complex, a strong labilizing of the other ligands is produced by the π-bonding.

Postmus and King have also shown[27] that in the reaction of the aquo chromium(III) ion with thiocyanate ion, the hydroxo complex $Cr(H_2O)_5OH^{+2}$ is more reactive than $Cr(H_2O)_6^{+3}$. This can be explained in terms of a dissociation mechanism with a five-coördinated intermediate stabilized by π-bonding. A similar situation exists for the acid hydrolysis of $SbCl_6^-$ which is less reactive than $SbCl_5OH^-$.[28] In short, there is no reason to believe that π-bonding is not a common occurrence in all octahedral complexes regardless of the nature of the central atom.

Acknowledgment.—The authors are indebted to Dr. R. E. Meeker for the measurements reported in Table I and Drs. Meeker and H. M. Neumann for stimulating discussions in connection with this paper.

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(27) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).

(28) H. M. Neumann, THIS JOURNAL, **76**, 2611 (1954).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions in Complex Ions. XI.[1] Rates of Hydrolysis and Racemization of Difluoro-bis-(ethylenediamine)-cobalt(III)[2,3]

BY FRED BASOLO, WILLIAM R. MATOUSH AND RALPH G. PEARSON

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The rates of acid and base hydrolysis of *trans*-$[Coen_2F_2]^+$ were determined and found to be much slower than the corresponding rates of reaction of *trans*-$[Coen_2Cl_2]^+$. In addition, unlike the dichloro complex, the rate of acid hydrolysis of the difluoro compound is acid catalyzed. A mechanism is proposed to account for this which involves the intermediate formation of a protonated complex. Finally the loss of optical rotation of *d-cis*-$[Coen_2F_2]^+$ was found to proceed in two steps. The first step is a mutarotation due to the formation of *d-cis*-$[Coen_2H_2OF]$ and this then slowly undergoes racemization.

The synthesis and reactions of some fluoroamminecobalt(III) complexes, as well as the resolution of *racemic* isomers, was described earlier.[4] Investigations on these complex ions have now been extended to kinetic studies of hydrolysis reactions and the mutarotation and racemization of optically active isomers. These data are presented here and compared with similar data for the corresponding chloro and bromo complexes.

Experimental

Compounds.—The coördination compounds used were prepared as previously described;[4] all other compounds were commercially available and of reagent grade.

Kinetic Methods for Rates of Acid Hydrolysis.—Three different methods were used to follow the rate of acid hydrolysis. The selection of a method depended, to some extent, on the nature of the complex under investigation.

1. **Spectrophotometric Method.**—This method was applicable to a study of *trans*-$[Coen_2F_2]^+$, since there is a large difference in the optical density of this complex and the product, $[Coen_2H_2OF]^{2+}$, at 500 mμ. The change in optical density at this wave length was followed until the replacement of one fluoride ion was substantially complete and a "leveling off" of the rate was observed. The second fluoride is replaced much more slowly than the first and therefore does not interfere greatly with the determination of the rate of the first step. All measurements were made on a Beckman Model DU Spectrophotometer using cells of 1-cm. path length. Temperature control to within ±0.1° was achieved by pumping water from a constant temperature bath through the compartment surrounding the cells. At low temperatures where the reaction is quite slow, the reaction mixture was kept in the thermostat and aliquots were periodically withdrawn for measurement of optical density. The data obtained gave good first order plots of t *vs.* log $(D_\infty - D)$ and the rate constant k was estimated from the slope of the line (Table II).

2. **Chemical Method.**—The spectrophotometric method was not applicable to the *cis*-difluoro complex because of only negligible spectral changes during hydrolysis. It was therefore necessary to devise a method to follow this reaction by determining the fluoride ion concentration in these colored solutions. This chemical method was also used to check the results obtained by the spectrophotometric method for the *trans* isomer; results by the two methods were in good agreement.

