilled orbital will be the $6p_z$ which is very close in energy to the set of $dsp^2$ hybrid orbitals and can therefore take part in bond formation to give the fully-bonded intermediate. This $p_z$ orbital is spatially suitable to form a square pyramidal structure with the $dsp^2$ square planar bonds and Haake [49] has obtained evidence of this in the replacement of chloride by nitrite ion in *cis*-$[Pt(NH_3)_2Cl_2]$. Kinetic studies of bimolecular nucleophilic substitution in fluorine complexes of platinum(II) are in progress so that the application of the generalisation of group mobility factors to inorganic systems may be tested more thoroughly.

## EXPERIMENTAL

*Preparations.*—Fluoropentamminecobalt(III) nitrate was prepared and purified by the method of Basolo and Murmann.[50] The crystals were purified by dissolving in a minimum of water at 45°, filtering, adding solid ammonium nitrate, and cooling; they were dried at 90° {Found: $F^- = 6·6$. Calc. for $[Co(NH_3)_5F](NO_3)_2$: $F^- = 6·6\%$}. Chloropentamminecobalt(III) perchlorate was prepared from the corresponding chloride by dissolving in cold 3M-sulphuric acid and adding ice-cold concentrated perchloric acid, purified by dissolving in ice-cold water and precipitating with cold perchloric acid, and dried at 110° {Found: $Cl^- = 9·3$. Calc. for $[Co(NH_3)_5Cl](ClO_4)_2$: $Cl^- = 9·4\%$}. Bromopentamminecobalt(III) perchlorate was prepared from the corresponding bromide in the same manner, and dried at 110° to constant weight. {Found: $Br^- = 18·8$. Calc. for $[Co(NH_3)_5Br](ClO_4)_2$: $Br^- = 18·9\%$}. Iodopentamminecobalt(III) perchlorate was prepared from the corresponding chloride by trituration with cold concentrated perchloric acid,[51] and purified by dissolving in water and rapidly filtering the solution into an equal volume of ice-cold 50% perchloric acid {Found: $I^- = 27·0$. Calc. for $[Co(NH_3)_5I](ClO_4)_2$: $I^- = 27·0\%$}.

*Analytical Procedures.*—(a) *Fluorine determinations.* An appropriate amount of the

---

[48] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 246.
[49] P. Haake, *Proc. Chem. Soc.*, 1962, 278.
[50] F. Basolo and R. K. Murmann, *Inorg. Synth.*, 1953, **4**, 171.
[51] R. G. Yalman, *J. Amer. Chem. Soc.*, 1955, **77**, 3219.

cobalt(III) complex was treated with excess of sodium hydroxide until replacement of the co-ordinated fluorine was complete. The solution was passed through a cation exchange column (Amberlite IR 120; sodium form), and the ionic fluorine in the effluent and washings titrated with thorium nitrate solution, sodium alizarin sulphonate as indicator. The thorium nitrate solution was calibrated with standard sodium fluoride solutions of various concentrations within the range employed.

(b) *Determinations of other halogens.* The cobalt(III) complex was treated as described for the determination of fluorine, and the solutions passed through Amberlite IR 120 resin (acid form). The corresponding halogen acid in the effluent and washings was estimated by Volhard's method.

*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. The water was freed from dissolved carbon dioxide by boiling and cooling under an atmosphere of nitrogen. Samples were withdrawn from time to time and passed through a cation exchange resin (Amberlite IR 120; sodium form for the fluoro-complex, acid form for the others). In all cases the resin column was surrounded by ice–water to reduce reaction of the adsorbed complex, and the resin was flushed continually with water between separations. For reactions below room temperature, the pipettes used for sampling were jacketed.

The fluoropentammine complex was supplied as the nitrate and the reaction samples were quenched by rapid cooling in a freezing mixture. The ionic strength of the solutions was adjusted to the desired value with sodium nitrate and the reaction was followed by titrating the fluoride ions in the effluent and washings from the exchange column with thorium nitrate,[52] 0·1% aqueous sodium alizarin sulphonate as indicator. Basolo and his co-workers [32] 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 and the acid form of Amberlite IR 120 since the release of the co-ordinated fluorine is acid-catalysed.[53] This difficulty could be avoided by using the sodium form of the resin, obtained by passing a solution of sodium nitrate through the column.

The ionic strength of solutions of the chloropentammine complex was adjusted to the desired value with sodium perchlorate and the reaction was followed by withdrawing portions of the reaction mixture by means of a fast-running, jacketed pipette and delivering into a sight excess of cold perchloric acid. The ionic chloride was separated from the complex cation by means of the cation exchange resin and was determined by Volhard's method.

The same methods were employed for following the reactions of the bromopentammine and iodopentammine complexes. Effluents containing hydriodic acid were analysed immediately as decomposition into iodine and water occurred on standing. Complications resulting from background aquation could be neglected.

Typical plots for the determination of $k_2$ and $E_{\text{act}}$ determinations are given in Figures **3** and **4** (for the fluoro-compound).

For experiments at 0°, a large Dewar flask filled with crushed ice and water was used. The thermostats used above room temperature were of the conventional design ($\pm 0{\cdot}05°$). The thermostat for temperature between 0° and room temperature incorporated an intermittent cooling unit and colourless kerosene was used to fill the tank ($\pm 0{\cdot}1°$). Light was carefully excluded from the reactions by adding black ink to the water in the thermostat bath; for ice and kerosene baths, the reaction vessels were blackened.

The authors thank the Committee on Higher Degrees and Research Grants of the University of Hong Kong for financial assistance.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF HONG KONG,
HONG KONG, B.C.C.

[*Received, June 1st,* 1964.]

---

[52] H. H. Willard and O. B. Winter, *Ind. Eng. Chem. Analyt.*, 1933, **5**, 7.
[53] S. C. Chan, *J.*, 1964, 2375.