disappearance of N^- was shown to be second order in respect to N^- and an addition of naphthalene causes a decrease in the rate. The following mechanism is proposed to account for these observations

$$P_n^* \rightleftarrows P_{n-1}^* + S \quad K_{e1}\text{(rapidly established equilibrium)}$$

$$N^- + S \rightleftarrows S^- + N \quad K_{e2}\text{(rapidly established equilibrium)}$$

$$2S^- \longrightarrow {}^-S\text{-}S^- \ldots\ldots k_2 \text{ (a slow reaction)}$$

This scheme leads to the expression

$$-\mathrm{d}N^-/\mathrm{d}t = k_2(K_{e1}K_{e2})^2 \times (N^-/N)^2,$$

agreeing well with the experimental findings. Furthermore, when sodium biphenyl was added instead of sodium naphthalene, the rate of disappearance of biphenyl$^-$ radical-ion was found to be greater than that of naphthalene$^-$ radical ion. This is accounted for by the proposed mechanism since K_{e2} is greater for biphenyl than for naphthalene. Further studies of the depropagation of "living" polymers are being continued.

The last series of experiments, preliminarily reported here, confirms the relative slowness of the dimerization of S^- radical-ions. Of course, the conditions of these experiments were such that the addition reaction

$$S^- + S \longrightarrow \cdot S - S^-$$

must be even slower, because of the exceedingly low concentration of the monomer. This is certainly not the case in the initial stages of the polymerization.

In conclusion, we wish to thank the National Science Foundation for financial support of these investigations through the grant No. G-2761.

HAIFA, ISRAEL
SYRACUSE, N. Y.

[CONTRIBUTION FROM THE BROOKHAVEN NATIONAL LABORATORY, AND THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

The D_2O–H_2O Solvent Effect on a Complex Ion Equilibrium*

BY HENRY TAUBE

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The change in solvent from H_2O to D_2O increases the equilibrium quotient for the reaction $(NH_3)_5CoOH_2^{+++} + Cl^- = (NH_3)_5ClOCl^{++} + H_2O$ by the factor 1.5. Comparisons of the effect observed here with that of the corresponding reaction, but with OH^- replacing Cl^-, are made.

The study of the influence of the change in solvent from H_2O to D_2O on the rate of electron transfer[1,2] has directed attention to the effect of this solvent change on some equilibria which are relevant to the problem of electron transfer. Thus it has been shown that K_{diss} for Fe^{+++} aq. is unchanged[1] by substituting D_2O for H_2O, and that K_{diss} for $(NH_3)_5CoOH_2^{+++}$ is decreased by a factor of 1.5 when this change is made in the isotopic composition of the solvent.[3] The hydrogen-isotopic solvent effects for these aquo ions are considerably smaller than those reported[4] for oxyacids having the same values of K_{diss}. In the context of these observations and considerations, it seemed of interest to measure the magnitude of the effect which the H_2O–D_2O solvent change has on a complex ion equilibrium which does not involve a proton-containing ligand as the group being replaced by H_2O. By comparing the results for such a system with those obtained for the corresponding one in which OH^- is replaced by H_2O, we can hope to assess the contribution to the isotope effect made by the OH bond in OH^-.

The reaction

$$(NH_3)_5CoOH_2^{+++} + Cl^- = (NH_3)_5CoCl^{++} + H_2O \quad (1)$$

was chosen for study. Because the rates of substitution are slow, but not too slow, the system is tractable and the equilibrium quotients can be measured readily by spectrophotometric means. The system has the added virtue that a complete description of the reaction is possible, at least insofar as the first sphere of coördination is concerned; for a substitution-labile system an equally complete description of the reaction is not always possible.