The standard procedure[5] of fluoride analysis by titration with thorium nitrate solution using a sodium alizarin sulfonate indicator was finally adapted to a study of these systems. The primary difficulty was that of visually detecting the end-point in these colored solutions. The possibility that the colored complex could be removed on a cation exchange resin and thus permit the usual determination of fluoride on the resulting colorless solution was first examined. The results obtained were not satisfactory as it appeared that adsorption of the complex on the resin induced the release of coördinated fluoride ion. A technique was finally developed that gave satisfactory results for solutions containing the colored complex ion. In a typical determination, two aliquots were withdrawn from the thermostated reaction mixture. One of these was used in combination with the standard indicator blank, such that on horizontally viewing through both solutions, an approximation to the end-point color was observed. The second aliquot was also placed in front of the standard indicator blank and in the same way viewed horizontally through both solutions. Titration was then carried out with thorium nitrate solution and the end-point detected by reference to the first aliquot plus indicator blank combination. Although this method was tedious, it did give satisfactory results for the first half-life of the reactions studied. Beyond this point the intensity of color increased and deviations in fluoride analyses became correspondingly larger. The data obtained gave good first order plots of t *vs.* log $(T_\infty - T)$, where T is the gross thorium nitrate titer, and the rate constant k was estimated from the slope of the line (Table IV).

3. **Fractional Life Method.**—An approximate but rapid method of determining the acid hydrolysis rate of the *trans* difluoro complex was to observe the time required for the originally green colored solution to become almost colorless or gray in color. This marked the point at which the combined optical absorption due to the green reactant, *trans*-$[Coen_2F_2]^2$, and the red product, $[Coen_2H_2OF]^{2+}$,

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(1) Previous paper in this series, R. G. Pearson and F. Basolo, THIS JOURNAL, **78**, 4878 (1956).

(2) This investigation supported by a National Science Foundation Grant (NSF-G58) and by the U. S. Atomic Energy Commission under Contract AT(11-1)-89—Proj. No. 2.

(3) Presented in part at the International Conference on Coordination Compounds in Amsterdam, April, 1955.

(4) W. R. Matoush and F. Basolo, THIS JOURNAL, **78**, 3972 (1956).

(5) H. H. Willard and O. B. Winter, *Ind. Eng. Chem. Anal. Ed.*, **5**, 7 (1933).

was approximately equal throughout the visible range. As the reaction proceeded beyond this point the solution became red in color. It was first necessary to determine the fractional life of the reaction which was represented by the colorless point, using as reference one of the other standard kinetic procedures. An expression relating the first order rate constant to a general fractional life, t_f, of a reaction is given by equation (1)

$$kt_f = \ln 1/(1 - f) \qquad (1)$$

Substitution of the values for the known rate constant and time required to reach this colorless point in (1) gave a value of $f = {}^1/_5$, this representing approximately the fifty-life of the reaction. Having established this it was then possible to estimate the rate constant of this reaction under a variety of experimental conditions by substitution in the specific expression (2)

$$k = 0.223/t_{1/5} \qquad (2)$$

Such a method is subject to somewhat greater errors than either of the other two methods described above but it has the advantage of being much more convenient. Usually several determinations were averaged, with the range of values of rate constants not exceeding ±10%.

Acid and Salt Dependence of Rate of Acid Hydrolysis.—A semiquantitative study of the dependence of the rate of acid hydrolysis on the acid concentration was made by the fractional life method. The solutions were 0.004 *M* in complex ion and the concentration of nitric acid was varied over the range 0.0001–4.0 *M*. Studies were also made with neutral solutions of the complex containing potassium nitrate over the concentration range 0.1–2.0 *M*. The results obtained are summarized in Table I.

TABLE I

RATES OF HYDROLYSIS OF *trans*-$[Coen_2F_2]^+$ AS A FUNCTION OF HYDROGEN ION CONCENTRATION

(A) Nitric acid solutions (25°)[a]

$[HNO_3]$	k(min.$^{-1}$) × 10^5
4.0	5000
3.5	3900
3.0	3400
2.5	2600
2.0	2100
1.0	680
0.5	300
0.1	52
0.01	10
0.001	6
0.0001	6
no HNO_3	6
0.1 to 2.0 *M* KNO_3	6

(B) Buffer solutions (59.3°)[b]

Buffer Solution	*p*H	k(min.$^{-1}$) × 10^3
KNO_3-HNO_3	1.01	85
KNO_3-HNO_3	2.04	11
$KHC_8H_4O_4$-HNO_3	2.54	8.0
$KHC_8H_4O_4$-HNO_3	2.98	7.2
$KHC_8H_4O_4$-NaOH	3.96	6.9
$KHC_8H_4O_4$-NaOH	4.98	7.6
$KHC_8H_4O_4$-NaOH	6.00	13
KH_2PO_4-NaOH	6.92	36
KH_2PO_4-NaOH	7.70	94

[a] Determinations were made by the visual fractional life method. [b] Spectrophotometric method was used and buffers are Clark and Lubs formulations.[6]

Since the aquofluoro reaction product is an acid, the acidity of the nitric acid solution changes during reaction, especially for those of low acidity. Therefore a second series of determinations were made using buffered solutions (*p*H 1.0–8.0)[6] and these results are also summarized in Table I.

