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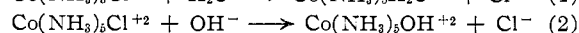
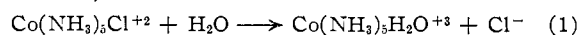
Deuterium Isotope Effects on the Acid Hydrolysis Rates of Chloro Complexes of Cobalt(III)¹

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Deuterium substitution both in the complex and in the solvent slows down the rate of acid hydrolysis of chlorocomplexes of cobalt(III). This is similar to what is observed in the solvolysis reactions of organic halides and the same explanations may be used. The isotope effect in the base hydrolysis of $\text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$ is consistent with, but does not prove, an $\text{S}_{\text{N}}1\text{CB}$ mechanism.

A recent paper² has discussed the effect of deuterium substitution, both in the complex and in the solvent, on the rates of reactions such as



The first of these reactions is called acid hydrolysis, or aquation, and the second is base hydrolysis. For both reactions it was found that deuterium systems reacted more slowly than light hydrogen systems by factors of 0.6 to 0.7. Particularly in the case of acid hydrolysis, where hydrogen exchange is slow, it was shown that deuteration both of the complex and of the solvent slowed down the rate. Surprisingly, deuteration both in the complex and in the solvent did not seem to produce a reaction rate slower than deuteration in the complex or in the solvent alone.

On the basis of these results, a rather detailed mechanism of the aquation process was proposed in which four water molecules are hydrogen bonded to both the Cl and an adjacent NH_3 group of the complex. The rate determining step was then the concerted motion of the chloride ion outward and a water molecule bonded to it inward. This picture has since been elaborated and extended.³ The effect of replacing hydrogen by deuterium was explained by assuming that hydrogen bonds are stronger than deuterium bonds. The failure to obtain a still lower rate when the complex and solvent were both deuterated was explained by the fact that deuteration was only 85–90% complete. Hence some light hydrogen bonds would always exist and offer a pathway for reaction. Partly on the basis of a report⁴ that the rates of hydrolysis of methyl halides was the same in H_2O and in D_2O , it was stated² that other detailed reaction mechanisms could not account for the isotope effects found for the cobalt complexes.

It has since been shown⁵ that the rates of hydrolysis of methyl halides are in fact slower in D_2O than in H_2O . For a large number of hydrolyzable organic derivatives of acids, ratios of $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$ ranging from 0.60 to near unity have now been observed.⁵ Furthermore, there does not seem to be any clear cut evidence as to whether hydrogen bonds or deuterium bonds are the stronger. Reports

in the literature are conflicting.⁶ It seems likely that the difference will be small enough so that the usual measurements of heats of hydrogen bond formation will not be sufficiently precise to supply an answer. A theoretical prediction in condensed media does not seem possible at present.⁷ It is certainly true that most physical properties indicate a greater degree of association for D_2O than for H_2O .⁸

In the case of base hydrolysis the rate of $\text{Co}(\text{ND}_3)_5\text{Cl}^{+2}$ in D_2O was only 0.60 that of $\text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$ in H_2O . The conclusion given² that this reduction in rate supports an $\text{S}_{\text{N}}1\text{CB}$ mechanism⁹ has been criticized¹⁰ on the grounds that a reaction going by a fast acid-base preequilibrium followed by a slow step, should be faster in D_2O than in H_2O . Several examples, such as the alkaline cleavage of diacetone alcohol and the reaction of chlorohydrins with hydroxide ion,¹¹ may indeed be cited in which $k_{\text{D}_2\text{O}} > k_{\text{H}_2\text{O}}$.

Because of these various objections, it was desirable to extend the studies of isotope effects in the hydrolysis of chloroamminecobalt(III) complexes to see to what extent the mechanisms proposed in reference 2 should be modified. The previous studies on acid hydrolysis also have been repeated. The two important changes are that a higher degree of deuteration of the complex ion $\text{Co}(\text{ND}_3)_5\text{Cl}^{+2}$ has been achieved (96%) and the rate studies have been done more carefully.

