560. *Mechanism, Kinetics, and Stereochemistry of Octahedral Substitutions. Part VI.* Bimolecular Basic Hydrolysis and Aquation of the Chloronitrobis(ethylenediamine)cobalt(III) Ions.*

By S. AŠPERGER and C. K. INGOLD.

The products and rates of the alkaline hydroxylation and of the aquation of *trans*- and of *cis*-chloronitrobis(ethylenediamine)cobalt(III), with displacement of the chlorine as chloride ion, are examined. Some errors in the literature concerning the products, and the proportions in which they arise in these reactions, are corrected. The *trans*-chloronitro-cation gives pure *trans*-aquonitro-cation on aquation, and 94% of the *trans*-stereoisomer in the alkaline substitution, these statements applying to first-formed products which have suffered no subsequent change. Similarly, the *cis*-chloronitro-cation gives the *cis*-product on aquation, and 66% of the *cis*-stereoisomer in the alkaline reaction. The alkaline hydroxylations obey second-order kinetics, and the aquations first-order. As compared with previously investigated ligands, which the nitro-group can be considered to replace, the latter has, for both reactions, a strong orienting effect, favouring predominating retention of configuration in place of extensive stereo-change. In the alkaline reaction, the changed orientation is associated with a mildly reduced rate of substitution. In aquation, the similar orientational change accompanies a considerably increased rate of substitution.

These observations are discussed. As to the alkaline reactions, reasons are given which support the conclusion of Part II that they are bimolecular nucleophilic substitutions, S_N2. The strong orienting effect of the nitro-group arises from its negative electromeric effect, exerted primarily on the *3d* non-bonding shell of the cobalt atom. The group retards substitution in all positions, but especially in those adjacent to itself. The mildness of the retardations is traceable to the simultaneity of bond-formation and bond-fission in these bimolecular anion exchanges. A theoretical classification is suggested of some orienting ligands, which have not yet been experimentally investigated. The stereochemical forms and relative energies of transition states for substitution without and with edge-displacement are considered qualitatively.

As to aquation, it is shown that, when, in an otherwise constant structure, an orienting ligand is so changed that its electron attraction in nucleophilic substitution is progressively increased, the rate of substitution at first falls and then rises. Recalling the demonstration of Part II that, with progressive reduction of the nucleophilic power in the reagent, the rate at first falls and then steadies, this further relation can be seen as a continued reproduction in octahedral substitutions of the pattern of kinetic effects which constituted the originally offered evidence of duality of mechanism in carbon substitutions. The aquations of the chloronitro-cations lie on the bimolecular branch of the rate curve. Their orienting effects are analogous to those of the alkaline reactions, but their rate effects are opposite and much larger, because the polarisation needed to secure the binding of water is the dominating constitutional requirement. It is suggested that *4d* orbitals play an intermediate rôle in this binding.

As noted in Part I,[1] Werner obtained all possible stereochemical results among the many octahedral substitutions of cobalt(III) which he studied. But he knew nothing of the mechanisms in operation, or even that his products were formed by only one substitution, and not, as many of them probably were, by two or more. It appears that no investigation, prior to ours, has started by characterising the mechanisms at work, and has

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* Part V, *J.*, **1956**, 1707.

[1] *J.*, **1953**, 2674.

then compared spatial orientation in single substitutions by a common mechanism—following the pattern mapped out 20 years ago for tetrahedral carbon substitutions. (A somewhat similar situation applies to square substitutions, to the study of which we hope to contribute later.)

In two preceding Parts [2] the steric course is described of several, kinetically controlled, bimolecular nucleophilic substitutions, S_N2, in which attacking hydroxide ion displaces a chloro-, bromo-, or nitrato-group from octahedral combination in a bis(ethylenediamine)-cobalt(III) ion. The complex ions used contained a single, characteristic, preserved ligand, which in some examples was the *iso*thiocyanate and in others the ammine group. It was noted that the proportions in which stereoisomers are formed in these substitutions are scarcely altered when either of these preserved ligands is exchanged for the other in the same position relatively to the group to be displaced. This result suggests either that the *iso*thiocyanato- and the ammino-group have no effect, or that they have equal effects, in controlling the spatial direction of substitution. And so the hitherto open question of whether spatial orientation by the retained groups is important in octahedral substitutions by the bimolecular nucleophilic mechanism is brought into the foreground.

Although the arguments through which one might derive guidance from organic chemistry are not wholly clear, the outstanding position of the nitro-group as an orienting group for bimolecular nucleophilic substitution in the aromatic series, suggested to us that, if any ligand is going to exert a notable orienting effect on the course of bimolecular nucleophilic substitution at octahedral cobalt, the nitro-ligand ought to do so. Accordingly we decided to study substitutions in which an entering group displaces chlorine as chloride ion from *cis*- and *trans*-chloronitrobis(ethylenediamine)cobalt(III) ions.

It has been inferred [1] from indications in the literature of complex salts, that water, although convenient as a solvent, is highly active towards them as a substituting agent; and furthermore, that water usually attacks a cobalt cation ahead of any possible anion, excepting the most nucleophilic of all that are stable, *viz.*, the hydroxide ion, which is thus the only anion able in water to effect a single-stage bimolecular displacement of, *e.g.*, a halogen atom, from combination with octahedral cobalt. It was in this belief that D.D. Brown used methyl alcohol as solvent when demonstrating mechanisms of substitution in an ion of octahedral cobalt,[3] notably, unimolecular substitutions by such weakly nucleophilic anions as the chloride and *iso*thiocyanate ions, and bimolecular substitutions by the successively more strongly nucleophilic nitrite, azide, and methoxide ions. Since then, our picture of the rôle of water in cobalt substitutions has been directly confirmed by Basolo and his co-workers [4] in the very examples with which we are now concerned. They examined the kinetics of the displacement of chlorine as chloride ion from both *cis*- and *trans*-chloronitrobis(ethylenediamine)cobalt(III) ions by substituting thiocyanate, nitrite, and azide ions, in water; and in every case they found that substitution proceeded *via* a preliminary aquation. Thus it was clear on specific grounds, as well as from general considerations, that, if we wished to observe simple bimolecular substitutions in these chloronitro-cations in water as solvent, the one anion available as substituting agent would be the hydroxide ion.

We describe below a combined study of the kinetics and products of the two aqueous reactions here formulated :

$$\left.\begin{matrix}\textit{cis}\\ \textit{trans}\end{matrix}\right\}\text{-[Co en}_2\text{(NO}_2\text{)Cl]}^+ + \text{OH}^- \longrightarrow (\textit{cis}\text{ and }\textit{trans})\text{-[Co en}_2\text{(NO}_2\text{)OH]}^+ + \text{Cl}^-$$

The conditions were so chosen that our results for these substitutions in the presence of the nitro-ligand are directly comparable with those already reported [2] for analogous substitutions in the presence of the *iso*thiocyanato- and ammino-ligands.

The kinetics of the reactions formulated have not been investigated before, but the products have, again by Basolo and his colleagues,[5] though only by analysis after completion

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[2] Parts IV and V, *J.*, 1956, 1691, 1707.

[3] Part II, *J.*, 1953, 2680.

[4] Basolo, Stone, Bergmann, and Pearson, *J. Amer. Chem. Soc.*, 1954, **76**, 3079.

[5] Basolo, Stone, and Pearson, *ibid.*, 1953, **75**, 819.

of the reactions. These authors reported that the *cis*-chloro-cation gave only the *cis*-hydroxy-cation, whilst the *trans*-chloro-cation gave equal proportions of the *cis*- and the *trans*-hydroxy-isomer. Even were these analyses correct, the method and conclusion would be dangerous, for the products finally found may not be original substitution products which have suffered no further change. A proof is required that, throughout the course of reaction, the substitution products appear in a constant ratio, which is identical with that observed finally. However, with all allowances made for possible error from methodological causes, we can neither confirm the reported results, nor explain them. These compositions of the product bear no resemblance to the compositions we obtained for original substitution products; and they are obviously not equilibrium compositions, set up by some subsequent reversible change, because they differ according to the starting substance.

The immediate product of the alkaline hydroxylation of either the *cis*- or the *trans*-chloronitro-cation is a mixture of the *cis*- and the *trans*-hydroxynitro-cation; but in our work these were always examined in the form of their conjugate acids, the *cis*- and the *trans*-aquonitro-cation, which are formed on acidification of the alkaline solutions.

(1) *Properties of the* cis- *and* trans-*Forms of the Chloro-, Hydroxy-, and Aquo-nitrobis(ethylenediamine)cobalt*(III) *Ions.*

(1.1) *The Chloronitro-cations.*—The *cis*- and the *trans*-isomer form well-characterised salts, as to the configurations of which there can be no doubt, salts of the *cis*-series having been optically resolved.[6] We obtained the two series by the action of sodium nitrite on *trans*-dichloro(bisethylenediamine)cobalt(III) chloride, as Werner describes,[7] isolating the *cis*-chloronitro-cation as its chloride, and the *trans*-chloronitro-cation as its nitrate.

