

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

## The Effect of Chelation and of Alkyl Substitution on the Rate of Hydrogen Exchange in Cobalt(III) Amines

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RECEIVED AUGUST 12, 1959

The rates of hydrogen exchange in an acetate buffer between various cobalt(III) amines containing hydrogen-1 and heavy water are reported. These rates were determined by following the increase in OH concentration by measurements in the near infrared and in a few cases by n.m.r. For the hexamine and pentamine series of cobalt(III) complexes studied, the rate of hydrogen exchange increases with an increase in chelation and with increasing alkyl substitution. A smaller ligand effect was observed for the oxalatotetramminecobalt(III) complexes. The rates of hydrogen exchange of the chloropentaminecobalt(III) complexes are approximately  $10^6$  times faster than their rates of base hydrolysis. This result shows that the base hydrolysis of these complexes may proceed by an  $S_N1CB$  mechanism.

The base catalyzed hydrogen exchange of metal amines in aqueous solution was first investigated by Anderson, Briscoe and Spoor.<sup>1</sup> They observed that  $Co(en)_3^{+3}$  exchanges more rapidly than does  $Co(NH_3)_6^{+3}$ .<sup>2</sup> Recent studies of Block and Gold<sup>3</sup> show that  $Co(NH_3)_4C_2O_4^+$  exchanges hydrogen more slowly than  $Co(NH_3)_6^{+3}$ . In both of these investigations it was found that the rate of hydrogen exchange is specific hydroxide ion catalyzed.

The results of hydrogen exchange studies on such systems may be used to test the  $S_N1CB$  mechanism proposed for the base hydrolysis of cobalt(III) amines.<sup>4</sup> For example this mechanism requires that the hydrogen exchange rate of a given complex exceed its rate of base hydrolysis. Furthermore it is of interest to know whether chelation and alkyl substitution affect the rate of hydrogen exchange in a way similar to that reported for the rates of base hydrolysis. Studies have therefore been made on the rate of hydrogen exchange for three different series of cobalt(III) complexes.

The techniques used previously<sup>1,3</sup> for such studies are rather time consuming and not readily adaptable to investigations of a large number of different types of complexes. Therefore it was necessary to devise a more convenient method of following the rate of hydrogen exchange, preferably one not involving the separation of complex from solvent. It was found that this could be done by determining the rate of formation of OH bonds in a solution containing light ammine complex and heavy water. The OH concentration was measured either by absorption in the near infrared or by n.m.r. (nuclear magnetic resonance).

### Experimental

**Preparation of Compounds.**—Most of the compounds used in this investigation are known compounds and were prepared by the methods previously described.<sup>5</sup> Analogous new compounds were prepared by essentially the same methods. In all cases the compounds were characterized by analysis as well as by their absorption spectrum.

(1) J. S. Anderson, H. V. A. Briscoe and N. F. Spoor, *J. Chem. Soc.*, 361 (1943).

(2) These various symbols are used for amines: en = ethylenediamine; pn = propylenediamine; *d,l*-bn = *d,l*-butylenediamine; *i*-bn = isobutylenediamine; N-Meen = N-methylethylenediamine; N-*n*-Pren = N-*n*-propylethylenediamine; trien = triethylenetetramine; tn = trimethylenediamine; dien = diethylenetriamine.

(3) H. Block and V. Gold, *J. Chem. Soc.*, 966 (1959).

(4) For original references and discussion see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," J. Wiley and Sons, Inc., New York, N. Y., 1958, pp. 124-132.

(5) Gmelin, "Handbuch der anorganischen Chemie," 58B (1930).