Experimental

The same procedures were used for the acid hydrolysis studies as had been reported previously.² A sufficiently large quantity of 99.5% D_2O was used to give 96.2% D content for the salt $[\text{Co}(\text{ND}_3)_5\text{Cl}]\text{Cl}_2$ based on random equilibration. This figure would not be changed much by any reasonable isotopic equilibrium constant for the exchange. The compound *trans*- $[\text{Co}(\beta\text{-picoline})_4\text{Cl}_2]\text{NO}_3$ had been prepared previously.¹² The compound $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4 \cdot \text{H}_2\text{O}$ was an analyzed sample obtained from J. W. Palmer.

Acid hydrolysis rates were studied at $49.4 \pm 0.1^\circ$ using the spectrophotometric method. The values of D_∞ needed were obtained from reference 2. In addition, the Guggen-

(6) (a) R. C. Herman and R. Hofstader, *J. Chem. Phys.*, **6**, 534 (1938); **7**, 460 (1939); (b) J. H. Hildebrand, R. W. Long and W. E. Morrell, *THIS JOURNAL*, **65**, 182 (1943).

(7) E. Whalley, *Trans. Faraday Soc.*, **53**, 1578 (1957).

(8) K. Wirtz, *Angew. Chem.*, **59**, 138 (1947); P. A. Giguère, O. Knop and M. Falk, *Can. J. Chem.*, **36**, 883 (1958).

(9) For a discussion see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 124–132.

(10) C. K. Ingold, Fifth Weizmann Memorial Lecture Series, The Weizmann Science Press of Israel, 1959, p. 11.

(11) (a) P. Ballinger and F. A. Long, *THIS JOURNAL*, **81**, 2347 (1959); (b) C. G. Swain, A. D. Ketley and R. F. W. Bader, *ibid.*, 2353.

(12) F. Basolo, J. G. Bergmann, R. E. Meecker and R. G. Pearson, *ibid.*, **78**, 2676 (1956).

(1) This investigation was supported by a grant from the U. S. Atomic Energy Commission under contract AT(11-1)-89, project No. 2.

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

(3) A. W. Adamson, *THIS JOURNAL*, **80**, 3183 (1958).

(4) C. G. Swain, R. Cardinaud and A. D. Ketley, *ibid.*, **77**, 935 (1955).

(5) R. E. Robertson and P. M. Laughton, *Can. J. Chem.*, **34**, 1714 (1956); **35**, 1319 (1957).

heim method¹³ was used in a number of cases. The same rate constants were obtained by the two methods. The change in optical density at 550 m μ was followed for both light and heavy [Co(NH₃)₅Cl]Cl₂. For [Co(β -pic)₄Cl₂]NO₃, a peak at 640 m μ was found and the reaction was followed at 660 m μ , since the reaction product had nearly zero absorptivity at this wave length. Except for a scattering of the first few points, the first order plots were linear up to one half-life, beyond which the reactions were not followed. Two to four runs were made for each case.

The solubilities of the chloropentammines in H₂O and in D₂O could not be determined at 49° because of hydrolysis during saturation. The solubilities were determined at 27°, in which case the aequation was slow. Excess solid was shaken with the solution for one half hour to attain equilibrium. A longer contact time up to 75 min. did not change the results nor did changing the amount of excess solid. Analysis was made by determining the optical density of 2 cc. of saturated solution diluted to 5 cc.

The pK_a of Pt(NH₃)₆⁺⁴ in H₂O and of Pt(ND₃)₆⁺⁴ in D₂O was measured by a potentiometric titration using a quinhydrone electrode, a saturated calomel electrode and a KCl salt bridge. The apparatus was standardized using acetic acid in H₂O and in D₂O since the isotope effect in this case is known.¹⁴ The known ratio for K_{HA} in H₂O and K_{DA} in D₂O then was used to calculate E^0 for the electrodes in D₂O, including any junction potentials. The value of E^0 was found to be 0.4864 volt at 25°. The pK_a was calculated from the simplified equation

$$pK_a = pH - \log \frac{[\text{salt}]}{[\text{acid}]} \quad (3)$$

Determination of the pK_a of acetic acid in H₂O before and after using the assembly in D₂O did not produce any changes. It was not possible to titrate Pt(NH₃)₆⁺⁴ all the way to the equivalence point because the solution became too alkaline for quinhydrone to function. Two or three separate titrations were made for each case.