The methods of spectral characterisation of these cations were conditioned, as much of our procedure has been, by the considerable speed with which, in neutral or acidic aqueous solution, either chloro-cation loses chloride ion, and becomes an aquonitro-cation. Such are the rates of these aquations that it was impossible to examine by photometer an extensive region of the spectrum of an aqueous solution of either chloro-cation before appreciable aquation set in.

For practical purposes of identification, and the checking of purity, however, we found that we could satisfactorily scan the spectrum given by a solution, freshly made at 0°, of either chloro-salt, from 2700 to 4000 Å on a Cary quartz recording spectrophotometer within 3 minutes, a period in which aquation is appreciable though not very extensive, as could be shown by immediately retracing the spectrum over the next 3 minutes. In this way, we could obtain a series of spectral curves which were reproducibly ***characteristic*** of the introduced pure isomers, even though they are not spectra *of* the pure isomers.

For record, we can quote the extinction coefficient at a fixed wavelength, as measured at 0° on a calibrated Unicam quartz spectrophotometer S.P. 500 and corrected for aquation by extrapolation back to zero time. At 3290 Å, the wavelength used in most of this work, the extinction coefficient of the *cis*-chloro-cation is 1554, and that of its *trans*-isomer is 1455 cm.$^{-1}$ mole^{-1} l. A more striking difference between the isomers is provided by the way in which, in consequence of aquation, the extinctions, which start at these points, move with time, in opposite directions, and at different speeds, as recorded in Sections 2.1 and 2.3.

(1.2) *The Aquonitro-cations.*—The *cis*- and the *trans*-aquo-cation are easily distinguished by their absorption spectra; and there is no doubt about which is which, because Mathieu has converted optically active *cis*-chloronitrobis(ethylenediamine)cobalt(III) ion by direct aquation into an optically active *cis*-aquonitro-cation, which he characterised by its absorption spectrum and rotatory dispersion.[8]

The *cis*- and *trans*-aquonitro-cations may be obtained in pure form in solution by direct aquation of the *cis*- and *trans*-chloro-cations, respectively, in neutral or dilute acid aqueous solution at or below room temperature. In aqueous solution at higher temperatures, these aquo-cations undergo reversible interconversion, as is established in Section 1.4.

[6] Werner, *Ber.*, 1911, **44**, 3272.

[7] *Idem, Annalen*, 1912, **386**, 252.

[8] Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 476.

It seems not to have been recognised before that this isomerisation may interfere with purity in the preparation of the very soluble crystalline salts of the isomeric aquo-cations with simple inorganic anions. Following the procedure used by Meyer and Rampoldt,[9] except that the recommended evaporations on the water-bath were omitted, salts being crystallised by cooling, and temperatures being kept below 25° throughout, the *cis*- and *trans*-aquo-cations were prepared by aquation of the chloro-cations, and crystallised first as their naphthionates (4-aminonaphthalene-1-sulphonates). These salts were unsuitable for our work, and were therefore converted with sulphuric acid into sulphates, which, after removal of the precipitated naphthionic acid, were induced to crystallise. The sulphates are much more soluble than naphthionates, and *cis*-isomers are more soluble than *trans*-isomers.

A plot of the absorption spectrum of the crystallised sulphate of the *trans*-aquo-cation at pH 4·55 is given in Fig. 1, and some further observational points are there added in order to show that the spectrum remains the same when the pH is lowered to 2·52 by addition of perchloric acid. It follows that, even at pH 4·55, the aquo-cation is present as such, and not to any extent as its conjugate base, the *trans*-hydroxy-cation. Fig. 1 also shows the absorption curve of a solution of the *trans*-aquo-cation, which was prepared from the nitrate of the *trans*-chloro-cation by aquation in water in the dark at 0° for 6 days, a time shown spectrally to suffice for the completion of that process, but not to allow opportunity for any appreciable isomerisation of the aquo-product. The solution was acidified to pH 1·2 with perchloric acid before the spectrum represented was measured. This spectrum coincides with that of the crystallised sulphate sufficiently closely to show that the aquation was complete, and that it gave the pure *trans*-aquo-cation. The deviation apparent at the short-wave end of the range signifies only the presence of a small amount of naphthionate as an impurity in the sulphate crystals.

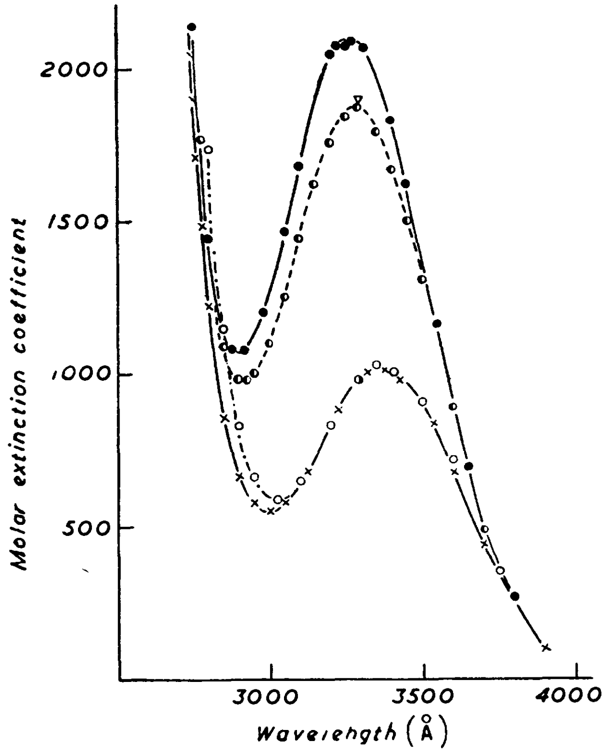

FIG. 1. *Absorption spectra of* 0·0004M-*aqueous solutions :*

× *of* trans-[Co en$_2$(NO$_2$)OH$_2$]$^{2+}$ *at* pH 1·2, *as obtained from* trans-[Co en$_2$(NO$_2$)Cl]$^{+}$NO$_3^{-}$ *by aquation and subsequent addition of* HClO$_4$; ○ *of crystallised* trans-[Co en$_2$(NO$_2$)OH$_2$]$^{2+}$SO$_4^{2-}$ *at* pH 4·55; ◑ *of the same, brought to* pH 2·52 *by addition of* HClO$_4$; ● *of* cis-[Co en$_2$(NO$_2$)OH$_2$]$^{2+}$ *at* pH 1·3, *as obtained from* cis-[Co en$_2$(NO$_2$)Cl]$^{+}$Cl^{-} *by aquation and subsequent addition of* HClO$_4$; ◑ *of crystallised* cis-[Co en$_2$(NO$_2$)OH$_2$]$^{2+}$SO$_4^{2-}$ *at* pH 5·30; ∇ *of the same, brought to* pH 2·27 *by addition of* HClO$_4$.

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[9] Meyer and Rampoldt, *Z. anorg. Chem.*, 1933, **214**, 1.

In spite of some improvement resulting from stricter control of temperatures in preparation, we were never able to obtain the crystalline sulphate of the *cis*-aquo-cation free from its *trans*-isomer, because of the great solubility of both sulphates, especially the *cis*-salt. The spectrum of a typical preparation is in Fig. 1. A spectrum which we take to be that of the pure *cis*-aquo-cation is represented by the uppermost curve in Fig. 1. It is the spectrum of a solution prepared from the chloride of the *cis*-chloronitro-cation by aquation in the dark at 20° for 3 days, a time shown spectrally to allow completion of that process, without permitting an appreciable isomerisation: the solution was acidified with perchloric acid to pH 1·3 before measurement of the spectrum.

The greatest difference of absorption between the *cis*- and *trans*-aquo-isomers occurs at 3290 Å. This, therefore, was the wave-length used for measurements of the composition of the product of the reaction of hydroxide ion with either chloro-cation, and also for following the kinetics of their alkaline hydrolysis, and the kinetics of their aquation. The extinction coefficients ε_{3290} are: *cis*-$[\mathrm{Co\,en_2(NO_2)OH_2}]^{2+}$, 2100; *trans*-$[\mathrm{Co\,en_2(NO_2)OH_2}]^{2+}$, 975 cm.$^{-1}$ mole^{-1} l. It was shown that, at this wavelength, and at the concentrations involved, salts of both these cations obey the Beer–Lambert law, so that concentrations and compositions can be calculated from observed absorptions with the aid of the usual linear relations.

