At 3.85×10^7 counts, an average of 359 molecules of ethanol were destroyed per electron. After 1.365×10^8 counts the average effective yield for ethanol was 180, since the products being formed were also being decomposed in the discharge. The mechanism of dissociative recombination whereby an organic molecule is neutralized at the cathode by an electron and dissociates from the excitation of ion recombination is expected to have an effective electron yield of approximately unity. If the mechanism of decomposition were photoexcitation, where the electron transfer between an argon ion and a molecule of the organic quenching agent produces a photon which is then absorbed by another organic molecule to give an excited intermediate, the effective electron yield is again expected to be unity. But the mechanism of electron collision in the gas phase, in which an electron collides with an organic molecule in traveling to the anode and loses some of its energy in excitation of the molecule, but which in being accelerated toward the anode acquires more energy for another collision, must have an effective electron yield much greater than unity. The primary mechanism, considering the large observed effective electron yield, is concluded to be that of electron collision in the gas phase.

Stating the mechanism of electron collision in terms of an equation

$$CH_3CH_2OH + \bar{e} \xrightarrow{\text{gas}} (CH_3CH_2OH)^+ + \bar{e}$$

it is seen then that the subsequent steps may be any or all of the following

$$(CH_3CH_2OH)^+ \longrightarrow \cdot CH_3 + \cdot CH_2OH$$
$$(CH_3CH_2OH)^+ \longrightarrow \cdot CH_2CH_3 + \cdot OH$$
$$(CH_3CH_2OH)^+ \longrightarrow \cdot C_2H_4OH + \cdot H$$

Various propagation and termination steps may then be written involving free radical reactions. In a system of this kind it is clear that many reactions are possible. The stoichiometry of the observed decomposition, as seen from Table II, may be approximated by

$$24CH_3CH_2OH \longrightarrow 16CH_3OH + 15C_2H_4 + CH_4 + CO_2 + H_2 + 6H_2O$$

The authors wish to thank Mr. R. W. Hannah for the infrared analyses.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions in Complex Ions. VII. Base Hydrolysis of Some Cobalt(III) Complex Ions[1,2]

BY RALPH G. PEARSON, ROBERT E. MEEKER AND FRED BASOLO

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The rates of base hydrolysis of a number of inorganic coördination complexes such as *cis*- and *trans*-dichlorobisethylenediaminecobalt(III) chloride have been determined. These reactions are quite rapid, generally having half-times of fractions of a second at room temperature. A simple flow apparatus utilizing electrical conductivity measurements for fast reactions is described. From the effect on reaction rate of various structural modifications in the complex molecule, an S_N1CB mechanism is proposed in which the reaction proceeds by dissociation of a chloride ion from the conjugate base of the complex cation. This mechanism is consistent with the expected acidities and rates of dissociation of the various complex ions. The data are correlated by applying the rule that rates of base hydrolysis should parallel rates of acid hydrolysis for a series of complex ions of cobalt(III) unless a marked change occurs in the acidities of some members of the series.

The mechanism of base hydrolysis of complex ions such as

$$[Co(NH_3)_5Cl]^{+2} + OH^- \longrightarrow [Co(NH_3)_5OH]^{+2} + Cl^- \quad (1)$$

has been considered by Brown, Ingold and Nyholm[3] to be a direct displacement of halide ion by hydroxide ion (an S_N2 process). This is in agreement with the observed kinetics of such reactions which are first order in hydroxide ion and first order in complex ion.

Others[4] have considered the mechanism to involve a prior acid–base equilibrium followed by release of halide ion from the conjugate base of the complex cation (an S_N1CB process).

$$[Co(NH_3)_5Cl]^{+2} + OH^- \underset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2Cl]^+ + H_2O \quad (2)$$

$$[Co(NH_3)_4NH_2Cl]^+ \xrightarrow[\text{slow}]{H_2O} [Co(NH_3)_4NH_2H_2O]^{+2} \xrightarrow[\text{fast}]{} [Co(NH_3)_5OH]^{+2} \quad (3)$$

This mechanism is in agreement with the recent observation that complexes containing no acidic protons release their replaceable ligands at a rate independent of the *p*H of the solution.[5] In such compounds step (2) cannot occur.

The way in which water replaces chloride ion in step (3) is presumably the same as for aquation of the parent ion under acid conditions (acid hydrolysis).

$$[Co(NH_3)_5Cl]^{+2} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{+3} + Cl^- \quad (4)$$

Earlier papers in this series[1,7] have reported the rates of acid hydrolysis as in (4) for a large number of complex ions of cobalt(III). Evidence has been presented to show that (4) probably involves a dissociation mechanism (S_N1) in which a pentacoördinated intermediate is formed.