Results and Discussion

Table I gives the rate constants found for acid hydrolysis. For comparison the results of the previous investigation² also are shown. These have been corrected from 52 to 49.4 by means of the known activation energy. Two definite conclusions can be drawn from these data. One is that deuteration of both the complex and the solvent produces the greatest retardation as would reasonably be expected. Further in the region of a system containing 90 mole % D and 10 mole % H there is no abnormally high rate. The second conclusion is that the retardation in rate does not depend on a cooperative effect involving hydrogen bonding by a solvent molecule both to the chloro group and to an acidic proton in the complex. This conclusion follows from the similar results in D₂O for Co(β -pic)₄Cl₂⁺ and Co(NH₃)₅Cl⁺². Accordingly the data cannot be said to give specific support for the mechanism of ref. 2.

TABLE I
RATES OF ACID HYDROLYSIS OF
CHLOROAMMINECOBALT(III) COMPLEXES AT 49.4°

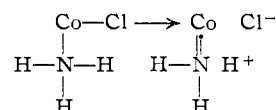
| Complex | Solvent | $k \times 10^3$, min. ⁻¹ | |
|--|---|--------------------------------------|--------|
| | | This work | Ref. 2 |
| [Co(NH ₃) ₅ Cl]Cl ₂ | H ₂ O | 1.91 ± 0.02 | 1.90 |
| [Co(NH ₃) ₅ Cl]Cl ₂ | D ₂ O | 1.34 ± .02 | 1.24 |
| [Co(ND ₃) ₅ Cl]Cl ₂ | H ₂ O | 1.45 ± .02 | 1.37 |
| [Co(ND ₃) ₅ Cl]Cl ₂ | D ₂ O | 1.15 ± .01 | 1.42 |
| [Co(ND ₃) ₅ Cl]Cl ₂ | 90% D ₂ O-10% H ₂ O | 1.14 ± .03 | .. |
| [Co(β -pic) ₄ Cl ₂]NO ₃ | H ₂ O | 42 ± 1 | .. |
| [Co(β -pic) ₄ Cl ₂]NO ₃ | D ₂ O | 33 ± 1 | .. |

(13) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(14) S. Korman and V. K. LaMer, *THIS JOURNAL*, **58**, 1396 (1936), give a value of 3.3 for the ratio K_{HA}/K_{DA} at 25° and 3.16 at 29°.

In fact the behavior of these inorganic systems is identical with that of organic halides. In solvolysis reactions it has been found that deuteration of the solvent reduces the rate, as already mentioned⁵ and deuteration of the halide also reduces the rate.¹⁵ The magnitude of the rate reduction in the latter case depends on the mechanism, being greater for S_N1 reactions than for S_N2 reactions.¹⁶ The factor 1.32 for k_H/k_D given by the first and third entries in Table I are in the mid-range of those reported for organic halides. The factor by which the rate is reduced in going from H₂O to D₂O is not diagnostic of mechanism being similar for alkyl halides ranging from methyl to *t*-butyl.⁵

The various explanations given for the isotope effects in organic systems are possible explanations for the inorganic systems. The generally accepted theory for the deuterium effect when located β to the halogen in the reacting molecule is that of hyperconjugation in the transition state.¹⁵ Such an explanation is certainly possible for the cobalt system



The details of this method for explaining lower reaction rates on deuterium substitution are given by Streitwieser.¹⁷ The treatment also could apply to the cobalt case.

There are two explanations for the slower rate of solvolytic type organic reactions in D₂O compared to H₂O. One, due to Robertson and Laughon,⁵ stresses stronger bonding in D₂O than in H₂O. Thus in order to solvate the ions as they are formed from neutral molecules, it is necessary to break up "icebergs" of ordered water around the reactants. This is more difficult in D₂O than in H₂O, hence slower reaction occurs. The other explanation is given, for example, by Pritchard and Long.¹⁸ This stresses the idea that D₂O is less effective than H₂O in solvating ions. Hence reactions producing ions will go more slowly in D₂O. The evidence for the poorer solvating properties for D₂O, in spite of a dielectric constant virtually the same as for H₂O, is that salts are less soluble in heavy water. Table II shows that this is true for the cobalt complexes also. There is in fact fair correlation between the relative solubilities in H₂O and in D₂O and the relative rates of hydrolysis for any one complex.