(1.3) *The Hydroxynitro-cations and their Relation to the Aquonitro-cations.*—The reversible interconversions of the *cis*- and *trans*-aquo-cations, and of the *cis*- and *trans*-hydroxy-cations, are extremely slow in aqueous solution at room temperature. Therefore in these conditions, acid–base equilibria between corresponding aquo- and hydroxy-cations are established in the *cis*- and *trans*-series independently.

In the near ultraviolet region, both hydroxy-cations are more weakly absorbing than are their conjugate acids, the aquo-cations. At 3290 Å the extinction coefficients of the hydroxy-cations are: *cis*-$[\mathrm{Co\,en_2(NO_2)OH}]^{+}$, 1020; *trans*-$[\mathrm{Co\,en_2(NO_2)OH}]^{+}$, 625 cm.$^{-1}$ mole^{-1} l. Therefore, when an initially alkaline solution of either hydroxy-cation, say at pH 12, is progressively acidified, the absorption at this wavelength rises from the appropriate hydroxy-value to the aquo-value. The ranges of intensity of absorption covered by these changes in the *cis*- and the *trans*-series do not overlap. But the changes occur in a similar pH range, and for both acid–base systems the rise in absorption, indicating conversion into the aquo-form, is complete at about pH 5.

Uémura and Hirasawa have recorded[10] a spectrophotometric examination of the acidic functions of *cis*- and *trans*-aquonitrobis(ethylenediamine)cobalt(III) ions. Their results are not inconsistent with the conclusion last stated, but their spectrophotometric data differ markedly from ours. One group of differences, the lower absorptions observed by them in the *cis*-series, can be understood, inasmuch as their basic material in this series was a crystalline nitrate of the *cis*-aquo-cation, which was prepared by Meyer and Rampoldt's unmodified method, and therefore probably contained a considerable proportion of the *trans*-isomer. However, their finding that, when an initially alkaline solution of the *trans*-hydroxy-cation is progressively acidified, absorption in the region near 3290 Å at first rises and then falls, passing through a maximum near pH 7·2, seems unintelligible and could not be confirmed.

(1.4) *Reversible Isomeric Conversion of the* cis- *and* trans-*Aquonitro-cations.*—This isomerisation occurs in water, but only at such temperatures that it did not disturb our measurements at 0° of the rates of alkaline hydrolysis and of aquation of the *cis*- and *trans*-chloronitro-cations, and did not change the composition of the first-formed products of these reactions during the period of the experiments. Accordingly, we had no need to measure the rate of the isomerisation; but in establishing its occurrence at temperatures near 90°, we determined the composition at its equilibrium.

Solutions, all 0·0004M, of the *trans*-aquo-cation, either made up directly from its sulphate, or prepared by aquation of the *trans*-chloro-cation as nitrate, were heated at about 90°. The extinction coefficients at 3290 Å at first rose, but after 2 hours remained constant at the mean value 1256 cm.$^{-1}$ mole^{-1} l. Solutions of the *cis*-aquo-cation, prepared in the

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[10] Uémura and Hirasawa, *Byull. Chem. Soc., Japan*, 1938, **13**, 377.

corresponding two ways, were heated similarly. Their extinction coefficients at first fell, but after 2 hours remained constant at the mean value 1275 cm.$^{-1}$ mole^{-1} l. The average of these two figures corresponds to the following isomer ratio at equilibrium : *cis*-aquo-, 31% : *trans*-aquo-, 69%.

(2) *Kinetics and Products of Aquation and of Alkaline Hydrolysis of the* cis- *and* trans-*Chloronitrobis(ethylenediamine)cobalt*(III) *Ions.*

The high rates of aquation of the nitro-cations were responsible for a considerable change of method from that of the corresponding investigation of *iso*thiocyanato- and ammino-cations, described in Parts IV and V. The instability of the chloronitro-cations in neutral and acid aqueous solution, even at 0°, puts difficulties in the way of the plotting of long absorption curves of either, and therefore of trying to prove by the finding of common intersections in changing absorption curves, that reaction products are appearing in fixed ratios. Such proof, and the values of the ratios, have to be extracted from kinetic data : in short, kinetics and products must be studied together. Moreover, as the rate of aquation is not always negligible in comparison with the rate of alkaline hydrolysis, the kinetics of these processes must to some extent be treated together.

All timed reactions were conducted in darkened vessels, since visible light has a small accelerating effect. The solvent was water throughout.

(2.1) *Rate and Product of Aquation of the* trans-*Chloro-cation.*—The chloro-cation was introduced as its weighed nitrate, the concentrations being, to within 1%, 0·0004M in work at 0° and 0·00667M in work at higher temperatures. Rates of aquation were measured over the temperature range 0—30° at pH 5, and also at 0° for pH values reduced by the addition of perchloric acid. The measurement was of the extinction coefficient at 3290 Å, which ran from the initial value 1455 appropriate to the *trans*-chloro-cation, to a final value of 975 cm.$^{-1}$ mole^{-1} l., a figure which shows that the pure *trans*-aquo-cation is being produced.

The reaction follows the first-order rate-law to within the accuracy of the measurements. The rate-constants entered in Table 1, show that the aquation process is insensitive to acid catalysis. The variation of rate with temperature may be represented by the equation, $k_1 = B_1 \exp(-E/\boldsymbol{R}T)$, where $B_1 = 6{\cdot}0 \times 10^{12}$ sec.$^{-1}$ and $E = 21{\cdot}5$ kcal./mole.

TABLE 1. *First-order rate constants* (k_1 *in sec.*$^{-1}$) *for aquation of the* trans-*chloronitrobis(ethylenediamine)cobalt*(III) *ion in water.*

Run	103	104	116	117	205	206	207
Temp.	0·0°	0·0°	0·0°	0·0°	14·0°	20·0°	30·0°
pH	5·07	5·07	1·95	1·52	~5·0	~5·0	~5·0
10^5k_1	3·64	3·62	3·71	3·57	28·2	52·8	149

(2.2) *Rate and Products of Alkaline Hydrolysis of the* trans-*Chloro-cation.*—In these experiments the *trans*-chloro-cation was supplied as its nitrate, always at a concentration of 0·0004M, and sodium hydroxide was introduced in the series of concentrations, 0·005, 0·01, 0·02, 0·04, 0·08 and 0·12N, all to within 1%. In timed samples, the alkaline reaction was stopped by acidification with perchloric acid, and the absorption at 3290 Å was then measured at 0° : this could be done with sufficient dispatch to avoid error from continuing aquation.

The observed changes of extinction are illustrated in Fig. 2, though most of the runs were followed for longer periods than can be represented on that diagram. The uppermost curve applies to aquation at pH 5, whilst the lower curves represent the successively faster reactions which occur with successively increased concentrations of alkali.

The extinction curves for the alkaline reactions do not run down to the aquation asymptote of 975, but stop at their own asymptote, or close group of asymptotes, at 1045 ± 3 cm.$^{-1}$ mole^{-1} l. The small amount of aquation that must accompany the hydroxide-ion reaction in these experiments can affect the position of individual asymptotes only within the range indicated, which is of the order of the error of measurement : the corresponding uncertainty in composition of product is only 0·3%. The final extinction quoted shows that alkaline hydrolysis of the *trans*-chloro-cation is producing 94% of *trans*-hydroxy- and 6% of *cis*-hydroxy-cation.

In all alkaline runs except the two most dilute in sodium hydroxide, this reagent, being in 50-fold or greater excess, suffers only a negligible change of concentration. In any one such run, the change of extinction coefficient follows the first-order rate law to within the observational accuracy, as is exemplified by the logarithmic plot in Fig. 3. This simple kinetic form shows that the reaction products contributing to the measured absorption are being produced simultaneously in a constant ratio.