For the hexamine series, the complexes  $[Co(d,l\text{-}bn)_3]I_3$ ,  $[Co(dien)_2]I_3$  and  $[Co(N\text{-}Meen)_3]I_3$  had not been reported previously. These were all prepared by the reaction of  $[Co(NH_3)_5Cl]Cl_2$  with an excess of diamine in the presence of a charcoal catalyst. The synthesis of  $[Co(d,l\text{-}bn)_3]I_3$  can be used to illustrate the general method of preparation. A reaction mixture containing 2 g. of  $[Co(NH_3)_5Cl]Cl_2$ , 3.5 g. of *d,l*-butylenediamine, 0.3 g. of activated charcoal and 25 cc. of water was digested on a steam-bath and occasionally stirred for a period of about 4 hr. At the end of this time the charcoal was removed on a filter and the orange colored filtrate was cooled in an ice-bath. To this cold solution was added 10 cc. of a saturated solution of KI to precipitate the desired iodide. The orange precipitate was collected on a filter and washed with a small amount of cold water, then by alcohol and ether. After drying overnight at 65° the salt weighed 2.5 g. (44% yield).

*Anal.* Calcd. for  $[Co(d,l\text{-}bn)_3]I_3$ : N, 11.9; I, 54.2. Found: N, 12.3; I, 54.5.

*Anal.* Calcd. for  $[Co(dien)_2]I_3$ : N, 13.0; I, 58.9. Found: N, 13.6; I, 59.0.

*Anal.* Calcd. for  $[Co(N\text{-}Meen)_3]I_3$ : C, 16.3; H, 4.54; I, 57.3. Found: C, 16.3; H, 4.7; I, 57.9.

The synthesis of  $[Co(trien)NH_2Cl](ClO_4)_2$  was described previously.<sup>6</sup>

For the oxalatotetrammine series, the complexes  $[Co(pn)_2C_2O_4]I \cdot 2H_2O$ ,  $[Co(i\text{-}bn)_2C_2O_4]Cl \cdot HCl$  and  $[Co(N\text{-}n\text{-}Pren)_2C_2O_4]I \cdot 4H_2O$  had not been reported previously. These were all prepared by the reaction of the appropriate dichlorotetrammine with a calculated amount of  $Ag_2C_2O_4$ . The synthesis of the dichlorotetrammine complexes was reported earlier.<sup>7</sup> The synthesis of the propylenediamine compound is typical of the method used. A reaction mixture containing 1.0 g. of *trans*- $[Co(pn)_2Cl_2]Cl$ , 1.8 g. of  $Ag_2C_2O_4$  and 15 cc. of water was heated on a steam-bath and occasionally stirred for a period of about 30 min. At the end of this time the  $AgCl$  was removed on a filter and the filtrate was cooled in an ice-bath. Addition of 5 cc. of a saturated solution of KI precipitated the pink colored iodide. This precipitate was collected on a filter, washed with a minimum amount of cold water, then with alcohol and ether. After drying at 65° the salt weighed 0.8 g. (45% yield).

*Anal.* Calcd. for  $[Co(pn)_2C_2O_4]I \cdot 2H_2O$ : N, 12.2. Found: N, 12.2.

*Anal.* Calcd. for  $[Co(i\text{-}bn)_2C_2O_4]Cl \cdot HCl$ : C, 30.4; H, 6.34. Found: C, 29.8; H, 6.32.

*Anal.* Calcd. for  $[Co(N\text{-}n\text{-}Pren)_2C_2O_4]I \cdot 4H_2O$ : N, 10.2. Found: N, 10.1.

**Determination of Rates of Hydrogen Exchange.**—The rates of hydrogen exchange were determined by measuring the increase in concentration of OH with time of a solution that originally contained the light complex in an acetate buffered heavy water solution. Most of these measurements were made by studies in the near infrared and a few were made by n.m.r. The two methods gave results that are in reasonably good agreement.

(a) **Infrared Method.**—Since  $D_2O$  does not absorb extensively in the near infrared, this region can be used for hydrogen exchange studies between hydrogen-1 metal am-

(6) R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, 59, 304 (1955).

(7) F. Basolo, *THIS JOURNAL*, 75, 227 (1953).