Studies in Deuterium Oxide.—The rates of acid hydrolysis of *trans*-$[Coen_2F_2]^+$ were determined in light and heavy water under comparable reaction conditions. In each case the reaction mixture contained 0.004 *M* complex and 0.1 *M* *p*-toluenesulfonic acid and the rates were followed spectrophotometrically at 25° ± 0.1°. Since only small volumes were used, the reaction solutions were sealed with paraffin in 1-cm. quartz cells, and these were partly immersed in a thermostated bath during the intervals between spectral readings. The deuterium oxide was obtained from the Stuart Oxygen Co. and had an assay of 99.8%. The results obtained are shown in Table III.

Rates of Base Hydrolysis.—The flow apparatus and technique employed to determine rates of base hydrolysis were described in a previous publication.[7] The base hydrolysis data are included in Table II.

TABLE II

RATES OF ACID HYDROLYSIS (0.1 *N* HNO_3) AND OF BASE HYDROLYSIS OF *trans*-$[Coen_2X_2]^+$ AT 25°

Complex	Acid hydrolysis k_{H_2O} (min.$^{-1}$)	Acid hydrolysis E_a (kcal.)	Base hydrolysis k_{OH^-} (1 mole^{-1} sec.$^{-1}$)
trans-$[Coen_2F_2]^+$	5.5×10^{-4}	29	64
trans-$[Coen_2Cl_2]^+$	1.9×10^{-3}[a]	27[a]	3.0×10^3[b]
trans-$[Coen_2Br_2]$	8.4×10^{-3}	26	1.2×10^4

[a] R. G. Pearson, C. R. Boston and F. Basolo, THIS JOURNAL, **75**, 3089 (1953). [b] See reference 7.

Kinetics of Mutarotation and Racemization.—The rate of loss of optical activity of aqueous acid solutions of *d-cis*-$[Coen_2F_2]NO_3$ was examined. A Bellingham and Stanley polarimeter was used to determine the optical rotations of the reaction solution, which was contained in a 1-dm. polarimeter tube. This tube was kept in a thermostated bath with a temperature control of ±0.1° and removed only briefly while making the rotational determinations. Rotations were measured at the sodium D line and each rotation was the average of at least five separate determinations. The complex concentrations were of the order of 0.003 *M*.

The kinetic data were plotted for a first order process, $\log -(\alpha_\infty - \alpha)$ *vs.* t where α is the observed angle of rotation. Although the rotation at infinite time, α_∞, is zero, the data obtained for a 0.1 *N* nitric acid solution fell into two linear portions (Fig. 1). By extrapolation of the second leg of the plot back to zero time, the approximate rotation of the intermediate product, *l-cis*-$[Coen_2H_2OF]^{2+}$, was determined from the intercept. Recalculation of the first portion of the data, using this estimated infinity value, yielded the rate of the first step. Both this rate of mutarotation and that of racemization of the second step are shown in Table IV.

Results and Discussion

The largest amount of ionic character in a metal halogen bond is ascribed to M–F. In general, it is believed that the greater the ionic character of a chemical bond, the more labile it will be.[8] However, this gross generalization is not without exception.[9] The rates of acid and base hydrolysis reported here (Table II) for the haloamminecobalt(III) ions afford another striking illustration that the more "ionically bonded" ligand is the least labile.

It was found that the lability of the Co–X bond increases in the order $F^- << Cl^- < Br^-$ which is analogous to the trend in C–X reported for organic compounds.[10] It will be noticed that in alkaline solution variations in rate between the fluoro and chloro complexes is much greater than that between the corresponding chloro and bromo compounds, *i.e.*, ratio of base hydrolysis rates are Cl/F∼50 and Br/Cl∼4. The acid hydrolysis data shown in Table II are misleading in this respect as they show both ratios to be approximately four. These data were obtained at a *p*H of 1 which, as will be discussed later, is in fact an acid catalyzed rate for the difluoro complex. A slightly better comparison would be with the minimum rate reached at *p*H 3–5 which then gives a ratio of rates, Cl/F∼30. An even better comparison would be with the rate obtained by extrapolation of the

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[6] N. A. Lange, ed., "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1949, Seventh Ed., pp. 1127–8.