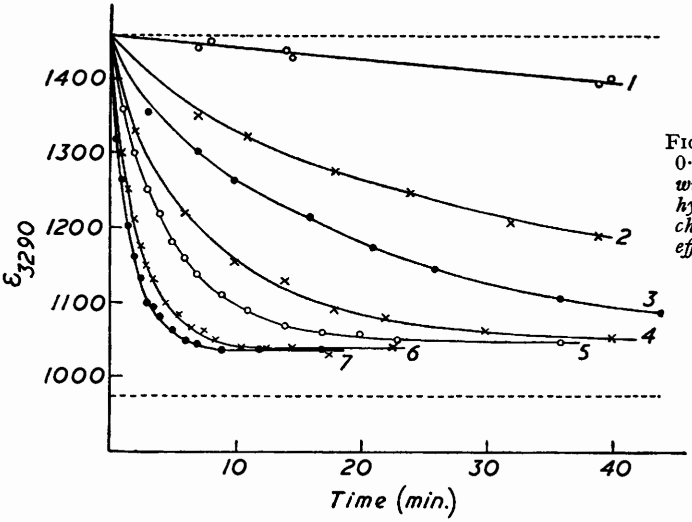

FIG. 2. *Kinetics of the reactions of* 0·0004M-trans-[Co $en_2(NO_2)Cl]^+NO_3^-$ *with water and aqueous sodium hydroxide at* 0°, *as followed by the change in the molar extinction coefficient at* 3290 Å :

Curve 1, *at* pH 5·07; *and Curves* 2, 3, 4, 5, 6, and 7, *with* 0·005, 0·01, 0·02, 0·04, 0·08, *and* 0·12N-*sodium hydroxide respectively.*

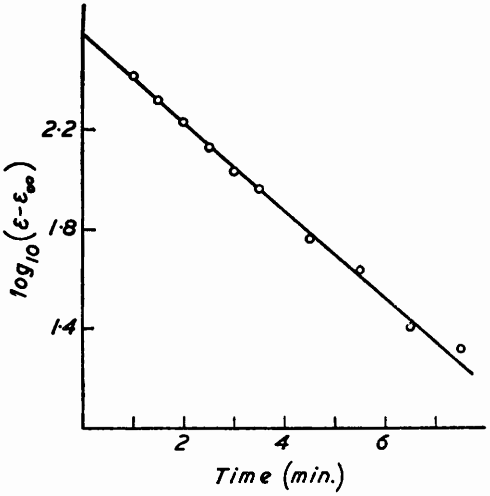

FIG. 3. *Logarithmic plot of the falling molar extinction coefficient in the reaction of* 0·0004M-trans-[Co $en_2(NO_2)Cl]^+NO_3^-$ *with aqueous* 0·08N-*sodium hydroxide at* 0° (*Run no.* 122).

The first-order rate constants, obtained by this procedure from the runs to which it is applicable, were found to be proportional to the concentrations of hydroxide ion. This shows that the alkaline hydrolysis is a reaction of second-order overall. Having established this, we broadened our procedure for the extraction of second-order rate constants, so that it remained applicable at the lower alkali concentrations, when aquation is not a negligible constituent of the measured process. This was simply a question of making appropriate allowances for aquation, the specific rate of which had been independently determined (Sect. 2.1). A general procedure for calculating individual rate constants from observations on mixed reactions of different orders has previously [11] been given.*

The second-order constants for the destruction by alkaline hydrolysis of the *trans*-chloro-cation are in Table 2. They reveal no definite salt effect, but two points are to be noted in this connexion. First, the relatively high rate of aquation caused us to use higher alkali concentrations than we might have chosen, and thus our range of ionic strengths is far from the region where rate (as log k_2) is most sensitive to ionic strength (as $\mu^{\frac{1}{2}}$). Secondly, most of the reactions are fast (often with half-change times of a very few minutes) and so considerable casual errors could not be avoided.

TABLE 2. *Second-order rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.) for the reaction of hydroxide ion with* trans-*chloronitrobis(ethylenediamine)cobalt*(III) *in water at* 0°.

Run	107	106	105	121	122	123
$[OH^-]_0$	0·005	0·01	0·02	0·04	0·08	0·12
k_2	0·074	0·077	0·083	0·079	0·083	0·081

Mean k_2 = 0·080 sec.$^{-1}$ mole^{-1} l.

(2.3) *Rate and Product of Aquation of the* cis-*Chloro-cation.*—This isomer, supplied as its weighed chloride, was made up in 0·0004M- or 0·00667M-solution in water, as described in Sect. 2.1 for the *trans*-isomer, with or without added perchloric acid, and the change of absorption intensity at 3290 Å with time was measured over the temperature range 0—40°. The extinction coefficient ran from the value 1554, appropriate to the *cis*-chloro-cation, to 2100 cm.$^{-1}$ mole^{-1} l.; and this we interpret to mean that the pure *cis*-aquo-cation is being produced.

The change followed a first-order law to within the observational error. It appeared to be insensitive to acid catalysis. The measured rate constants, in Table 3, show that, at the investigated temperatures, the aquation of the *cis*-chloro-ion is 7—10 times slower than of the *trans*-isomer. The variation of the rate of aquation of the *cis*-chloro-ion with temperature is expressed by the equation $k_1 = B_1 \exp(-E/\boldsymbol{R}T)$, where $B_1 = 2{\cdot}8 \times 10^{12}$ sec.$^{-1}$, and $E = 22{\cdot}35$ kcal./mole.

TABLE 3. *First-order rate constants (k_1 in sec.$^{-1}$) for aquation of the* cis-*chloronitrobis(ethylenediamine)cobalt*(III) *ion in water.*

Run	108	115	203	204	202
Temp.	0·0°	0·0°	20·0°	30·0°	40·0°
pH	5·14	2·08	~5·0	~5·0	~5·0
10^5k_1	0·365	0·332	6·06	20·5	66·6

(2.4) *Rate and Products of Alkaline Hydrolysis of the* cis-*Chloro-cation.*—Except that the *cis*-chloro-cation was supplied as weighed chloride, the initial conditions in this series of experiments corresponded exactly to those of the series on the alkaline hydrolysis of the *trans*-chloro-cation.

The observed changes in the extinction coefficient at 3290 Å of acidified timed samples are illustrated in Fig. 4; but most of the runs were followed over longer periods than can

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* It can be simplified in the present application. If k_2^* and k_1^* are the inexact second- and first-order "constants," calculated by the usual integrated equations, for a reaction consisting of mixed second- and first-order components, of which the true rate constants are k_2 and k_1, respectively, then, quite generally,

$$k_2 = k_2^* - k_1/(b - x) + t\mathrm{d}k_2^*/\mathrm{d}t$$

But in all the present examples it is a sufficient approximation to write

$$k_2 = k_2^* - k_1/(b - x)$$

and in several of them this equation can be simplified to

$$k_2 = (k_1^* - k_1)/(b - \tfrac{1}{2}x_\infty)$$

It must be remembered that our measured spectral intensity is a more sensitive indicator of aquation than of the alkaline reaction in the average ratio 1·34 : 1, so that we must write $1{\cdot}34k_1$, instead of k_1 when calculating k_2 directly from spectral intensities.

[11] Hughes, Ingold, and Shapiro, *J.*, 1936, 231.

be accommodated to that diagram. The lowest curve applies to aquation at pH 5, and the succession of curves above it represent the successively faster reactions which occur as increasing quantities of hydroxide ion are introduced. The illustrated crossing of two curves is not accidental: more crossings would be seen if the diagram were extended towards the right.

The asymptotic extinction coefficient for aquation lies far above the diagram at 2100 cm.$^{-1}$ mole^{-1} l. The alkaline reactions run to much lower asymptotes, which are not coincident, but are spread over the small range 1712—1736 cm.$^{-1}$ mole^{-1} l., the faster runs ending on lower values: that is how the crossings occur. About one-third of the spread in the asymptotes can be understood as arising from the varying proportions in which aquation occurs, and the differing compositions of the products of the alkaline reaction and of aquation. But we calculate that, if aquation could be fully suppressed, the asymptotes would still be spread over the range 1712—1728 cm.$^{-1}$ mole^{-1} l. The mean value, 1720 cm.$^{-1}$ mole^{-1} l., corresponds to production, by alkaline hydrolysis of the *cis*-chloro-cation, of an average of 66% of the *cis*-hydroxy- and 34% of the *trans*-hydroxy-cation. The range of ±8 cm.$^{-1}$ mole^{-1} l. in the extinction coefficient corresponds to a variation of ±0·7% in composition of product; and this we take to be a medium effect of the alkali on the direction of reaction: it is, or course, a very small effect.

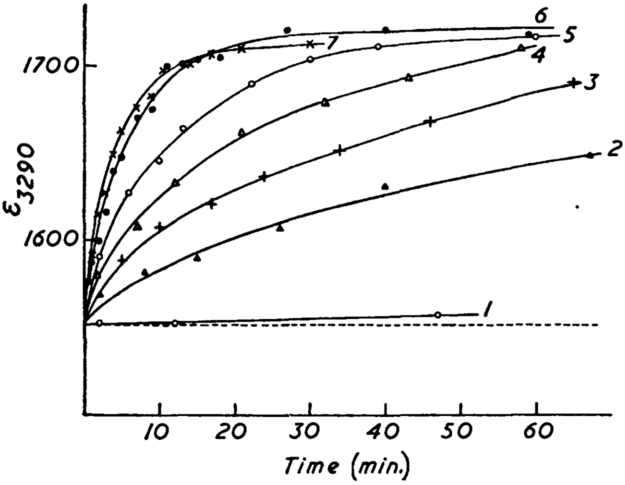

FIG. 4. *Kinetics of the reaction of* 0·0004M-cis-$[\mathrm{Co\,en_2(NO_2)Cl}]^+\mathrm{Cl}^-$ *with water and aqueous sodium hydroxide at* 0°, *followed by the change in the molar extinction coefficient at* 3290 Å:

Curve 1, *at* pH 5·14; *and Curves* 2, 3, 4, 5, 6, *and* 7, *with* 0·005, 0·01, 0·02, 0·04, 0·08 *and* 0·12N-*sodium hydroxide, respectively.*

Just as before, we showed that, with the hydroxide ion in constant excess, the absorption intensity follows a first-order rate law, and yields first-order rate constants proportional to the concentrations of hydroxide ion. Obviously we were again dealing with a second-order reaction, the light-absorbing products of which were being formed simultaneously in a fixed ratio. We then calculated second-order rate constants for the hydroxide-ion reaction, with due allowance for the accompanying aquation, using the procedure described in Sect. 2.2.*

The second-order constants for destruction of the *cis*-chloro-cation are in Table 4.