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(1) Previous paper in this series, R. G. Pearson, P. M. Henry, J. G. Bergmann and F. Basolo, THIS JOURNAL, **76**, 5920 (1954).

(2) This investigation supported by the U. S. Atomic Energy Commission under Contract AT(11-1)89- Proj. No. 2.

(3) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2678 (1953).

(4) (a) F. J. Garrick, *Nature*, **139**, 507 (1937); (b) J. S. Anderson, H. V. A. Briscoe and N. F. Spoor *J. Chem. Soc.*, 361 (1943).

(5) R. G. Pearson, R. E. Meeker and F. Basolo, *J. Inorg. Nuc. Chem.*, in press.

$$[Co(NH_3)_5Cl]^{+2} \rightleftharpoons Co(NH_3)_5^{+3} + Cl^- \qquad (5)$$
$$Co(NH_3)_5^{+3} + H_2O \xrightarrow[\text{fast}]{} [Co(NH_3)_5H_2O]^{+3}$$

The forward process in (5) is rate determining.

If the S_N1CB mechanism for base hydrolysis is correct, then the observed second-order rate constant is equal to the product of the equilibrium constant for (2) times the rate constant for (3). Since the rate of reaction (3) for a series of complex ions should be closely proportional to the rate of reaction (4), it is clear that we could predict the rates of base hydrolysis from the known rates of acid hydrolysis if we had knowledge of the acid ionization constants of the complex ions. These constants are in fact unknown, even $[Co(NH_3)_6]^{+3}$ being too weak an acid to measure reliably. That reaction (2) does occur is shown by deuterium exchange studies.[6] In alkali, exchange is complete in a time much less than that for the over-all hydrolysis.

In spite of the unavailability of data on the actual acid strengths, we can still formulate, as a working hypothesis, the rule that *rates of base hydrolysis should parallel rates of acid hydrolysis for a series of complex ions of cobalt(III) unless a marked change occurs in the acidities of some members of the series.* Data on model compounds of measurable acidity can be used as a guide for predicting changes in acid strength. As an illustration of the above rule the relative rates of base hydrolysis and acid hydrolysis for the series $Co(NH_3)_5X^{+2}$ ($X = Cl^-$, Br^-, NO_3^-) should be essentially constant. This is in fact true and formed the basis for assigning an S_N2 mechanism to the acid hydrolysis reaction on the assumption that the base reaction is S_N2.[3] However, as we shall see, the constancy of relative rates is not invariant and hence the assignment of a common S_N2 mechanism is invalid.

Our purpose in this paper is to report the rates of base hydrolysis (1) for a series of cobalt(III) complexes and to compare the rates to those of acid hydrolysis (4).

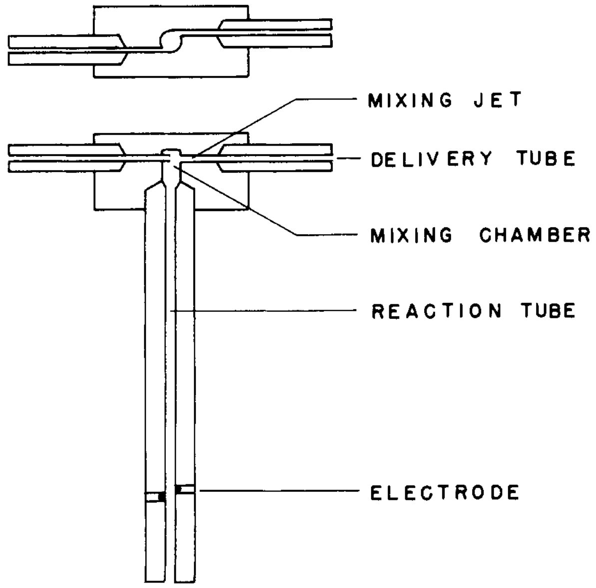

Fig. 1.—Flow apparatus.

Experimental

Preparation of Compounds.—The compounds used were prepared as previously described.[7]

Apparatus.—A simplified flow apparatus based on the method introduced in 1923 by Hartridge and Roughton was employed. Roughton[8] has reviewed existing flow techniques. A diagram of the reaction cell is shown in Fig. 1. The delivery tubes are 1 mm. glass capillary, and the reaction tube is 1 or 1.5 mm. glass capillary. The mixer block is Lucite plastic.