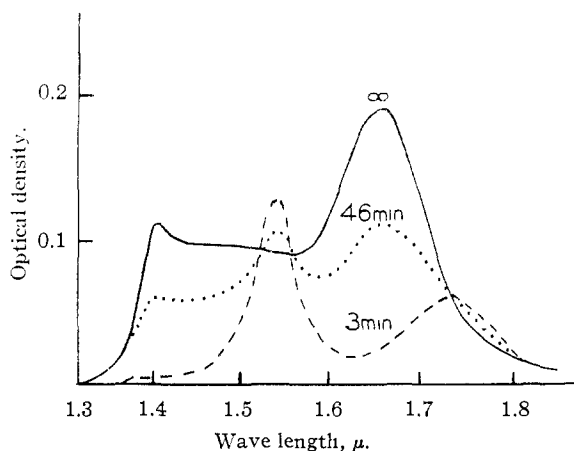


Fig. 1.—Change in the near infrared absorption spectrum of an acetate buffered  $D_2O$  solution of  $0.11 M Co(NH_3)_6^{+3}$  at  $25^\circ$ .

amines and the solvent  $D_2O$ . During the progress of hydrogen isotope exchange in these solutions, the NH absorption peak at  $1.53 \mu$  disappears and OH peaks form at  $1.65$  and  $1.40 \mu$  (Fig. 1). The rate of exchange is determined by following the disappearance of the NH absorption band or the appearance of the OH bands. Data collected at these three wave lengths are in good agreement. However the largest change in absorption occurs at  $1.65 \mu$  so that most of the measurements were made at this wave length.

All of the hydrogen exchange studies were carried out in  $D_2O$  buffered with sodium acetate and deuterium acetate. The buffer solution was prepared by adding anhydrous sodium acetate and acetic anhydride to 99.5%  $D_2O$  to give  $0.1 M NaC_2H_3O_2$  and  $0.1 M DC_2H_3O_2$ . Measurements were made with a Beckman Model DK-2 recording spectrophotometer which was equipped with a cell holder maintained at constant temperature ( $\pm 0.1$ ) by circulating water through it from a thermostatic water-bath. The buffer solutions were placed in glass stoppered 1 cm. quartz cells and allowed to come to equilibrium temperature. At this time a weighed amount of the ammine complex was added to one of the cells and dissolved by vigorous shaking. The absorption spectrum ( $1.4$ – $1.8 \mu$ ) of the solution then was recorded at various times.

The rates of hydrogen exchange were determined by plotting  $\log(H_\infty - H_t)$  versus  $t$  where  $H_\infty$  is the optical density at infinite time and  $H_t$  is the optical density at time  $t$ . The pseudo first order rate constants,  $k_{obsd.}$ , in these buffered systems are obtained by multiplying the slopes of these curves by  $-2.3$ . Thus the second order rate constants,  $k$ , reported are determined by  $k = k_{obsd.}/[OD^-]$ . The values of  $k$  are determined with a precision of 15%. Cobb and Anderson<sup>8</sup> have observed that  $Co(NH_3)_6^{+3}$  has a marked effect on the pH of a phosphate buffer solution. Likewise Block and Gold show that in these solutions it is more reliable to use the  $OH^-$  activity as calculated from the pH determination than the value estimated from the buffer ratio. Therefore the pH of acetate buffered  $H_2O$  solutions of each complex at exchange conditions was determined. In no case was the buffer pH decreased by more than 0.2 pH unit by the addition of complex at the concentrations used for hydrogen exchange studies. These small variations in pH were used in each case to adjust the values of  $[OD^-]$  calculated on the basis of a  $pK_a$  of 5.26 for  $DC_2H_3O_2$  and a  $K_f$  for  $D_2O$  of  $0.15 \times 10^{-14}$ . For complexes 8, 12 and 16 that exchange rapidly in the acetate buffer solution, the rates were also determined in  $0.1 M DC_2H_3O_2$ . The complex concentrations varied between 0.02 and 0.18  $M$ ; however, the rate constant for exchange does not depend on the concentration of complex.