TABLE 4. *Second-order rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.) for the reaction of hydroxide ion with* cis-*chloronitrobis(ethylenediamine)cobalt*(III) *in water at* 0°.

Run	114	112	109	113	124	125
$[\mathrm{OH}^-]_0$	0·005	0·01	0·02	0·04	0·08	0·12
k_2	0·029	0·035	0·031	0·033	0·032	0·030

Mean k_2 = 0·032 sec.$^{-1}$ mole^{-1} l.

They show more scatter than do the corresponding values for the *trans*-chloro-cation. In the *cis*-series, the alkaline hydrolysis is 2·5 times slower, but the spectral indication of

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* The formulæ are the same, except that the sensitivity factor, to be multiplied into k_1, is now 5·76.

reaction progress is 2·5 times less sensitive, than in the *trans*-series. For reasons given in Sect. 2.2, it is not surprising that our results reveal no clear salt effect.

(3) *Summary and Discussion.*

(3.1) *Results.*—The main results reported in the preceding Sections are collected in Table 5.

(3.2) *Orientation in Bimolecular Hydrolyses.*—Of the three types of reaction distinguished in Table 5, the alkaline hydroxylations (*A*) belong to the type for which mechanism is best authenticated: having regard to the kinetic investigation of octahedral cobalt substitutions described in Part II,[3] and the observed kinetic form of the present alkaline hydroxylations, we can safely assign to them the bimolecular mechanism, S_N2. We recall that, in Part II, the other mechanism that would be consistent with the second-order form of the reaction, *viz.*, that which starts with an extraction by the basic reagent of a nitrogen-bound proton from an ethylenediamine ligand, was excluded, because this mechanism requires that the rate with different reagents should run parallel to their proton-affinity, indeed, it should be proportional to their base strength, whereas the rates observed showed no kind of parallelism to base strength.

TABLE 5. *Rate and steric course of reactions in water of bis(ethylenediamine)cobalt(III) ions containing the nitro-ligand.*

Reaction type	Kinetic order	Displaced group (X)	Temp.	Rate constant	Products (%)	
					cis	*trans*
(*A*) *cis*- or *trans*-$[Co\,en_2(NO_2)X]^+ + OH^- \longrightarrow$ *cis*- and *trans*-$[Co\,en_2(NO_2)OH]^+ + X^-$				k_2 (sec.$^{-1}$ mole^{-1} l.)		
S_N2	2	*trans*-Cl	0°	0·080	6	94
	2	*cis*-Cl	,,	0·032	66	34
(*B*) *cis*- or *trans*-$[Co\,en_2(NO_2)X]^+ + OH_2 \longrightarrow$ *cis*- and *trans*-$[Co\,en_2(NO_2)OH_2]^{2+} + X^-$				10^5k_1 (k_1 in sec.$^{-1}$)		
Aquation	1	*trans*-Cl	0°	3·63	0	100
	,,	,,	30	149	0	100
	,,	*cis*-Cl	0	0·365	100	0
	,,	,,	30	20·5	100	0
(*C*) *cis*- or *trans*-$[Co\,en_2(NO_2)X]^{2+} \longrightarrow$ *cis*- and *trans*-$[Co\,en_2(NO_2)X]^{2+}$						
Isomerisation	—	*trans*-OH_2	~90°	—	31	69
		cis-OH_2	,,	—		

This conclusion requires further remark, because it is the starting point of our present argument, and it has recently been challenged,[12] though, as we think, groundlessly. The stated grounds are that the replacement, in cations such as *trans*-dichlorobis(ethylenediamine)cobalt(III), of the bis(ethylenediamine) by either tetrapyridyl or bis-αα-dipyridyl residues, which have no nitrogen-bound hydrogen, leads to an easy aquation, which is not appreciably accelerated by alkali up to pH 9·18. It was inferred that the absence of nitrogen-bound hydrogen in these aromatic complexes has excluded the normal mechanism of alkaline hydrolysis, thus leaving aquation in control. This is a most dubious conclusion. The high rates, especially in the dipyridyl complexes, where the chelate ligand is sterically more comparable to ethylenediamine (for the possibility of steric hindrance has to be remembered), point clearly to a promoted aquation, *i.e.*, to a mechanism facilitated, rather than to one excluded, by the bond properties of the aromatic groups. We would explain this on the basis that the facilitated aquation is a unimolecular solvolysis (cf. Sect. 3.2), as of a diphenylmethyl halide, and that it is facilitated for a like reason, *viz.*, that the aromatic π-electrons are conjugated with the electrons of the breaking bond. In the matter of formal conjugation, the replacement of an ethylenediamine ligand in a chloro-cobalt(III) complex by two pyridyl ligands is like passing from a *cyclo*pentyl halide to a diphenylmethyl halide, a change which, as we know, gives greatly increased prominence to unimolecular reactions.

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[12] Pearson, Meeker, and Basolo, *J. Inorg. Nucl. Chem.*, 1955, **1**, 341.

The present work provides a further reason why the challenge offered cannot be considered successful. This is that its authors would have obtained essentially the same result had they derived their material from *trans*-dichlorobis(ethylenediamine)cobalt(III) by leaving the ethylenediamine ligands in position, and simply replacing one chlorine atom by a nitro-group: this would have given the *trans*-chloronitro-cation, which is as familiar to them [3, 4] as it is to us. Now the greatest hydroxide concentration which they used when searching for the alkaline reaction in their pyridine and dipyridyl complexes was 333 times smaller than the smallest that we employed for the purpose of measuring the alkaline reaction of the chloronitro-complex. It will be obvious from Fig. 2 (p. 2868), by imagining the gap between the top two curves to be narrowed to 1/333 of its present width, that, had these authors included the chloronitrobis(ethylenediamine) complex in their comparisons, its alkaline reaction also would have been undetectable at their alkalinities, *viz.*, up to pH 9·18. Yet nitrogen-bound protons are here available. Indeed, if the alkaline reaction really depended on their extraction, it should appear, not merely with its previous prominence, but with an increased prominence, because the electron-attracting nitro-substituent must increase the susceptibility of the protons to extraction by basic reagents.

Since the above was written, two further papers claiming support for the proton extraction mechanism have come to hand. Their arguments are unsatisfying. In the first,[13] the principal new observation is that second-order chlorine-displacement from the chloropentamminecobalt(III) ion by the action of OD^- in D_2O is appreciably slower than by OH^- in H_2O. Now, the known hydrogen-exchange rates of cobaltammines [12] show that, in the proposed mechanism, the initial hydrion loss could not be rate-determining: it could occur only as a pre-equilibrium, yielding a complex ion which slowly and spontaneously loses a chloride ion. The authors do not make it clear that, in this, its only possible, form, their proposed mechanism does not predict their observed rate order. This mechanism would be similar to the known mechanism of the alkaline splitting of diacetone alcohol, which is effected faster by OD^- in D_2O than it is by OH^- in H_2O [15]: here the alcoholic hydrion is rapidly and reversibly partitioned with the external base, to leave an organic ion which slowly and spontaneously loses an anion.

In the other paper,[16] the central observation is that, when, in the chloropentamminecobalt(III) ion, four ammonia groups are replaced by two ethylenediamine ligands, and thereafter by one triethylenetetramine ligand, the alkaline hydrolysis rates successively rise, while the aquation rates successively fall. There are several possible explanations of this: one is that, as more hydrocarbon ties stretch across the surface of the ion, the compactness of its aqueous solvation shell is reduced, so that penetration by an external anion becomes easier, while the water reaction itself becomes less easy. The authors assume, without alternative, that the hydrocarbon loops make proton extraction easier, and therefore make the alkaline rate greater: arguing backward, they claim that this supports their mechanism. We shall show below that the indubitably acid strengthening nitro-group reduces alkaline hydrolysis rate, though it accelerates aquation.