Experimental

$(NH_3)_5CoOH_2(ClO_4)_3$ prepared as described earlier[5] and purified by repeated crystallization was the source of the ion $(NH_3)_5CoOH_2^{+++}$, and the salt $(ND_3)_5CoCl_3$, similarly purified, was the source of the chloro-complex. The extinctions coefficients of the deutero forms of the complex ions are sufficiently different[6] from those of the ordinary forms so that it was necessary to determine them also. The deutero form of the aquo ion was prepared simply by dissolving $(NH_3)_5CoOH_2(ClO_4)$ in the deuterated solvent and waiting for exchange equilibrium. $(NH_3)_5CoCl_3$ was prepared by the method described by Adamson and Basolo.[6]

The equilibrium quotients were determined by measuring the optical densities of the limiting forms ($(NH_3)_5CoOH_2^{+++}$ and $(NH_3)_5CoCl^{++}$), having the isotopic composition of the ions the same as that of the media, and comparing these optical densities with those measured for solutions which had reached equilibrium. At 25° a period of one month was allowed for equilibration, but at 51° a period of 2 days suffices, and at the highest temperature 80° a period of 3 hours. Solutions equilibrated at the higher temperatures were cooled rapidly to freeze the equilibrium. Measurements of optical density always were made at room temperature so that no corrections for the change in extinction coefficients with temperature were needed. The optical densities reported were measured with a Cary spectrophotometer, Model 14, the range from 650 to 310 mμ being covered.

The deuterium enriched solutions contained 87% D_2O All solutions were made 0.003 M in $HClO_4$ (acid is added to

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[1] J. Hudis and R. W. Dodson, THIS JOURNAL, **78**, 911 (1956).

[2] A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959).

[3] D. J. Bearcroft, D. Sebera, A. Zwickel and H. Taube, to be published.

[4] G. Schwarzenbach, *Z. Elektrochem.*, **44**, 46 (1938).

[5] A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 835 (1952)

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

suppress the dissociation of $(NH_3)_5CoOH_2^{+++}$; this ion has a dissociation constant of about 10^{-6} under the experimental conditions).

Table I contains a report of the positions of the maxima and the extinction coefficients at the maxima for the various species of interest in this work.

TABLE I

A COMPARISON OF EXTINCTION COEFFICIENTS OF THE AQUO AND CHLORO COMPLEXES IN H_2O AND 87% D_2O (ϵ IN CM.^{2} MOLE^{-1}, BASE 10 LOGARITHM)

	Max. at λ (mμ)	ϵ	Max. at λ (mμ)	ϵ
Aquo in H_2O	491	47.5	345	44.8
Deuteroaquo in D_2O	488	46.2	342	43.2
Chloro in H_2O	432	51.0	363	48.3
Deuterochloro in D_2O	431	49.2	362	47.0

The fractional change in ϵ between the deutero and hydrogen forms is even greater on the long wave length sides of the two absorption bands in the visible than it is at the maxima. Thus at 370 mμ, ϵ increases 14%, and at 550 mμ, 11%, in going from the deutero to the hydrogen forms. On the short wave length sides of the two absorption bands the extinctions almost coincide for the two isotopic forms. There is a noticeable difference in absorption when $(NH_3)_5CoOH_2^{+++}$ dissolved in H_2O is compared to the same ion in D_2O (if the latter system is measured a short time after mixing, only the hydrogens in the coördinated water have undergone exchange). The change amounts to perhaps a 4% decrease in ϵ at λ 550 mμ in going from H_2O to D_2O as solvent, and there is a barely detectable shift in the maxima toward shorter wave lengths. The isotopic effects on ϵ for the aquo ion which are reported here agree satisfactorily with those reported by Adamson and Basolo.[6] However, for the chlorocomplex they report an increase in ϵ in making the comparison for which we report a decrease. Also, the present results do not duplicate the large decrease (14%) they report for ϵ at 550 mμ when $(NH_3)_5CoOH_2(ClO_4)_3$ is dissolved in D_2O rather than in H_2O.

Results

Table II contains a summary of results obtained in calculating the equilibrium quotient at a variety of wave lengths from the data obtained for a medium 0.300 M in NaCl.