It is of interest that the heavy complex turns out to be more soluble in either solvent than the light complex. This may be explained either by the lattice energy of the light complex being greater or by the hydration energy of the ions of the light complex being less. In the same way, the lower solubility of salts in D₂O in general may be due to either stronger bonding of the solvent so that the intrusion of ions becomes more difficult or to weaker interaction of the ions with the solvent.¹⁹

(15) V. J. Shiner, Jr., *ibid.*, **75**, 2023 (1953); E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954).

(16) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(17) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *THIS JOURNAL*, **80**, 2326 (1958).

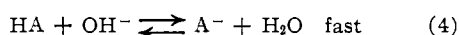
(18) H. G. Pritchard and F. A. Long, *ibid.*, **78**, 6008 (1956).

TABLE II
SOLUBILITY OF CHLOROAMMINECOBALT(III) COMPLEXES IN
H₂O AND D₂O AT 27.2°

| Complex | Solv. | Solubility, mole/l. | Relative values | |
|--|------------------|------------------------|-----------------|------|
| | | | Solu- bility | Rate |
| [Co(NH ₃) ₅ Cl]Cl ₂ | H ₂ O | 0.0224 | 1.00 | 1.00 |
| [Co(NH ₃) ₅ Cl]Cl ₂ | D ₂ O | .0166 | 0.74 | 0.70 |
| [Co(ND ₃) ₅ Cl]Cl ₂ | H ₂ O | .0256 | 1.14 | .76 |
| [Co(ND ₃) ₅ Cl]Cl ₂ | D ₂ O | .0193 | 0.86 | .60 |
| [Co(β-pic) ₂ Cl ₂]NO ₃ | H ₂ O | .0397 | 1.00 | 1.00 |
| [Co(β-pic) ₂ Cl ₂]NO ₃ | D ₂ O | .0342 | 0.86 | 0.79 |

In summary, there are several explanations for the isotope effects on rates of aqution of the cobalt complexes. One possible explanation is that originally proposed by Adamson and Basolo.² This depends upon the rather dubious assumption that hydrogen bonds are weaker than deuterium bonds. However, it cannot be said that the mechanism of ref. 2 is excluded by the data. That is, the transition state may be as shown and the isotope effects may be due to the causes cited for organic halides.

Turning to the case of base hydrolysis, it is necessary to consider the steps of the proposed S_N1CB mechanism in detail to predict the isotope effect. In brief we have for such a mechanism



The rate then is given by

$$\text{Rate} = k(K_a/K_w)[\text{HA}][\text{OH}^-] \quad (6)$$

where k is the rate constant for step 5. Now it can be seen that isotope effects for the three constants k , K_a and K_w may be expected. The observed isotope effect will be

$$\frac{k_H}{k_D} = \frac{(kK_a/K_w)_H}{(kK_a/K_w)_D} \quad (7)$$

In the case under discussion HA is Co(NH₃)₅Cl²⁺ and A⁻ is Co(NH₃)₄NH₂Cl⁺. In D₂O solvent each of these species will be exchanged rapidly to Co(NH₃)₅Cl²⁺ and Co(ND₃)₄ND₂Cl⁺ under basic conditions.² The observed isotope effect, as mentioned earlier, is $k_H/k_D = 0.60$ (averaged between 2.5 and 18°). This must be interpreted in terms of changes in K_a , K_w and k on deuteration. For the rate constant k a reasonable prediction can be made. It should show an effect approximately the same as for acid hydrolysis of Co(ND₃)₅Cl²⁺ in D₂O. From Table I this is seen to be $(1.15)/(1.91) = 0.60$.

Accordingly, for the mechanism to agree with the facts, it is necessary that isotope effects in K_a , the acid ionization constant of the complex ion, and K_w , the ion product of water, be equal to each other. K_w is known in D₂O²⁰ to be 0.154×10^{-14} at 25°. Thus the isotope effect on K_w is 6.5. The isotope effect on K_a remains to be determined. Unfortunately this is not possible because the complex is too weak an acid to measure directly.