(b) N.m.r. Method.—Nuclear magnetic resonance techniques have been used to determine rates of hydrogen exchange in various systems.<sup>10</sup> However, these methods

generally have been used to study extremely rapid exchange reactions. The method described here is used to follow exchanges having rates that can be determined by conventional kinetic techniques. As described earlier, the systems under investigation involve hydrogen-1 metal amines and  $D_2O$ . Proton resonance measurements were made with a Varian High Resolution 40 m.c. Spectrometer. Because of quadrupole coupling with the nitrogen nucleus, the N-H proton signal is flat and not well resolved. It remains much the same during the period of exchange. However, the O-H proton signal is very sharp and intense so that the rate of hydrogen exchange is determined readily from the increase of the O-H signal with time (Fig. 2).

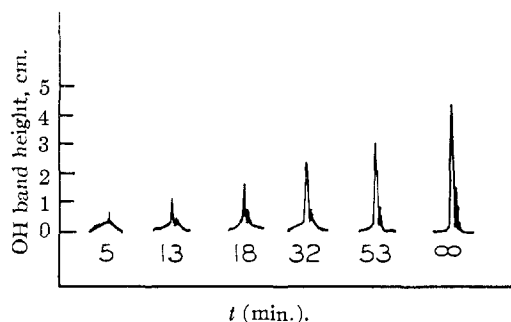


Fig. 2.—N.m.r. measurements of changes in the OH proton signal for a solution of  $Co(NH_3)_6^{+3}$  in buffered  $D_2O$  at  $25^\circ$ .

A weighed amount of complex was placed in a 5 mm. n.m.r. sample tube and about 2/3 of the tube was submerged in a Dry-Ice-acetone bath. To the cold tube was added 0.5 cc. of buffered  $D_2O$  which freezes before coming in contact with the solid complex. The tube then was sealed and placed horizontally in a water-bath at the desired temperature during which time the solid and liquid do not come in contact with each other. After the equilibrium temperature was reached, the tube was shaken to form the reaction solution and immediately placed in the RF receiver coil. Measurements of the spectrum were made at various times. The rate constants were determined as before from plots of  $\log(H_\infty - H_t)$  versus  $t$  where  $H_\infty$  is the OH peak height in mm. at infinite time and  $H_t$  is the peak height at time  $t$ . The results obtained by this method were in reasonably good agreement with the infrared method (Fig. 3). However since the n.m.r. technique was more difficult experimentally, the data reported here were largely collected by means of infrared studies.

## Results

Except for *cis*- $Co(en)_2(NH_3)_2^{+3}$  the hexammine series of complexes all gave linear plots of the hydrogen exchange data. Linear plots also were obtained for  $Co(NH_3)_5Cl^{+2}$  and  $Co(NH_3)_4C_2O_4^{+}$  but the other compounds gave a curved line. The result obtained for *cis*- $Co(en)_2NH_3Cl^{+2}$  is shown in Fig. 4. Making use of the method described by Frost and Pearson,<sup>11</sup> both fast and slow first order rate constants were evaluated. Similarly two rate constants were obtained for *cis*- $Co$ -(trien) $NH_3Cl^{+2}$  and *cis*- $Co(en)_2(NH_3)_3^{+3}$ . Only the initial average rate constants are reported for the oxalato series of compounds where the curvature observed was much less.

The second order rate constants, determined as described in the Experimental section, are tabulated in Tables I and II.

## Discussion

This investigation was carried out in an attempt to test the validity of the  $S_N1CB$  mechanism pro-

(8) L. H. Cobb and J. S. Anderson, *Trans. Faraday Soc.*, **40**, 145 (1943).

(9) S. Korman and V. K. La Mer, *THIS JOURNAL*, **58**, 1403 (1936). R. Kingerley and V. K. La Mer, *ibid.*, **63**, 3260 (1941).

(10) A. Berger, A. Lowenstein and S. Meiboom, *ibid.*, **81**, 62 (1959).

(11) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 150.