[7] R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 709 (1956).

[8] C. H. Johnson, *Trans. Faraday Soc.*, **31**, 1612 (1935).

[9] F. Basolo, J. C. Hayes and H. M. Neumann, THIS JOURNAL, **76**, 3807 (1954).

[10] W. T. Miller, Jr., and J. Bernstein, *ibid.*, **70**, 3600 (1948).

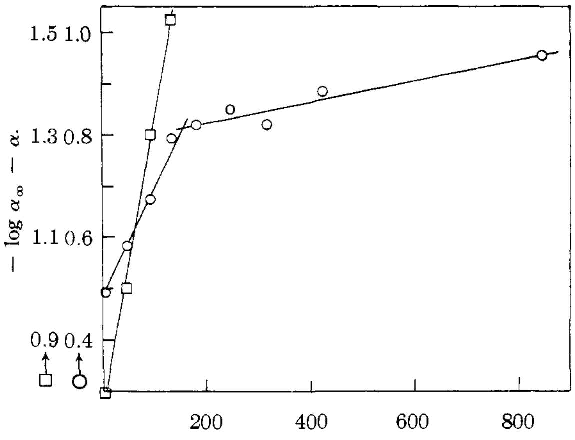

Fig. 1.—Mutarotation and racemization of *d-cis*-$[Coen_2F_2]NO_3$ in 0.1 *N* nitric acid at 35°: original plot -○——○-, plot of mutarotation using adjusted infinity value -□——□-.

linear portion of the acid catalyzed acid hydrolysis and base hydrolysis (Fig. 2) until these lines intersect, this presumably would give the rate of the acid hydrolysis without any acceleration due either to acid catalysis or base hydrolysis. Although this extrapolation cannot be too accurate it does give, as an order of magnitude, the ratio of rates Cl/F∼ 300. It is of interest to note that these rates do correlate the crystal field strengths of the coördinated halide ions which decrease in the order $F^- > Cl^- > Br^-$.[11]

The acid hydrolysis of *trans*-$[Coen_2F_2]^+$ was found to be acid catalyzed (Table I), whereas it is known[12] that chloro and bromo complexes react at a rate independent of hydrogen ion concentration at a *p*H below 4. This means that the hydrolysis of fluoroamminecobalt(III) ions is unique in being both acid and base catalyzed (Fig. 2). Base catalysis is normal and is a result of increasing contribution of the rapid base hydrolysis reaction to the total observed rate of hydrolysis. Acid catalysis is believed to be due to the greater base strength and hydrogen bonding tendency of the fluoride ion compared to chloride or bromide ions. Thus, it is postulated that the complex is first protonated and then that this species is much more reactive than the non-protonated form

$$[Coen_2F_2]^+ + H^+ \rightleftarrows [Coen_2F_2H]^{2+} \quad (3)$$

$$[Coen_2F_2H]^{2+} + H_2O \xrightarrow{\text{slow}} [Coen_2H_2OF]^{2+} + HF \quad (4)$$

According to this mechanism step (3) is a rapid acid–base equilibrium and the rate determining step, (4), is therefore dependent on the first power of the concentration of the complex and also of the hydrogen ion. That this is essentially correct is shown by the unit slope of the straight line obtained from a plot of log *k vs.* log $[H^+]$.

Additional support that the acid catalysis is due to an acid–base equilibrium (3) is obtained from the rates of reaction in hydrogen oxide compared to deuterium oxide (Table III). The greater (45%) rate in heavy compared to normal water is attributed to a larger concentration of the reactive intermediate, since it is known that weak acids are less dissociated in heavy water.[13] Some organic reactions that exhibit specific hydrogen ion catalysis are also reported to be more rapid in heavy than in ordinary water.[14] It is further significant that the acid hydrolysis of chloro and bromo complexes which do not proceed by this mechanism are slower in heavy water than in light water.[15]