In constructing the cell a $^1/_{16}$ in. diameter hole is first drilled in the Lucite block for the mixing chamber. The mixing jets are then drilled with a No. 60 drill so as to enter the mixing chamber tangentially. The holes for the mixing jets and chamber are counterdrilled just undersize for the delivery tubes and reaction tube, respectively. The ends of these glass tubes are ground to a taper to match the bottoms of the counterdrilled holes in the plastic block. The tubes are sealed into the block by heating the tip of the glass just to redness in a flame, allowing it to cool in the air for a few seconds, and then thrusting it into the drilled hole in the block. The assembly is held carefully in position for a minute or two until the plastic solidifies around the glass, forming a very strong seal. The assembly should be allowed to cool slowly to avoid strains in the plastic. The platinum wire electrodes are sealed into the reaction tube before it is joined to the block. Two slots just wide enough to accommodate the electrodes are ground into the reaction tube until the bore of the capillary is just exposed on either side. These slots are not placed directly across from each other, but rather are staggered a couple of millimeters for structural strength. The electrode wires are sealed in the slots with apiezon wax. The seal is coated with Glyptal varnish which forms a tough outer film to withstand the fluid pressures which may be encountered during operation of the cell. The whole assembly is carefully heated in an oven at 100°. This softens the wax so that it flows into all crevices around the electrodes, and hastens the drying of the varnish. For structural strength, a wooden brace a few centimeters long is fastened along the reaction tube bridging the electrode slots. The protruding electrode wires are bent down so as to fit into small mercury cups for electrical contact.

In operation the reactant solutions are driven by air pressure from their reservoirs (aspirator bottles) through the delivery tubes, and into the mixing chamber. Reaction occurs as the mixture flows through the reaction tube, where a steady state for each point is set up under conditions of constant flow rate. The extent of reaction at the electrode position remains constant as long as the constant flow rate is maintained. The electrical resistance of the solution flowing past the electrodes is measured. The equivalent reaction time corresponding to this resistance reading is the time required to flow from the mixing chamber to the electrodes, or the cell volume divided by the flow rate. The cell volume is determined by weighing the amount of mercury it will hold, and the flow rate is determined by measuring the volume of effluent collected from the cell in a given time. Resistance readings for various constant flow rates yield data for a complete kinetic determination. Five or more experimental points can be obtained with as little as 100 ml. of each reactant solution. Final resistance values are obtained by collecting the effluent from the cell and running it back through the cell after the reaction is complete. Initial resistance values may be obtained by measuring the resistance of the separate reactant solutions and applying the parallel resistance law, remembering that each solution is diluted by a factor of two in the mixing chamber, or by extrapolating the data back to zero time in certain cases.

It is important that the delivery rates from each reservoir be equal and remain equal for the various flow rates used. The first of these conditions is checked by measuring the resistance when one reservoir contains a dilute electrolyte and

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(6) See 4b and A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

(7) R. G. Pearson, C. Boston and F. Basolo, THIS JOURNAL, **75**, 3089 (1953); *J. Phys. Chem.*, **59**, 304 (1955).

(8) "Rates and Mechanisms of Reactions, Vol. VIII, Techniques of Organic Chemistry," Interscience Publishers, New York, N. Y., 1953, Chapter X.

the other contains water, and then interchanging the reservoirs and seeing that the resistance remains constant. The second condition is checked by seeing that the resistance is independent of flow rate when one reservoir contains only water. These conditions were obeyed to $\pm 1\%$.

Thermostatting is accomplished by immersing the reservoirs and delivery tubes in a constant temperature waterbath, and circulating water from this bath through a water jacket around the reaction tube.

Three different cells were constructed, having volumes of 0.132, 0.427 and 0.702 ml., respectively. With these three cells equivalent reaction times in the range from 30 milliseconds to a few seconds were attained. The range could have been extended to smaller times if necessary.

Electrical resistances were measured with a Jones Conductivity Bridge using alternating current of 1000 cycles per second and two volts. A cathode ray oscilloscope was used for balance point detection.

Calibration.—The apparatus was tested by reproducing rate measurements for two fast reactions whose rates are known. The rate constant for the decomposition of carbonic acid is reported by Roughton[9] at several temperatures. By interpolation from a plot of log k *versus* $1/T$ the values 20.9 and 28.2 sec.$^{-1}$ are obtained for the rate constant at 22 and 25°, respectively. For several runs in the concentration range from 0.003 to 0.01 M, average values of 20.0 and 27.9, respectively, were obtained at the two temperatures in our apparatus. Figure 2 shows a plot of the data for one of these calibrated runs.