For these reasons, we shall base further discussion on the conclusion of Part II, that the hydroxide-ion reactions are bimolecular substitutions, S_N2. Now it was noted in Part I that, independently of mechanism, in such octahedral substitutions as ours, the occurrence of stereo-change, in the form described as edge-displacement in the individual molecular acts of substitution, is only conditionally reflected in the observable stereochemical result of the substitution. A *trans*-factor, substituted with microchemical stereo-change, will give a macrochemical *cis*-product, and without it, will give a *trans*-product. However, a *cis*-factor, substituted with microchemical stereo-change, may give macrochemically either a *cis*- or a *trans*-product, but without it, will certainly give a *cis*-product.

The results which we report for S_N2 substitution by hydroxide ion of the *trans*-form

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[13] Adamson and Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261.

[14] Anderson, Briscoe, and Spoor, *J.*, 1943, 361.

[15] Nelson and Butler, *J.*, 1938, 957.

[16] Pearson, Meeker, and Basolo, *J. Amer. Chem. Soc.*, **1956**, **78**, 709.

of the chloronitro-cation can therefore be exactly translated into molecular terms: 94% of the individual molecular acts of substitution proceed with retention of configuration, and only 6% of them take place with edge displacement. From the data for the corresponding S_N2 substitution of the *cis*-chloronitro-cation, only the less definite inference can be drawn that not more than 66% of the individual molecular transactions retain configuration, and at least 34% of them involve edge displacement.

A question of some interest is answered by the contrast between these results and those reported in Parts IV and V [2] for the corresponding reaction of analogous halogeno*iso*thiocyanato- and halogenoammine-cations, especially the results applying to *trans*-structures, which yield the more definite molecular conclusions. The investigation which led to the present work was begun with the knowledge that all S_N2 carbon substitutions involve exclusive stereo-change. It was then observed that S_N2 cobalt substitutions in the *iso*thiocyanato- and ammino-structures proceed with predominating, but not exclusive, stereo-change. As far as could be seen at that stage, a less exclusive version of the rule for S_N2 carbon substitutions might have been the effective rule for bimolecular octahedral substitutions. However, we now see that this is not so, since substitution in the *trans*-nitro-structure proceeds mainly with retention of configuration. Though the previous results might have suggested the contrary, an orientation phenomenon is undoubtedly involved in the directional control of S_N2 cobalt substitutions, the place of the entering group, in relation to that of the expelled group, depending on groups whose state of binding is not disturbed.

In the study of orientation in aromatic substitution, much enlightenment followed from a consideration of the relation of orientation to rate of substitution. Although we have only a few data, it seems not too early to begin applying the same method to cobalt substitutions, and therefore Table 6 has been constructed, which gives the partial rates of formation of the separate products of bimolecular displacement of halogen by hydroxide ion from bis(ethylenediamine)cobalt(III) ions, each containing a characteristic "orienting" group. The data are from Parts IV and V, as well as from this paper.

TABLE 6. *Second-order rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.) for the formation of individual isomers by substitution in bis(ethylenediamine)cobalt(*III*) ions by hydroxide ions in water at* 0°.

Structure of Co en$_2$-complex			Total rate, k_2	Product		Partial rates	
				cis (%)	*trans* (%)	k_2 (*cis*)	k_2 (*trans*)
trans	NCS	Cl	0·34	76	24	0·26	0·080
"	NH_3	"	1·25	76	24	0·95	0·30
"	NO_2	"	0·080	6	94	0·005	0·075
trans	NCS	Br	1·95	81	19	1·58	0·37
cis	NCS	Cl	1·40	82	18	1·15	0·25
"	NH_3	"	0·50	84	16	0·42	0·08
"	NO_2	"	0·032	66	34	0·021	0·011
cis	NH_3	Br	3·32	85	15	2·82	0·50

On the special subject of this paper, a question which one might ask is whether, in the substitution of *trans*-complexes (to deal with the simpler situation first), the nitro-ligand orients so differently from the *iso*thiocyanato- and ammino-ligands because, relatively to them, it accelerates substitution with retention of configuration, or because relatively to them, it retards substitution with edge displacement. The answer, indicated by Table 6, is that the nitro-group exerts its orienting effect by selective *inhibition*: it inhibits entry of the substituting agent in any position that would require a stereo-change. An equivalent statement is that the nitro-group inhibits entry adjacent to itself. And of these two statements, we believe the second to be the more significant, because we have to take into account the data for the substitutions of the *cis*-complexes. These figures show that the nitro-group does not oppose stereo-change *as such*, as it might conceivably have done, *e.g.*, by causing a tighter anchoring of those ethylenediamine ligands which have to shift during stereo-change. In fact, the amount of demonstrable stereo-change in the substitution of the *cis*-nitro-complex is considerable, and is comparable to that of any of the *cis*-complexes. The rate figures for the *cis*-structures suggest further that the nitro-group may have some retarding effect on substitution in all positions as well as a selective inhibition of substitution in positions adjacent to itself.

The electronic characteristic which in organic chemistry singles out the nitro-group from most other groups is its great constitutional capacity conjugatively to combine with unsaturation electrons, so increasing the multiplicity of its own binding, and at the same time polarising the system supplying the electrons. We may plausibly suppose that the nitro-group acts thus on the cobalt atom, increasing the multiplicity of its binding to cobalt, and polarising the cobalt atom with respect particularly to its outer layer of six unshared *d* electrons. This electron shell will, then, be displaced in the direction of the nitro-group. The first effect to be expected of such a displacement is an inhibition of anion attack in positions adjacent to the nitro-group, and hence an orientation of the attack towards the other side of the cobalt atom. Here, the polarisation of cobalt should provide more open access to the reagent; and, if that were all that we had to take into account, the reaction should go faster. But the same polarisation of cobalt will oppose heterolysis of the departing halogen: as always in bimolecular nucleophilic substitution, the question of whether a polar substituent will accelerate or retard reaction depends on a balance of opposing effects, in particular, on whether the importation of electrons by the substituting agent, up to the stage described as the transition state, needs only a smaller, or is conditional on a larger, simultaneous release of electrons towards the departing group. Both sorts of balance are found in bimolecular nucleophilic substitutions on carbon. Our present results suggest that, in these substitutions on cobalt, the electron release is slightly the more important of the two processes of electron transfer which are involved in the formation of the transition state. The case is analogous, for example, to bimolecular nucleophilic substitutions of benzyl and of allyl halides by anions, where also an excess of electron release is required to produce the transition state.

Conjugative binding of unshared metal electrons by a ligand has been suggested by Chatt in explanation of *trans*-substitution to certain ligands, *e.g.*, ethylene, in square platinous complexes.[17] Here the directing ligand appears to have a large accelerating effect, but as yet there has been no kinetic study of mechanism in such clear cases, although second-order kinetics have been established for some probably related square platinous substitutions.[18]

The above picture of orientation in bimolecular substitution by anions at octahedral cobalt suggests the existence of two broad classes of orienting groups, probably with a certain degree of merging. Cyano- and carbonyl groups are likely to exhibit, though not to the same quantitative extent, tendencies similar to that of the nitro-group, towards the promotion of substitution, probably at somewhat reduced rates, remotely from the orienting group, and thus with predominating retention of configuration when a *trans*-group is displaced. Halogeno-, azido-, and aquo-groups are likely broadly to resemble the *iso*thiocyanato- and the ammino-group in not restricting substitution in their neighbourhood, thereby allowing substitution to proceed with extensive stereo-change, and, when a *trans*-group is displaced, with predominating stereo-change.

It is here implied that there are two transition states for these bimolecular octahedral substitutions, and that their bonding energies are not very different, although, in the absence of conjugative disturbances to the bonding, the transition state for substitution with edge-displacement is more stable than that for substitution with a preserved configuration. It is not necessary to construe this polar interpretation as a denial that steric effects may in some circumstances be important for octahedral orientation, *i.e.*, that a complete theory would add the non-bonding energy to the bonding.

In most published discussions of the steric course of octahedral substitution, the reagent is represented as attacking within a face of the octahedron, and the expelled group as departing from a corner. This is not a useful approach to the structure of the transition state, because the principle of microscopic reversibility requires that, in that state, the

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[17] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456, and references there cited.

[18] Zuyagintsev and Karandasheva, *Doklady Akad. Nauk U.S.S.R.*, 1955, **101**, 93.

attacking and displaced groups will have a like geometrical relation to the rest of the structure: an octahedron elaborated in one face does not fulfil the symmetry condition for a transition state. A recent suggestion is that the transition state has the form of a pentagonal bipyramid with attacking and displaced groups symmetrically located.[5] This figure imports more symmetry than the principle of microscopic reversibility demands, and it has the objection that five bond-angles are reduced to 72°, the remaining ten angles being unreduced, whereas we should expect smaller deviations from the normal 90° among angles between full bonds, and deviations more evenly spread among angles between bonds of a like kind.