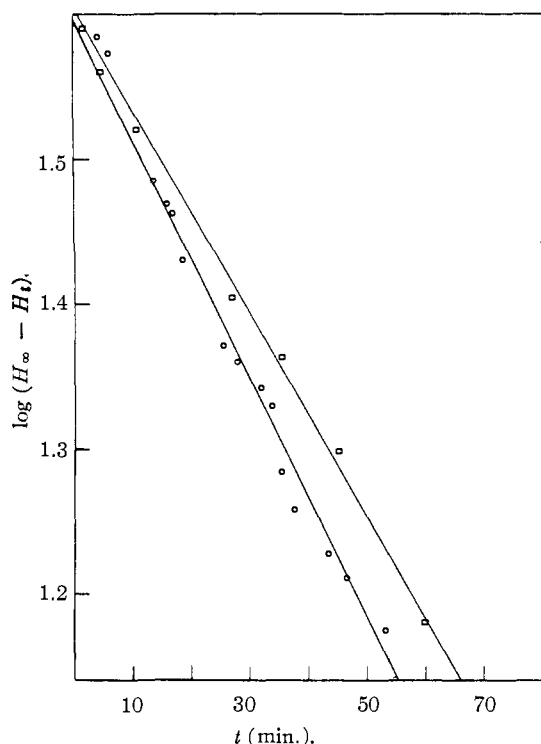
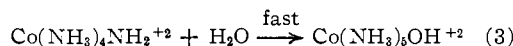
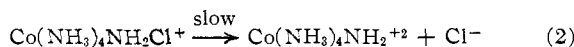
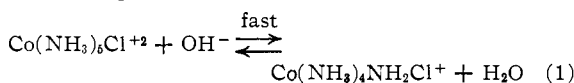


Fig. 3.—Comparison of hydrogen exchange rate data on the system  $\text{Co}(\text{NH}_3)_6^{+2}-\text{D}_2\text{O}$  as collected by the infrared method ( $\square$ ) and by n.m.r. ( $\circ$ ).

posed for the base hydrolysis of cobalt(III) amines. The reaction scheme for such a mechanism may be represented as



Therefore this mechanism requires that equilibrium (1) be more rapid than the rate of base hydrolysis. Since (1) leads to hydrogen exchange, this rate can be determined by measuring the rate of hydrogen exchange. It was only possible to make such a

TABLE I  
EFFECT OF CHELATION ON THE RATES OF HYDROGEN EXCHANGE OF SOME COBALT(III) AMMINES WITH ACETATE BUFFERED  $\text{D}_2\text{O}$  AT  $25^\circ$

| No.            | Complex  | Concn., $M$ | $k$ , $M^{-1}$ , $\text{sec}^{-1}$                 |
|----------------|--|-------------|--|
| 1              | $\text{Co}(\text{NH}_3)_6^{+3}$                        | 0.11        | $1.6 \times 10^6$                                  |
| 2              | $\text{cis-Co}(\text{en})_2(\text{NH}_3)_2^{+3}$       | .15         | $2 \times 10^7$ ( $1.3 \times 10^6$ ) <sup>a</sup> |
| 3              | $\text{Co}(\text{en})_3^{+3}$                          | .16         | $2.5 \times 10^6$                                  |
| 4              | $\text{Co}(\text{tn})_3^{+3}$                          | .16         | $1.1 \times 10^7$                                  |
| 5              | $\text{Co}(\text{dien})_2^{+3}$                        | .10         | $1.4 \times 10^7$                                  |
| 6 <sup>b</sup> | $\text{Co}(\text{NH}_3)_6\text{Cl}^{+2}$               | .06         | $1.5 \times 10^5$                                  |
| 7 <sup>b</sup> | $\text{cis-Co}(\text{en})_2\text{NH}_3\text{Cl}^{+2}$  | .18         | $1 \times 10^6$ ( $5 \times 10^4$ ) <sup>a</sup>   |
| 8 <sup>b</sup> | $\text{cis-Co}(\text{trien})\text{NH}_3\text{Cl}^{+2}$ | .10         | $5 \times 10^7$ ( $2 \times 10^5$ ) <sup>a</sup>   |

<sup>a</sup> Rapid rate is the rate of exchange of the  $\text{NH}_3$  hydrogens and the slow rate is that for the exchange of the N-H hydrogens of the chelating group. See Fig. 6 and text for the significance of these values. <sup>b</sup> The base hydrolysis rate constants for these complexes at  $25^\circ$  are: 6,  $8.5 \times 10^{-1} M^{-1} \text{sec}^{-1}$ ; 7,  $5.4 \times 10^{-1} M^{-1} \text{sec}^{-1}$ ; 8,  $1.6 \times 10^2 M^{-1} \text{sec}^{-1}$ .