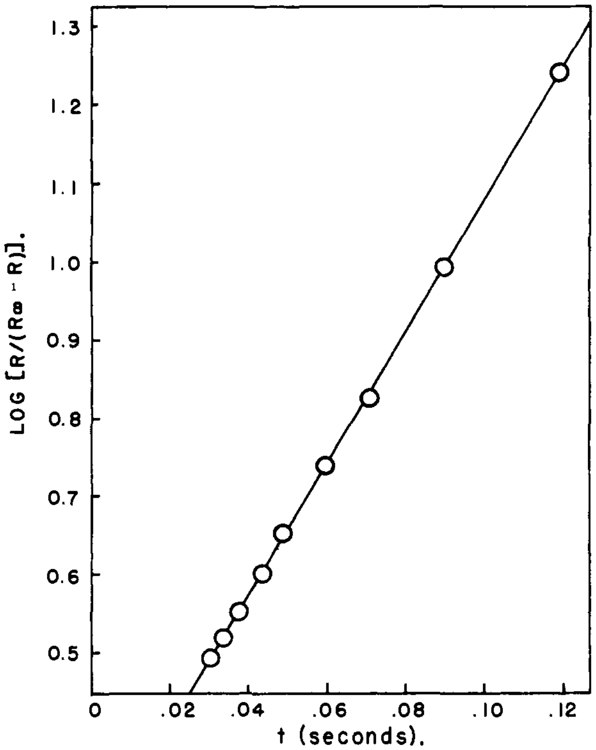

Fig. 2.—Calibration of flow apparatus: decomposition of carbonic acid at 22°.

The rate of the base-catalyzed ionization of nitroethane is reported by Bell and Clunie[10] to be 350 mole^{-1} min.$^{-1}$ at 25°. This reaction is too slow to be studied conveniently in our apparatus. However, under pseudo first-order conditions in excess nitroethane our flow method gave values of 370 and 390.

That the different cells yield self-consistent data was shown by running the same second order reaction in different cells, varying the concentrations so that the rate was suitable for the equivalent time range of each cell. Rate constants obtained in this way agreed within a few per cent.

Treatment of Data.—First-order rate constants in all reactions studied were determined by plotting $\log_{10}((R_\infty - R)/R)$ as ordinate *versus* t as abscissa. Then $k = 2.303$ (slope), where R is the resistance at time t, R_∞ is the final resistance, and k is the first-order rate constant.

Rate constants for second-order reactions with equal concentrations of reactants were determined by plotting $(R\cdot(R_\infty - R))$ as ordinate *versus* f as abscissa. Then, $k = (R_\infty - R_0)$ (slope)$/aR_0$, where a is the initial concentration of each reactant and R_0 is the initial resistance.

For second-order reactions with unequal concentrations of reactants $\log_{10}\{(R_\infty + [(n - 1)(R_\infty/R_0)] - n(R)/(R_\infty - \mathrm{R})\}$ is plotted as ordinate *versus* t as abscissa. The $k = 2.303$ (slope)$/(b - a)$ where b and a are the initial concentrations of the two reactants and n is defined by $b = na$. For a particular run the ordinate function reduces to the form $\log_{10}(R_\infty - cR)/(R_\infty - R)$, where c is a constant.

The compounds containing two replaceable chloro groups present a special problem in that two competitive, consecutive reactions are involved, as indicated in the equations

$$\text{dichloro complex} + \text{OH}^- \xrightarrow{k_1} \text{chlorohydroxo complex} + \text{Cl}^- \quad (7)$$

$$\text{chlorohydroxo complex} + \text{OH}^- \xrightarrow{k_2} \text{dihydroxo complex} + \text{Cl}^- \quad (8)$$

The ratio $1/K = k_1/k_2$ was found to have values ranging from 3 to 15 for the compounds studied. Values of k_1 were determined from data obtained during the early part of the reaction, before the intermediate chlorohydroxo complex had been formed in sufficient concentration for k_2 to interfere. To determine k_2 two methods were employed. The time ratio method of Frost and Schwemer[11] was most convenient for processes having small values of $1/K$. The second method involved adding enough hydroxide ion to replace both chloro groups, and plotting the data as for a simple second-order reaction with $n = 2$. k_1 was determined from the slope of the straight line through the first few points, and K was determined from the deviations, Δ, of subsequent points from this straight line by the relation