In order to provide such angles, it is necessary to satisfy the symmetry condition only in a minimal way; and this is done in the two transition states which we assume for these substitutions. Some idea of them can be conveyed by indicating, as is done in Fig. 5, the relation between the points occupied and the octahedral corners from which the occupying groups have come or to which they will go. Transition state (I) is for substitution with retention of configuration: it might be set up if the electrons of the nucleophilic reagent were to engage in a lateral attack on the main lobe of the cobalt bond orbital to the displaced group. Transition state (II) is for substitution with edge displacement: it could arise from attack by the reagent on the backward pointing cap-shaped member of the bond orbital.[19]

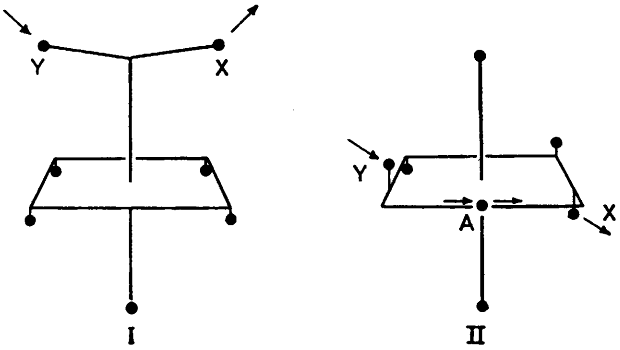

FIG. 5. *Geometry of bimolecular transition states in octahedral substitution,* I *without, and* II *with edge displacement.* Y *is the entering,* X *the departing, and* A *the internally displaced group. The positions of these groups, and of the undisplaced groups, in the transition state are shown in qualitative relation to the octahedral positions of the initial and final states.*

(3.2) *Mechanism of Aquation.*—Despite an original intention to have nothing to do with aquation until easier mechanistic problems had been solved, we have been unable to avoid either making observations on it, as noted already, or forming opinions about it, which may be worth indicating, though the supporting observations are less systematic than if they had been planned.

The main suggestions emerge when we analyse rates of aquation, somewhat as we did those for alkaline hydrolysis. This is done in Table 7, in which many of the rate figures are only approximate, because we need to compare rates at common temperatures, and the measurements were made at various temperatures providing in some cases only a rough basis for the extrapolations involved. Some figures are approximate for other reasons explained in the notes below the Table. Figures are included which are derived, directly or indirectly, from the work of other investigators, notably of Mathieu. Indirect derivations are explained in the notes. We are able to cite, in addition to the main series of values applying to bis(ethylenediamine)cobalt(III) ions, some further values relating to analogous tetra-amminecobalt(III) ions.

When the theory of duality of mechanism in nucleophilic substitution at saturated carbon atoms was advanced 20 years ago, the main arguments in support of that concept were expressed in two schematic diagrams,[20] one showing that, as electron release from influencing substituents was changed in a progressive way, rate of substitution passed through a minimum, and the other that as the nucleophilic power of the substituting agent was progressively decreased, the rate at first fell and then remained constant, each

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[19] Ingold, *Chem. Soc. Spec. Publ. No.* 1, p. 10.
[20] Gleave, Hughes, and Ingold, *J.*, 1935, 236.

of these changes of rate trend being associated with a change of kinetic order, whenever order depended on mechanism. In Part II of this series,[3] a diagram corresponding to the second of these was shown to express the dependence of rate of substitution at a cobalt atom on the nucleophilic power of the substituting agent; and on this evidence, the theory of duality of mechanism was extended to octahedral substitutions. On examining Table 7,

TABLE 7. *Comparison of first-order rate constants* (k_1 *in* sec.$^{-1}$) *and proportions of products for aquation of bis*(*ethylenediamine*)*- and tetrammine-cobalt*(III) *ions in water.*

$$[CoR_4YX]^{n+} + H_2O \longrightarrow [CoR_4YOH_2]^{(n+1)+} + X^-$$

$R_4 = en_2$			10^5k_1		Products (%)			
	Y	X	0°	30°	*cis*	*trans*	Ref.	Note
cis	OH	Cl	~2·3	~90	—	—	Mathieu	*a*
trans	Cl	,,	0·075	6·2	0	~100	,,	*b*
cis	,,	,,	0·44	25	100	0	,,	*b*
trans	NCS	,,	0·000043	0·010	—	—	Part IV	—
trans	NH_3	,,	0·00097	0·067	—	—	Part V	—
cis-	,,	,,	~0·0024	~0·091	—	—	,,	*c*
trans	NO_2	,,	3·63	149	0	100	Part VI	—
cis	,,	,,	0·365	20·5	100	0	,,	—
trans	NCS	Br	0·00021	0·043	43	57	Part IV	—
cis	NH_3	,,	0·0053	0·30	—	—	Part V	—
cis	NH_3	NO_3	0·036	2·8	—	—	,,	—
R = am_4			20°					
trans	Cl	Cl	72		—	—	Ovenston	*d*
cis	,,	,,	82		—	—	,,	*d*
trans *cis*	NH_3	,,	0·083		—	—	Garrick	*e*
trans *cis*	NH_3	Br	0·65		—	—	Brown	*f*

(*a*) The rate is from observations by Mathieu (*Bull. Soc. chim. France*, 1936, **3**, 2121, 2152) on the variation of the rate of aquation of *cis*-$[Co\,en_2(OH_2)Cl]^{2+}$ with its concentration in water, and with pH in aqueous buffers, at 30°, together with the acid strength for the above cation, as he determined it with a glass electrode at 20°, assuming a zero heat of aqueous dissociation of the acidic cation, and 20 kcal./mole as the activation energy for the aquation, a value adopted after making a survey of known activation energies for aquation in the bis(ethylenediamine)cobalt(III) series. The stereochemistry of the product $[Co\,en_2(OH)(OH_2)]^{2+}$ must be regarded as unknown, because the *cis*- and the *trans*-form of this cation have been shown to undergo reversible interconversion at a rate which must be comparable with that of their collective formation at the relevant pH values (Basolo, *J. Amer. Chem. Soc.*, 1950, **72**, 4393; J. Bjerrum and Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1265).

(*b*) Rate data by Mathieu (*locc. cit.*) have been halved, since we require the rate of displacement of one particular chlorine for comparison with the other rate figures in the Table. The products must be at least approximately as stated, because Mathieu (*Bull. Soc. chim. France*, 1936, **3**, 2121; 1937, **4**, 687) has shown that *cis*-$[Co\,en_2Cl_2]^+$ gives first *cis*-$[Co\,en_2Cl(OH_2)]^{2+}$, and then a diaquo-product containing much *cis*-$[Co\,en_2(OH_2)_2]^{3+}$, whilst Bjerrum and Rasmussen have preparatively converted *trans*-$[Co\,en_2Cl_2]^+$ by aquation into *trans*-$[Co\,en_2(OH_2)_2]^{3+}$ (*loc. cit.*), presumably by way of the isomeric intermediate *trans*-$[Co\,en_2Cl(OH_2)]^{2+}$, which Meisenheimer and Kinderlen prepared (*Annalen*, 1924, **438**, 238), and Uémura and Hirasawa showed to be fairly stable in acid solution (*Bull. Chem. Soc., Japan*, 1938, **13**, 377).

(*c*) An activation energy of 22 kcal./mole has been assumed, following a survey of analogous known activation energies.

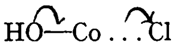
(*d*) Rates by Ovenston (Thesis, London, 1936) are halved as explained for a similar case under (*b*) above.

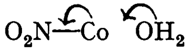
(*e*) Garrick, *Trans. Faraday Soc.*, 1937, **7**, 486.

(*f*) Brown (Thesis, London, 1952) with the aid of data by Lamb and Fairhill (*J. Amer. Chem. Soc.*, 1923, **45**, 378), and by Brönsted (*Z. phys. Chem.*, 1926, **122**, 383).

we find that a diagram similar to the first of the former ones will express the variation of rate of the cobalt substitutions with the electron release or attraction of the orienting substituent.