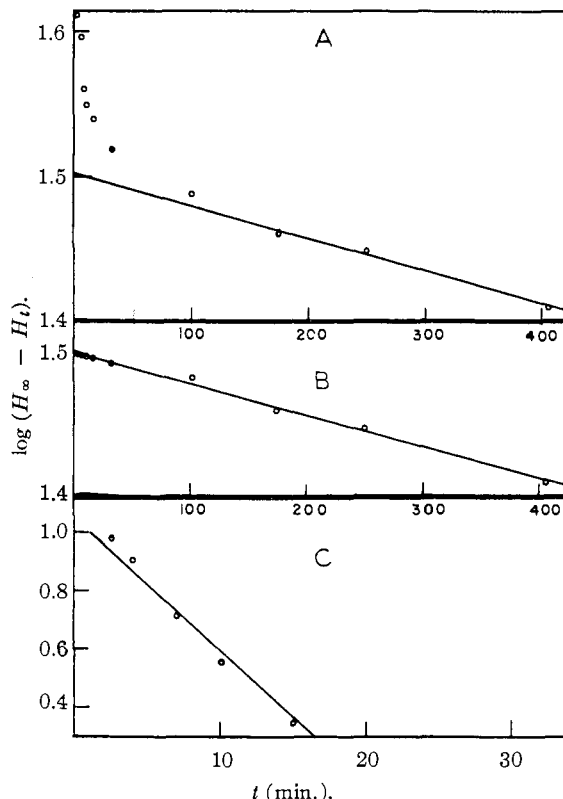


Fig. 4.—Rate of hydrogen exchange of  $\text{cis-Co}(\text{en})_2\text{NH}_3\text{Cl}^{+2}$  with buffered  $\text{D}_2\text{O}$  at  $25^\circ$ : A, experimental data; B, corrected slow rate; C, corrected fast rate.

direct comparison of rates for the chloropentamine complexes. For these complexes (6, 7 and 8 in Table I) the rapid rates of hydrogen exchange are approximately  $10^5$  times faster than their rates of base hydrolysis.

TABLE II  
EFFECT OF ALKYL SUBSTITUTION ON THE RATE OF HYDROGEN EXCHANGE OF SOME COBALT(III) AMMINES WITH ACETATE BUFFERED  $\text{D}_2\text{O}$

| No.             | Compound  | Concn., $M$ | Temp.      | $k$ , $M^{-1}$ , $\text{sec}^{-1}$ |
|-----------------|---|-------------|------------|------------------------------------|
| 9               | $\text{Co}(\text{en})_3^{+3}$                               | 0.16        | $25^\circ$ | $2.5 \times 10^6$                  |
| 10              | $\text{Co}(\text{pn})_3^{+3}$                               | .16         | $25^\circ$ | $4.5 \times 10^6$                  |
| 11              | $\text{Co}(d,l\text{-bn})_3^{+3}$                           | .02         | $25^\circ$ | $5 \times 10^6$                    |
| 12              | $\text{Co}(\text{N-Meen})_3^{+3}$                           | .05         | $25^\circ$ | $3 \times 10^6$                    |
| 13 <sup>a</sup> | $\text{Co}(\text{en})_2\text{C}_2\text{O}_4^{+b}$           | .12         | $35^\circ$ | $8 \times 10^6$                    |
| 14 <sup>a</sup> | $\text{Co}(\text{pn})_2\text{C}_2\text{O}_4^+$              | .12         | $35^\circ$ | $1 \times 10^6$                    |
| 15 <sup>a</sup> | $\text{Co}(i\text{-bn})_2\text{C}_2\text{O}_4^+$            | .12         | $35^\circ$ | $1 \times 10^6$                    |
| 16 <sup>a</sup> | $\text{Co}(\text{N-}n\text{-Pren})_2\text{C}_2\text{O}_4^+$ | .10         | $35^\circ$ | $4 \times 10^7$                    |