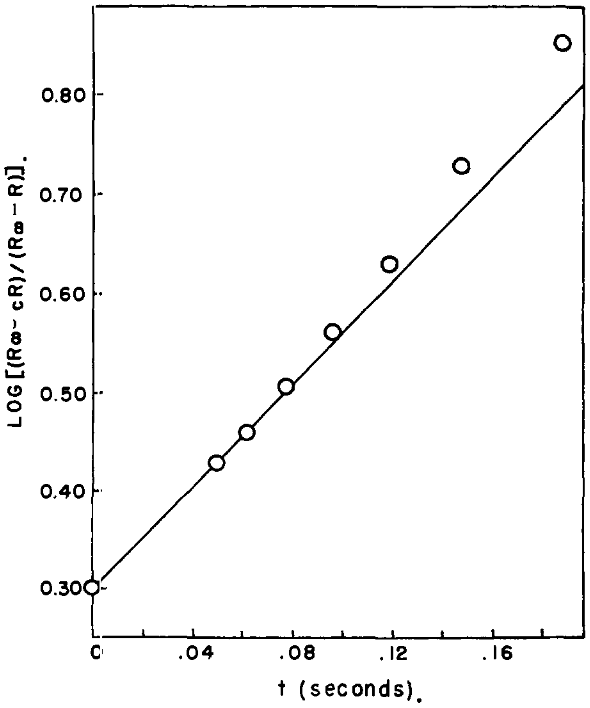

Fig. 3.—Base hydrolysis of *trans*-Coen$_2$Cl$_2^+$ at 25° showing deviations due to hydrolysis of second chloro group.

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(9) F. J. W. Roughton, THIS JOURNAL, **63**, 2930 (1941).

(10) R. P. Bell and J. C. Clunie, *Proc. Roy. Soc.* (*London*), **212**, 16 (1952). See also R. G. Pearson and L. Piette, THIS JOURNAL, **76**, 3087 (1954).

(11) A. A. Frost and W. C. Schwemer, *ibid.*, **74**, 1268 (1952); W. C. Schwemer and A. A. Frost, *ibid.*, **73**, 4541 (1951).

$K = 2.303\Delta/2(e^{\tau} - \tau e^{\tau} - 1)$ where $\tau = ak_1t$. Figure 3 shows such a plot for the base hydrolysis of the *trans*-Coen$_2$-Cl$_2^+$ ion. The two methods are in good agreement. For example, when applied to the data of Fig. 2, the time ratio method gives $1/K = 15.0$, and the deviation method gives $1/K = 15.5$.

Values of k_1 for dichloro complex were confirmed in some cases by using a 1:1 mole ratio of reactants. A method for calculating R_∞ from $R = f(t)$ data was developed and applied to experiments such as this where subsequent reactions prevented direct measurement of R_∞. The equation used was

$$\lambda_\infty = (2\lambda\lambda'' - \lambda''\lambda' - \lambda\lambda')/(\lambda + \lambda'' - 2\lambda') \quad (9)$$

where λ is the value of any physical property proportional to concentration, and where λ, λ′ and λ″ are values separated by a constant time interval. Since it is conductance which is proportional to concentration, the lambdas are taken as reciprocal resistances.[12]

Whenever possible R_∞ was determined experimentally by collecting the effluent from the flow cell, and measuring its resistance after the reaction had gone to completion. For experiments using a 2:1 mole ratio or hydroxide ion to dichloro complex the experimental final resistance corresponds to replacement of both chloro groups by hydroxide ion. The R_∞ appropriate to the hydrolysis of the first chloro group only was taken as that resistance corresponding to half the total conductivity change.

Buffer Studies.—Some of the *trans*-dichloro complex ions aquated so rapidly in the reservoir that the flow method could not be used. In these cases the base hydrolyses were studied in buffered systems of such hydroxide ion concentrations that the half-lives were in the order of a few seconds. Advantage was taken of the fact that the *trans*-dichloro complex ions are green while their hydrolysis products are red. At the time of half reaction the solution becomes momentarily colorless or gray. Rate constants k_1 were thus approximated by noting the time for the colorless appearance in buffer solutions of the complexes. Buffers used were 0.050 *M* Na$_2$B$_4$O$_7$ having a *p*H of 9.18 at 25° and 0.10 *M* (CH$_3$)$_3$N partially neutralized with HCl and having a *p*H of 9.51 at 25°. Using known compounds this method worked well if the simple relationship $[\mathrm{OH}^-] = \text{antilog}\ (p\mathrm{H} - 14.0)$ was used. Table I shows some results with knowns. For unknowns k_1 was calculated as equal to $0.693/[\mathrm{OH}^-]t^{1/2}$.