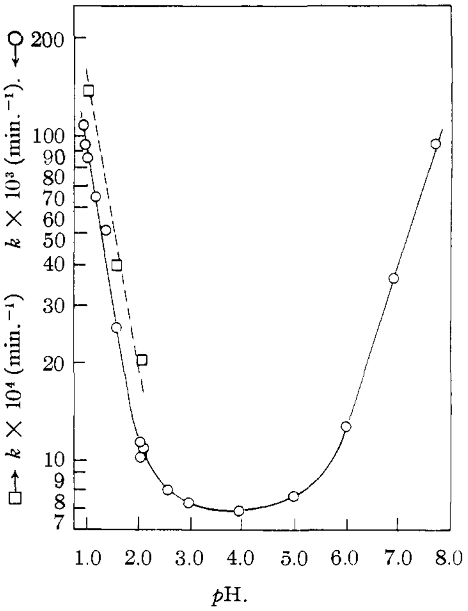

Fig. 2.—*p*H dependence in the acid hydrolysis of *trans*-$[Coen_2F_2]NO_3$ at 59.3° (-○——○-) and 45.4° (-□ - - - □-)

TABLE III

RATES OF ACID HYDROLYSIS IN LIGHT AND HEAVY WATER

Complex	Temp., °C.	Solvent	k(min.$^{-1}$)
trans-$[Coen_2F_2]^{+a}$	25	H_2O	7.7×10^{-4}
	25	D_2O	1.1×10^{-3}
$[Co(NH_3)_5Cl]^{2+b}$	52	H_2O	2.53×10^{-3}
	52	D_2O	1.65×10^{-3}

[a] Spectrophotometric method on solutions 0.0004 *M* in complex and 0.1 *M* in *p*-toluenesulfonic acid. [b] See reference 15.

Although acid catalyzed hydrolysis of haloamminecobalt(III) ions is limited to the fluoro compounds, it is not uncommon for reactions of complex ions. The hydrolyses of carbonato and sulfito complexes are greatly accelerated by increased hydrogen ion concentration[16] as is also the exchange of radiocyanide with some cyano complexes.[17] The rates of dissociation of fluoride and of cyanide ions from ferrimyoglobin fluoride and cyanide are acid catalyzed.[18] Similarly the rates of dissocia-

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(11) K. Fajans, *Naturwiss.*, **11**, 165 (1923); R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388, 436 (1938); L. E. Orgel, *J. Chem. Soc.*, 4756 (1952); J. Bjerrum, C. J. Ballhausen and K. Jørgensen, *Acta Chem. Scand.*, **8**, 1275 (1954); H. Hartmann, *Z. physik. Chem.*, **4**, 376 (1955).

(12) A. B. Lamb and J. W. Marden, THIS JOURNAL, **33**, 1873 (1911).

(13) For references see V. K. LaMer, *Chem. Rev.*, **19**, 363 (1936).

(14) For references see W. F. K. Wynne-Jones, *ibid.*, **17**, 115 (1935).

(15) A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

(16) A. B. Lamb and K. J. Mysels, THIS JOURNAL, **67**, 468 (1945).

(17) A. W. Adamson, J. P. Welker and M. Volpe, *ibid.*, **72**, 4030 (1950).

(18) P. George and G. I. H. Hanania, *Biochem. J.*, **56**, xxxviii (1954).

tion of certain 2,2′-bipyridine[19] and ethylenediamine[20] metal complexes were likewise observed to be acid catalyzed. Finally it is of interest to note that the rate of alcoholysis of benzyl fluoride is acid catalyzed but that of other benzyl halides is not;[10] this is analogous to the behavior of the haloamminecobalt(III) complex ions.

The rate of loss of optical activity of an aqueous solution of *d-cis*-$[Coen_2F_2]^+$ at a *p*H of 1 shows clearly that this proceeds in two distinct steps (Fig. 1). There is first a change in optical rotation followed then by a slower loss of optical activity. Within rather large limits of experimental error, the initial mutarotation proceeds at approximately the same rate as does the hydrolysis under these same conditions (Table IV). This suggests that *d-cis*-$[Coen_2F_2]^+$ is converted to *d-cis*-$[Coen_2H_2OF]^{2+}$ without extensive loss in optical rotation. The fluoroaquo product in turn undergoes racemization at a rate independent of the rate of release of the second fluoride. No detailed kinetic study was made of the hydrolysis of the second fluoride except to observe that it was very slow compared to the rate of loss of optical activity.

TABLE IV

RATES OF ACID HYDROLYSIS, MUTAROTATION AND RACEMIZATION OF *d-cis*-$[Coen_2F_2]^+$ GIVEN IN $k(min.^{-1})$.