It being assumed that, as is usually true for carbon substitutions, the strongest kinetic polar effects are electromeric, the extreme of electron release among the groups considered will be shown by the hydroxyl substituent, the unshared electrons of which can be conjugated through cobalt with the bond electrons of the departing ligand; and the extreme of electron attraction will be exhibited by the nitro-group, the unsaturation orbitals of which are available for conjugation with cobalt, and thence with the bonding electrons of the entering radical by a mechanism to be suggested below :





As to the remaining groups, we assume, on the basis of organic chemical analogies, that Cl will act most nearly like OH, and NH_3^+ most nearly like NO_2. The position of NCS is not theoretically unambiguous, but we might expect a behaviour intermediate between that of Cl and NH_3^+ on the empirical ground that the ready oxidation of this ligand with loss of sulphur suggests that its unsaturation electrons are concentrated on that atom, *i.e.*, that this ligand is present in cobalt complexes in a form approximating to $-\overset{+}{N}{\equiv}C{-}\overset{-}{S}$. We thus arrive at the polar series, OH, Cl, NCS, NH_3^+, NO_2 ; and, on examining the data we find that, in this series, the rate changes as is illustrated schematically in Fig. 6. Here the group NCS has been placed at the minimum, although all that we really know is that it is nearest to the minimum.

Although it has not the status of a proof, this continued reproduction in cobalt substitutions of the pattern of kinetic effects which constituted the originally offered evidence of duality of mechanism in carbon substitutions seems very significant. In Part II it was argued,[3] on the basis of a less complete reproduction of kinetic pattern than is now disclosed, that a similar duality of mechanism applies to octahedral substitution by anionic reagents. The present suggestion is that, just as a like duality applies, in organic chemistry to solvolysis, including aqueous solvolysis, which could alone provide a diagram like Fig. 6, so it applies, in the chemistry of octahedral complexes, to solvolytic aquation.

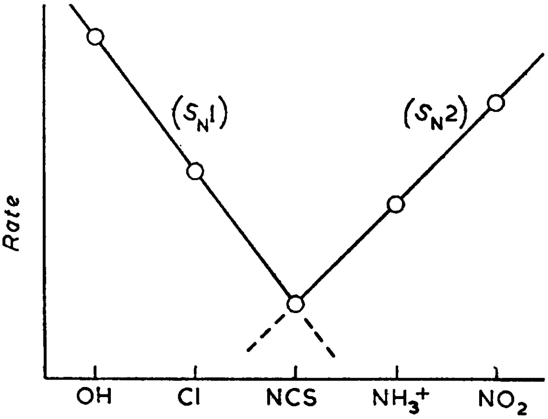


FIG. 6. *Schematic illustration of the variation of rate of aquation with the polar effect of the orienting substituent in substituted halogeno-bis(ethylenediamine)- and halogeno-tetra-ammine-cobalt*(III) *ions; illustrating the theory of duality of mechanism in octahedral solvolysis.*

Pearson *et al.* argued [21] in favour of the unimolecular mechanism of aquation when presenting data for the rate of aquation of *trans*-dichlorocobalt(III) complexes: they found that *C*-alkylation in an ethylenediamine residue increased the rate, and explained this as a steric acceleration. They noted that such an explanation on a purely steric basis must inevitably be incomplete, and that their interpretation had its difficulties, one of which was that *C*-alkylation in a trimethylenediamine residue produced a retardation. Brown *et al.* argued,[2] on the general grounds of the nucleophilic activity of water towards metal atoms, that the bimolecular mechanism should appear in aquation.

The decreasing rate along the S_N1 branch in Fig. 6 is easy to understand : electrons must be supplied to the seat of substitution in order to facilitate electron transfer to the departing ligand : no compensating electronic condition weakens this requirement, inasmuch as electron importation by the substituting agent does not occur in the rate-controlling stage of the unimolecular mechanism. The increasing rate along the S_N2 branch, and the accompanying orientational change from NCS to NO_2, require to be discussed.

[21] Pearson, Boston, and Basolo, *J. Amer. Chem. Soc.*, 1953, **75**, 3089.

First, as to rate—the picture is different from that presented by the S_N2 reaction with hydroxide ions. In this alkaline reaction, as we have seen already, all the rate effects are much milder, and for the nitro-group are mildly retarding. But now for aquation, we find a strong increase of rate along the series NCS, NH_3^+, NO_2. Hence we assume that there must be some difference of mechanism between alkaline hydrolysis and solvolytic aquation.

It will be clear that we cannot introduce the required difference by retaining the concept of bimolecular alkaline hydrolysis, and making aquation unimolecular in the series NCS, NH_3^+, NO_2. For that would require the diametrically opposite rate trend for aquation: the nitro-group should be very strongly retarding relatively to the other groups, whereas in fact it is very strongly accelerating.

We could understand the accelerating influence of the nitro-group if we could rationalise the assumption that aquation, when bimolecular, occurs as a form of S_N2 substitution in which, for some reason to be considered, the polarisation-demand of the binding of the water is much more important than that of the loosening of the displaced group. We could, of course, say, simply and fairly plausibly, that the water molecule is so much less strongly nucleophilic than the hydroxide ion that it needs more help from polarisation to bring it into reaction. But a more detailed, if speculative, description is suggested by the theory [22] that the weaker bonds of transition metals are formed with the participation of " higher " *d* orbitals. Outside the completely full 3*d* orbitals of the octahedral cobalt atom, and its fully occupied set of $3d^24s4p^3$ bond orbitals, but not much higher in energy, lie the empty 4*d* orbitals, which in principle provide weak binding sites for nucleophilic molecules. A site of this kind might have such an energetic value that it could " evaporate," and so bind, a water molecule from solvent water, even though it could not desolvate, and so bind, an aqueous anion, such as hydroxide ion. Clearly such a 4*d*-binding of water would be greatly assisted were the underlying 3*d*-shell to be pulled out of the way, as by a nitro-substituent. And once a water molecule had been so bound, it might be energetically easy for it, and a potentially anionic ligand, to exchange their forms of binding, with the result that the anion could be solvated, as by hypothesis it would be, and so could escape, whilst the water molecule would remain in the structure.

Secondly, concerning orientation—as for alkaline hydrolysis, so for solvolytic aquation, we find that a change of orienting group from NCS to NO_2 leads to increased retention of configuration; but that, relatively to alkaline hydrolysis, the orientation of aquation exhibits a general displacement in the direction of increased retention of configuration. The first of these points can be understood on the basis of the preceding picture; and so can the second, if we add the idea that the assumed exchange of bond types begins to be felt during the binding of the water, the more so if the exchanging bonds are in proximity.

EXPERIMENTAL

(4.1) *Preparations.*—*trans*-Chloronitrobis(ethylenediamine)cobalt(III) nitrate and *cis*-chloronitrobis(ethylenediamine)cobalt(III) chloride were prepared as outlined in Sect. 1.1, the former four times (Found: Co, 18·3; C, 14·9; H, 5·0; N, 26·1; Cl, 11·0. Calc.: Co, 18·2; C, 15·0; H, 5·0; N, 25·8; Cl, 10·7%), and the latter three times (Found: Co, 19·9; C, 16·2; H, 5·45; N, 23·7; Cl, 24·0. Calc.: Co, 19·95; C, 16·3; H, 5·8; N, 23·5; Cl, 23·8%). All the preparations gave good analyses, and all of the same salt gave identical absorption curves, as measured on the Cary instrument under the conditions described in Sect. 1.1.

The preparations of *trans*- and *cis*-aquonitrobis(ethylenediamine)cobalt(III) sulphates were accomplished as mentioned in Sect. 1.4 (Found for the *trans*-salt: Co, 17·25; C, 15·3; H, 5·4; N, 20·3; S, 9·8; Cl, 0·01. Found for the *cis*-salt: Co, 17·2; C, 14·7; H, 5·6; N, 20·4; S, 9·4; Cl, 0·3. Calc.: Co, 17·4; C, 14·2; H, 5·35; N, 20·65; S, 9·45; Cl, 0·0%). Both aquo-salts are difficult to prepare, and the analyses indicate the presence of impurities, which could not be removed. We know from its spectrum that the *trans*-sulphate contained a little naphthionate.

(4.2) *Spectrophotometry.*—Apart from the use already mentioned of the Cary Quartz Recording Spectrophotometer for purity control, all absorption intensity measurements were made with a Unicam quartz spectrophotometer S.P. 500, the 10-mm quartz cell being used. The windows of this were kept clear of mist with the aid of silica gel.

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[22] Taube, *Chem. Rev.*, 1952, **59**, 69; Burstall and Nyholm, *J.*, 1952, 3570; Nyholm and Sharpe, *ibid.*, p. 3579; Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

(4.3) *Kinetics.*—Ice-water in a large Dewar vessel served as the thermostat. The acid runs require no description. For the alkaline runs, the necessary amount of aqueous sodium hydroxide, and of the dry cobalt salt, were brought to reaction temperature in separate 500-ml. flasks, and then the alkaline solution was poured on to the cobalt salt, which dissolved immediately, at what then became the time-zero. Timed samples were subsequently delivered into cooled vessels containing a few drops of concentrated perchloric acid, and the absorption intensity at 3290 Å was measured at once, against similarly acidified blank solutions.

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William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.

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