These experiments in buffers are of value also in demonstrating that the rate of base hydrolysis depends only on the hydroxide in concentration and is not subject to general base catalysis. This result is required by the mechanism postulated in equations 2 and 3. Specifically it shows that removal of a proton from the complex ion is not the rate determining step.

Acid Strength Measurements.—Acid dissociation constants were determined for several aquo and diaquo complexes of cobalt(III). Hydroxo complexes were obtained in solution by adding a slight excess of NaOH to 0.015 *M* solutions of the chloro complexes. These were then titrated with 0.1028 *M* HCl using a micro-buret which could be read directly to 0.01 ml. The titration was followed with a Beckman Model G *p*H Meter which was standardized against Beckman standard buffers at *p*H 7.00 and 9.18 before and after each run. Sharp breaks in the *p*H titration curves were obtained corresponding to (1) the titration of the excess hydroxide ion and (2) the formation of the monoaquo complex. The end-point for the second H$_2$O group in diaquo complexes was obscure, but the two good breaks observed in each titration were sufficient to establish all equivalence points. pK_a values were then determined by substitution in the formula $pK_a = p\mathrm{H} + \log[\mathrm{HA}]/[\mathrm{A}^-]$ where the symbols are defined by the equilibrium $HA \rightleftarrows \mathrm{H}^+ + \mathrm{A}^-$.

TABLE I

COMPARISON OF HALF-TIMES FOR BASE HYDROLYSES OBSERVED IN BUFFER SOLUTION WITH VALUES CALCULATED FROM FLOW DATA FOR *trans*-[Co(AA)$_2$Cl$_2$]$^+$ AT 25°

	Na$_2$B$_4$O$_7$ buffer $t^{1/2}$, sec.		(CH$_3$)$_3$N–HCl buffer $t^{1/2}$, sec.	
(AA)[a]	Calcd.	Obsd.	Calcd.	Obsd.
en	15.0	15.8	7.0	8.6
pn	19.9	20.5	9.1	10.4
d,l-bn	21.9	21.4		
N-me·en	4.1	4.0	1.9	2.0
N-pr·en	2.2	2.0	1.0	<2

[a] en = ethylenediamine, pn = propylenediamine, *d,l*-bn = *d,l*-butylenediamine, N-me·en = N-methylethylenediamine, N-pr·en = N-*n*-propylethylenediamine.

Measurement of pK_1 values for the diaquo complexes is complicated because *cis-trans* isomerization occurs with an appreciable life time for the hydroxo-aquo form, and the isomers may have quite different pK_1 values. Fortunately the pK_2 values are only slightly different for the *cis* and *trans* forms. Bjerrum and Rasmussen[13] have studied the system *cis*- and *trans*-[Coen$_2$(H$_2$O)$_2$]$^{+3}$ in detail.

Since only relative values are needed for this work, *p*H readings were taken at an arbitary time after each addition of acid. The values obtained then are not necessarily equilibrium values, but were all obtained under standardized conditions. The data are shown in Table II.

TABLE II

ACID DISSOCIATION CONSTANT FOR SOME AQUO COMPLEXES OF COBALT(III) AT 25° (0.015 *M* complex)

Compound[c]	pK_1	pK_2
[Co(NH$_3$)$_5$H$_2$O]$^{+3}$	6.13	..
[Coen$_2$NH$_3$H$_2$O]$^{+3}$	5.96	..
[Co(trien)NH$_3$H$_2$O]$^{+3}$	5.88	..
[Co(N-pr·en)$_2$(H O)$_2$]$^{+3}$	4.51	7.64
[Co(N-me·en)$_2$(H$_2$O)$_2$]$^{+3}$	4.71	7.55
[Co en$_2$ (H$_2$O)$_2$]$^{+3}$	5.28[a]	7.87[a]
[Co pn$_2$ (H$_2$O)]$^{+3}$	5.39	7.78
[Co(*d,l*-bn)$_2$(HO)$_2$]$^{+3}$	5.48	8.05
[Co(m-bn)$_2$(H$_2$O)$_2$]$^{+3}$	5.64	7.83
[Co(NH$_3$)$_4$(H$_2$O)$_2$]$^{+3}$	5.79[b]	..

[a] Bjerrum and Rasmussen (ref. 13) report $pK_1 = 5.80$ and $pK_2 = 8.10$ for the equilibrium mixture of *cis* and *trans* in 1 *M* NaNO$_3$. [b] From the data in ref. 14 corrected for ionic strength by applying equation 11, and for temperature by applying the same factor as found for K_0 values of Co(NH$_3$)$_5$H$_2$O^{+3}. [c] trien = triethylenetetramine, m-bn = *meso*-butylenediamine.