<sup>a</sup> Reproducibility on duplicate runs is 30%. Values of  $k$  are estimated from data collected during the initial 30% of exchange, since the data show a slight curvature to slower rates with increasing time. <sup>b</sup> For comparison the values of  $k$  obtained for  $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$  at  $35^\circ$  is  $8 \times 10^6 M^{-1} \text{sec}^{-1}$ . Block and Gold<sup>8</sup> obtain a value of  $6 \times 10^4 M^{-1} \text{sec}^{-1}$  for  $\text{Co}(\text{ND}_3)_4\text{C}_2\text{O}_4^+$  at  $25^\circ$ .

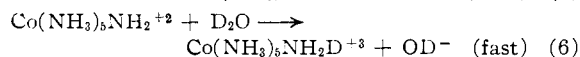
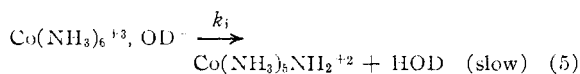
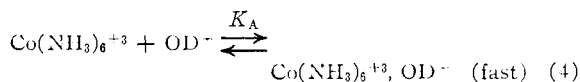
Unfortunately a similar direct comparison of rates could not be made for the dichlorotetramminecobalt(III) complexes. These compounds hydrolyze too rapidly at the conditions used for hydrogen exchange studies. Therefore any hydrogen exchange data would be of little meaning because of the net chemical reaction which proceeds

during exchange. Some oxalatotetramminecobalt(III) complexes were used in order to investigate hydrogen exchanges in univalent cationic species. While the equating of two chloro groups to one oxalato group is open to question, it can be seen from Table II that the rate of exchange is again much larger than the rates of base hydrolysis.<sup>4</sup>

It is of interest to note that the effect of chelation and of alkyl substitution on the rate of hydrogen exchange for cobalt(III) amines roughly parallels the effects observed on the rates of base hydrolysis. For example, data in Table I show that the rate of hydrogen exchange increased with increasing chelation. This is also the effect that chelation has on the rates of base hydrolysis of chloroamminecobalt(III) complexes. Similarly the effect of C-alkyl substitution in substituted ethylenediamine complexes is small both for exchange (Table II) and for base hydrolysis.<sup>4</sup> A much larger effect is observed for N-alkyl substitution, acceleration being observed for both hydrogen exchange and base hydrolysis.<sup>4</sup>

Although these effects are parallel for exchange and base hydrolysis rates, it should be made clear that this is not a necessary requirement of the  $S_N1CB$  mechanism. According to this process the rate determining step for base hydrolysis is the dissociation of chloride ion from the conjugate base, (2). This rate will of course be different for different compounds. The second factor that affects the rate of base hydrolysis according to this mechanism is the concentration of the conjugate base. Since this is expected to be related to its ease of formation, (1), it is reflected in the rate of hydrogen exchange. Still it follows that a small concentration of one conjugate base may dissociate more rapidly than a larger concentration of a different conjugate base. Furthermore there need not be a direct relationship between acidity of a complex and its rate of dissociation since steric factors, solvation effects, etc., may influence the forward and reverse steps of reaction 1. Accordingly there need not be an exact correlation between rates of base hydrolysis and rates of hydrogen exchange.

Another complication exists in that hydroxide ion forms an ion-pair with at least the trivalent complexes. It may well be this ion pair which reacts to produce the exchange.