$[HNO_3]$	Temp., °C.	Acid hydrolysis	Mutarotation	Racemization
no acid	25	1.8×10^{-4}	...	...
0.001	25	3.6×10^{-4}	4.9×10^{-4}	$\sim 2 \times 10^{-4}$
0.1	25	3×10^{-3a}	6.2×10^{-3}	3.9×10^{-4}
0.1	35	1×10^{-2a}	1.3×10^{-2}	4.7×10^{-4}

[a] The method of removal of complex on an ion exchange resin prior to titration of fluoride was employed. Because of difficulties described in experimental these data are only semi-quantitative.

This change in optical rotation of an acid solution of *d-cis*-$[Coen_2F_2]^+$ is analogous to the behavior which Mathieu[21] reports for *l-cis*-$[Coen_2Cl_2]^+$. He suggests that since the rate of racemization of *d-cis*-$[Coen_2H_2OCl]^{2+}$ is not dependent on the rate of replacement of the chloro group, it must involve a dissociation of the coördinated water to yield a symmetrical intermediate. Recently[22] it was shown that the loss of optical activity is primarily due to isomerization to the symmetrical *trans*-$[Coen_2H_2OCl]^{2+}$ which can in turn regenerate the *racemic cis* isomer. Tentatively it can also be concluded that the racemization of *d-cis*-$[Coen_2H_2OF]^{2+}$ likewise proceeds by an exchange of coördinated water with the solvent. Before more definite statements can be made, it must be determined whether or not the rate of water exchange is sufficiently rapid to permit such a mechanism. One final point of interest is that the rates of racemization for a series of complex ions of the type $[Coen_2H_2OX]$ decrease with changes of X in the order $Cl^- > F^- > NO_2^- \sim NCS^- >> NH_3$. If all that is involved in racemization is the water exchange, then it is surprising that the chloroaquo complex racemizes approximately 200 times faster than does the nitroaquo whereas the rate of acid hydrolysis of *cis*-$[Coen_2Cl_2]^+$ is only twice that of *cis*-$[Coen_2NO_2Cl]^+$. This can be understood if the replacement of water in the nitroaquo complex takes place a larger percentage of the time without loss of optical activity as compared to the chloroaquo compound. This is in agreement with the π-bonding hypothesis[1] which predicts that the contribution of π-bonding electrons from chloride to cobalt in the pentacoördinated intermediate, $[en_2Co{=}Cl]^{2+}$, enhances the formation of a trigonal bipyramid structure whereas the tetragonal pyramid structure is favored for $[en_2Co\text{-}NO_2]^{2+}$ which does not have this type of π-bonding.

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[19] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 736 (1950); F. Basolo, J. C. Hayes and H. M. Neumann, THIS JOURNAL, **75**, 5102 (1953).

[20] J. Bjerrum, K. G. Paulsen and I. Paulsen, "Symposium on Coordination Chemistry," Danish Chemical Society, 51 (1953).

[21] J. P. Mathieu, *Bull. soc. chim.*, [5] **4**, 687 (1937).

[22] R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 2673 (1956).

EVANSTON, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, AND UNIVERSITY OF CONNECTICUT]

The Mechanism of the Formation and Rearrangement of Nitritocobalt(III) Ammines[1]

BY R. KENT MURMANN[2] AND HENRY TAUBE[3]

RECEIVED MAY 2, 1956

The formation of a group of nitritocobalt(III) ammines from the aquo complexes proceeds in weakly acidic solutions without breaking the cobalt–oxygen bond. The formation of the nitro derivative from nitritopentammine–cobalt (III) ion proceeds in water solution by an intramolecular process involving either the formation of a pentacoördinated intermediate followed by instantaneous reaction with the group released or *via* a heptacoördinated activated state.

I. Introduction

The rate of substitution of a ligand for another on cobalt(III) and chromium(III) coördination compounds is often quite slow. Certain ions, however, substitute more rapidly and a correlation between the nucleophilic character of these reactants and the rate and mechanism of the reaction has been made.[4] A consideration of the literature values of the rates of substitution reactions reveals a group which seem to proceed more rapidly than one would anticipate on this basis. Comparison of the following rates indicates that the fast group consists of the reaction between an aquo-coördination compound and a labile-oxygen containing

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[1] This work was supported in part by the ONR under contract N6-ori-02026.

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[3] George Herbert Jones Laboratory, University of Chicago, Chicago, Illinois.

[4] D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953).