Brönsted and Volquartz[14] have studied the system Co(NH$_3$)$_x$(H$_2$O)$_y$$^{+3}$ ($x + y = 6$) by indirect methods at 15°. They report that ionic strength effects may be accounted for by the relation $\log K_a = \log K_0 - 2\sqrt{\mu} + \mu$, (11) for small values of μ where μ is the ionic strength and K_0 is the acid dissociation constant at zero ionic strength. For comparison they report $K_0 = 2.04 \times 10^{-6}$ for Co(NH$_3$)$_5$H$_2$O^{+3} at 15°. Our value is $K_0 = 1.95 \times 10^{-6}$ at 25°.

All kinetic and acidity studies were carried out at 25°.

Results and Discussion

Table III shows values of k_1 and $k_{\mathrm{H_2O}}$ (acid hydrolysis rates from earlier papers in this series) for three series of compounds showing increasing chelation. Rates for compound 4 and 5 are reported to only one significant figure because of difficulties with fairly rapid aquation for 4 and the high reaction rate in base for 5. It is observed in all three series that the compounds with the greater chelation have the faster rates of base hydrolysis. It is further observed that the trend in acid hydrolysis rates for each of the three series of compounds is in the opposite direction to the trend in base hydrolysis rates. Thus the criterion upon which Brown, Ingold and Nyholm[3] base their suggestion that both processes occur by the same mechanism is invalid here.

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[12] See W. E. Roseveare, THIS JOURNAL, **53**, 1651 (1931).

[13] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

[14] J. N. Brönsted and K. Volquartz, *Z. physik. Chem.*, **134**, 97 (1928).

TABLE III

EFFECT OF INCREASED CHELATION ON RATES OF BASE HYDROLYSIS (k_1) AND ACID HYDROLYSIS (k_{H_2O}) AT 25°

No.	Compound	k_1, mole sec.$^{-1}$	k_{H_2O}, sec.$^{-1}$
1	$[Co(NH_3)_5Cl^{+2}$	0.85^a	6.7×10^{-6b}
2	*cis*-$[Coen_2NH_3Cl]^{+2}$	5.4×10^1	1.4×10^{-6b}
3	*cis*-$[Co(trien)NH_3Cl]^{+2}$	1.6×10^2	6.7×10^{-7b}
4	*cis*-$[Coen_2Cl_2]^+$	1×10^3	2.5×10^{-4}
5	*cis*-$[Co(trien)Cl_2{}^+$	2×10^5	1.5×10^{-4}
6	*trans*-$[Co(NH_3)_4Cl_2]^+$	1.8×10^{3c}	1.8×10^{-2}
7	*trans*-$[Coen_2Cl_2]^+$	3.0×10^3	3.2×10^{-5}

[a] A. W. Adamson and F. Basolo, ref. 6; see also H. Puente and A. Lelong, *C.A.*, **37**, 6528 (1943); **40**, 3333 (1946); who report 1.3 for *k*. [b] 35°. [c] By buffer method.

These kinetic results can be explained on the basis of the S_N1CB mechanism if the acid strengths increase markedly with increasing chelation. There is, in fact, every reason to believe that this is so. Thus the acid dissociation constant for $Pt(NH_3)_6{}^{+4}$, $Pten(NH_3)_4$ and $Pten_3{}^{+4}$ are 1.2×10^{-8}, 7.1×10^{-7} and 3.5×10^{-6}, respectively.[15] Also, the rate of deuterium exchange is greater for $[Coen_3]^{+3}$ than for $[Co(NH_3)_6]^{+3}$.[4b]

Table II shows pK_a values for a series of aquo complexes of cobalt(III) at 25°. Those complexes with the greater chelation are seen to be somewhat more acidic, though the differences are rather small. It must be remembered, however, that the acidities reported here are for OH bonds. The expected changes for NH bonds would be considerably greater. This is because the OH bond is only indirectly affected.

Table IV shows the effect of alkyl substituents on the values of k_1, k_2 and k_{H_2O} for substituted *trans*-dichlorobisethylenediaminecobalt(III) complexes. Again the rate constants for base hydrolysis and acid hydrolysis follow different trends. Increasing C-alkylation increases the rate of acid hydrolysis markedly while the base hydrolysis is slowed down somewhat. This result can be explained by the S_N1CB mechanism if C-alkylation, by an inductive effect, reduces the acidity of the complex ion to compensate for the increased rate of dissociation.