The rate of hydrogen exchange is then a function of the concentration of ion pair which in turn depends upon the association constant  $K_A$  for equilibrium 4. Therefore the rate expression for exchange becomes,  $\text{Rate} = K_A k_i [\text{OD}^-]$ . Thus the values of  $k$  reported in Tables I and II are equal to  $K_A k_i$ . The association constant is known<sup>12</sup>

(12) J. A. Caton and J. E. Prue, *J. Chem. Soc.*, 671 (1956); R. G. Pearson and F. Basolo, *THIS JOURNAL*, **78**, 4878 (1956).

for some of the complexes investigated, e.g.,  $\text{Co}(\text{NH}_3)_6^{+3}$ , 72;  $\text{Co}(\text{en})_3^{+3}$ , 31;  $\text{Co}(\text{pn})_3^{+3}$ , 19;  $\text{Co}(\text{d,l bn})_3^{+3}$ , 11. In these cases the estimated values of  $k_i$  are  $2.2 \times 10^4$ ,  $8.0 \times 10^4$ ,  $4.2 \times 10^5$  and  $5 \times 10^5 \text{ sec.}^{-1}$ , respectively. That the value of  $k_i$  is larger for  $\text{Co}(\text{en})_3^{+3}$  than it is for  $\text{Co}(\text{NH}_3)_6^{+3}$  agrees with the observation<sup>13</sup> that  $\text{Pt}(\text{en})_3^{+4}$  is a stronger acid than  $\text{Pt}(\text{NH}_3)_6^{+4}$ .

Such a scheme has the advantage of explaining the specific hydroxide ion catalysis observed for these exchanges. Alternatively the explanation may be simply a large value of  $\beta$  in the Brønsted relationship,  $k_B = GK_B^\beta$ , between rate constant  $k_B$  and base dissociation constant  $K_B$ . Kinetically one cannot distinguish between a reaction of the ion pair as in (5) and (6) and a reaction between free complex ion and hydroxide ion as in (1). It may be mentioned that evidence for general base catalysis in the hydrogen exchange reactions of  $\text{Cr}(\text{en})_3^{+3}$  and *trans*- $\text{Pt}(\text{en})_2\text{Cl}_2^{+2}$  has been found.<sup>14</sup>

The complexes 5, 10 and 12 each contain different types of N-H hydrogens. However, this difference is not detected experimentally, since it is found that all of the hydrogens exchange at the same rate. Similarly all of the hydrogens of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$  exchange at the same rate. Instead the data for compounds 2, 7 and 8 clearly show (Fig. 4) that some hydrogens exchange at a fast rate and others at a slower rate. For *cis*- $\text{Co}(\text{en})_2\text{NH}_3\text{Cl}^+$ , approximately 25% of the hydrogens exchange rapidly whereas this value is about 30% for *cis*- $\text{Co}(\text{trien})\text{NH}_3\text{Cl}^+$  and 30% for *cis*- $\text{Co}(\text{en})_2(\text{NH}_3)_2^{+3}$ . These results suggest that it is the  $\text{NH}_3$  hydrogens that exchange rapidly. This agrees with  $\text{NH}_4^+$  being a stronger acid than  $\text{RNH}_3^+$ . It does not appear to agree with the fact that  $\text{Pt}(\text{en})_3^{+4}$  is a stronger acid than  $\text{Pt}(\text{NH}_3)_6^{+4}$ . However, the latter result has been explained on the basis of a solvation effect,<sup>15</sup> the ethylenediamine being a solvent blocking substituent which favors the expulsion of a positive charge from the complex. If the  $\text{NH}_3$  molecule is present in a complex containing such solvent blocking groups, then it logically follows that its more acidic proton will be lost more rapidly than that of the less acidic  $\text{RNH}_2$ .

It is of interest to note that the rates of exchange reported for the heavy ammine-light water systems<sup>1</sup> of  $\text{Co}(\text{NH}_3)_6^{+3}$  and  $\text{Co}(\text{en})_3^{+3}$  are respectively  $1.0 \times 10^6$  and  $1.7 \times 10^6 M^{-1} \text{ sec.}^{-1}$  compared to  $1.6 \times 10^6$  and  $2.5 \times 10^6 M^{-1} \text{ sec.}^{-1}$  for the corresponding light ammine-heavy water systems. The rates are not expected to be the same because of an isotope effect.<sup>16</sup>

**Acknowledgments.**—We wish to thank Dr. A. L. Allred for his help with the n.m.r. measurements. This investigation was supported by a National Science Foundation Grant (NSF-G5104).

EVANSTON, ILLINOIS

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