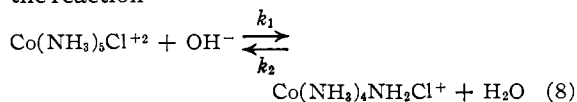
(19) It should perhaps be emphasized that differences in bonding between D and H are probably due chiefly to zero point energy effects. Some suggestions that inductive differences exist have been made; E. A. Halevi and M. Nussim, *Tetrahedron*, **1**, 174 (1957), for example.

(20) R. W. Kingerley and V. K. LaMer, *THIS JOURNAL*, **63**, 3256 (1941).

An estimate of the isotope effect can be made because of the well known generalization that the smaller the K_a , the larger the isotope effect.²¹ This rule can be given a theoretical justification, at least for a series of acids of a given type in which changes in K_a are accompanied by changes in the stretching frequency for the acidic proton.²²

The weakest acid other than water for which the isotope effect has been measured is 2-chloroethanol^{11a} where K_a in water is 4.9×10^{-15} and the ratio $(K_a)_H/(K_a)_D$ is 4.8, which is in accord with an extrapolation of the Rule and LaMer plot. This suggests that for an acid considerably weaker, an isotope effect of 6.5 may well be attained or even exceeded. Water, where K_a must be taken as 2×10^{-16} to be consistent, gives an unusually large effect probably because of special circumstances.

An estimate of K_a for Co(NH₃)₅Cl²⁺ may be made in the following way. It must be smaller than 10^{-13} since it is not measurable even for Co(NH₃)₆³⁺ which must be a stronger acid still.²³ Further the value must be greater than 10^{-21} since the rate of the reaction



can be measured, k_1 being about $1.5 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°. The product $k_2[\text{H}_2\text{O}]$ cannot exceed a figure of about 10^{12} sec^{-1} , assuming that reaction occurs on every suitably oriented collision. Since $k_1/k_2 = K_a/K_w$ for reaction 8, it can be seen that $K_a > 10^{-21}$.

The result of this line of argument suggests that K_a for Co(NH₃)₅Cl²⁺ should be in such a range that an isotope effect of 6.5 is not unexpected. In such a case it can be said that the observed isotope effect on the rates of base hydrolysis agrees with the S_N1CB mechanism. Again it must be admitted that it does not exclude other mechanisms, for example, a direct nucleophilic attack by hydroxide or deuterioxide ion.

The data in Table III are designed simply to show that the isotope effect on the acidity of an ammine complex is not abnormally small. In fact, if anything, the observed ratio, $(K_a)_H/(K_a)_D = 4.2$, is larger than might have been expected on the basis of the acidity of Pt(NH₃)₆⁴⁺.

| TABLE III ISOTOPE EFFECT ON THE K_a OF Pt(NH ₃) ₆ ⁴⁺ AT 29.0° | | |
|--|------------------|------------------------------|
| Compound | Solvent | K_a |
| [Pt(NH ₃) ₆]Cl ₄ ^a | H ₂ O | $6.9 \pm 1 \times 10^{-8}$ |
| [Pt(ND ₃) ₆]Cl ₄ ^a | D ₂ O | $1.6 \pm 0.7 \times 10^{-8}$ |
| CH ₃ COOH ^b | H ₂ O | $2.3 \pm 0.2 \times 10^{-8}$ |
| CH ₃ COOD ^b | D ₂ O | (0.70×10^{-8}) |

^a Concentration 0.01 M. ^b Concentration 0.04 M.

Acknowledgments.—The authors wish to acknowledge helpful discussions with Professors A. W. Adamson and F. A. Long.

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(21) C. K. Rule and V. K. LaMer, *ibid.*, **60**, 1974 (1938).

(22) O. Halpern, *J. Chem. Phys.*, **3**, 456 (1935); P. M. G. Bavin and W. J. Canady, *Can. J. Chem.*, **35**, 1555 (1957).

(23) Ref. 9, p. 388-389.

(24) Fred Basolo, J. W. Palmer and Ralph G. Pearson, *THIS JOURNAL*, **82**, 1073 (1960).