TABLE IV

EFFECT OF C- AND N-ALKYL SUBSTITUENTS ON THE RATES OF BASE HYDROLYSIS AND ACID HYDROLYSIS OF SUBSTITUTED *trans*-$[Coen_2Cl_2]^+$ COMPLEXES AT 25°

No.	Compound	k_1, mole sec.$^{-1}$	k_2, mole sec.$^{-1}$	k_{H_2O}, sec.$^{-1}$
7	$[Coen_2Cl_2]^+$	3.0×10^3	2.0×10^2	3.2×10^{-5}
8	$[Copn_2Cl_2]^+$	2.3×10^3	2.1×10^2	6.2×10^{-5}
9	$[Co(d,l\text{-}bn)_2Cl_2]^+$	2.1×10^3	2.2×10^2	1.5×10^{-4}
10	$[Co(m\text{-}bn)_2Cl_2]^+$	9.8×10^{3a}	....	4.2×10^{-3}
11	$[Co(i\text{-}bn)_2Cl_2]^{+b}$	9.8×10^3	....	2.2×10^{-3}
12	$[Co(N\text{-}me{\cdot}en)_2Cl_2]^+$	1.1×10^4	3.3×10^3	1.7×10^{-5}
13	$[Co(N\text{-}pr{\cdot}en)_2Cl_2]^+$	2.1×10^4	3.0×10^3	1.2×10^{-4}

[a] By buffer method. [b] i-bn = isobutylenediamine.

It is also observed that N-alkylation increases the rate of base hydrolysis over what would be expected from the rate of acid hydrolysis, while *trans*-$[Co(NH_3)_4Cl_2]^+$, included in Table II, reacts rather slowly in base compared to its reaction in acid. This latter result is expected from the discussion given in connection with Table III. The increased rate of the N-alkyl complexes must be attributed to a further increase in acidity upon replacing a second proton of NH_3 with an alkyl group. Thus the effect is a continuation of that found when a proton of NH_3 is replaced by $-CH_2CH_2NH_2$.

Such a result is not unreasonable when it is observed that the N-alkyl complex has only one proton left on the nitrogen, analogous to trimethylammonium ion which is well known to be a stronger acid than dimethylammonium ion. The inversion in the expected effect of an alkyl group on acidity has been explained by a reduction in the solvation energy of the positive ion to compensate for the inductive effect.[16]

The required influence of C- and N-alkylation on acidities is indeed observed, as shown in Table III, though again the effects are minimized since it is only the OH acidity which is measured.

Table V shows several other complex ions whose rates of base hydrolysis were measured in this work. In the case of the difluoro, dichloro and dibromo complexes of bis-ethylenediaminecobalt(III) where the acidity may not vary much, there is a fair parallelism between the rates of acid hydrolysis and base hydrolysis. The fluorine atom might have been expected to raise the acidity somewhat more than a bromine or chlorine atom. However, the hydrolysis of the difluoro complex in acid is catalyzed by acid[17] and the value given in Table V is the minimum rate constant observed at pH 3.

TABLE V

RATES OF BASE HYDROLYSIS AND ACID HYDROLYSIS FOR SOME MISCELLANEOUS *trans*-$[Co(AA)_2X_2]^+$ COMPLEXES AT 25°

No.	Compound	k_1, mole sec.$^{-1}$	k_{H_2O}, sec.$^{-1}$
14	$[Coen_2Br_2]^+$	1.2×10^4	1.4×10^{-4a}
15	$[Coen_2F_2]^+$	6.4×10^1	1×10^{-6a}
16	$[Copn_2F_2]^+$	4.3×10^1	....
17	$[Co(dan)_2Cl_2]^{+c}$	1.7×10^{4b}	3×10^{-3}

[a] Values from ref. 17. [b] By buffer method. [c] dan = $NH_2CH_2C(CH_3)_2CH_2NH_2$.

In conclusion, it is possible to explain the relative rates of acid and base reactions of a large number of complex ions of cobalt(III) by postulating an S_N1 mechanism for acid hydrolysis and an S_N1CB mechanism for base hydrolysis. The concept that both reactions are S_N2 processes seems ruled out by the variations in rate with structure. That the base hydrolysis is S_N2 appears to be excluded by the large increases in rate observed when easy access to a displacing reagent is prevented by either increased chelation or, to a lesser degree, by alkyl substitution. Further, the observation that a complex must have an acidic proton to react rapidly with base is incompatible with an S_N2 mechanism. This conclusion is in accord with interpretations of recent studies[6] on the deuterium effect and entropy of activation for base hydrolysis reactions.

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