TABLE II

DETERMINATION OF K_1 AS FUNCTION OF λ

(Co (III) = 0.0035 M, (NaCl) = 0.300 M, $HClO_4$ = 0.003 M)

λ =	560 mμ	540	370	310	Mean
K_1 at 25°	1.41	1.44	1.43	1.43	1.48
at 51°	2.20	2.24	2.30	2.13	2.22
at 80°	3.60	3.66	3.65	3.68	3.65

The system is evidently well-behaved, as is further demonstrated by the results of an experiment in which $(NH_3)_5CoCl_3$ rather than $(NH_3)_5CoOH_2(ClO_4)_3$ was used as starting material. This experiment gave values for the equilibrium quotient identical (within 3%) to those reported in Table II.

Other data which were obtained at 25° are

K_1 in D_2O (87%), 0.300 M NaCl = 2.0

K_1 in H_2O, 0.035 M NaCl, μ = 0.041 = 3.3

K_1 in H_2O, 0.100 M NaCl, μ = 0.106 = 2.4

Discussion

Garrick studied the rate of reaction 1 forward and reverse, but apparently made no direct determination of the equilibrium quotient.[7] Using the specific rates he reports for the forward and reverse reactions, the equilibrium quotient K_1 for a medium at ionic strength 0.32 (KNO_3 at 0.20 M) is calculated as 1.6. The agreement with the value reported in the present work, 1.43 ± 0.06 at $\mu = 0.31$ for a medium containing NaCl as the major electrolyte component, is satisfactory. While it cannot be claimed that the difference between the value reported in this paper and in Garrick's is real, some difference because of the change in electrolyte composition of the solvent can be expected.

The variation of K_1 with μ is described satisfactorily by the equation of Rabinowitch and Stockmayer,[8] proposed for the variation of the association constant of $FeCl^{++}$ with μ. The equation is modified by changing the value of the constant which corresponds to the dissociation constant at $\mu = 0$. The equation, adapted by fitting it to our data at $\mu = 0.31$

$$\log K_1 = 0.977 - \frac{3\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} + 0.295\,\mu$$

suggests 9.8 as the value of K_1 at $\mu = 0$. The values calculated from the equation for $\mu = 0.106$ and 0.041 are 2.3 and 3.3, to be compared with the measured values of 2.4 and 3.3. The variations of K_1 with μ which can be derived from Garrick's data are in reasonable agreement with ours.

An increase in K_1 by a factor of 1.40 is observed in changing from H_2O to 87% D_2O as solvent. For the purposes of the comparison which will be made presently, this ratio is corrected to 100% D_2O using a linear extrapolation, so that for 100% D_2O the value 1.47 will be used for the rate $K_1^{D_2O}/K_1^{H_2O}$. It is admitted that a linear extrapolation is not necessarily valid, but the error made in such an extrapolation will not materially affect the use to which the extrapolated value will be put.

Consider now the reaction corresponding to (1) but with OH^- in place of Cl^-.

$$(NH_3)_5CoOH_2^{+++} + OH^- = (NH_3)_5CoOH^{++} + H_2O \quad (2)$$

The equilibrium quotient for this reaction is obtained as the ratio K_{diss}/K_w where

$$K_{diss} = \frac{((NH_3)_5CoOH^{++})(H^+)}{((NH_3)_5CoOH_2^{+++})} \text{ and } K_w = (H^+)(OH^-)$$

The change in both K_{diss}[3] and K_w[9] caused by the change in solvent from H_2O to D_2O is known, so that $K_2^{D_2O}/K_2^{H_2O}$ is calculated as 6.54/1.5 = 4.4. Now it can be assumed that the ratio $K_1^{D_2O}/K_1^{H_2O}$ provides a fair measure of the H–D isotope effects in reaction 2 exclusive of those occasioned by the internal structure of OH^-, so that it can be concluded that this internal structure is the seat of an isotope effect of the magnitude of 4.4/1.47 = 3.0 (K_2 being greater in D_2O than in H_2O). An effect of this magnitude and in this direction can be explained[10] by reasonable frequency assignments to the bending and torsional modes for OH^- in Co–OH, without invoking any differences in the OH stretching mode between OH^- and $(NH_3)_5CoOH^{++}$. It is clear that a rationalization of the H–D isotope effect for reaction 2 at once provides a

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[7] F. J. Garrick, *Trans. Faraday Soc.*, **33**, 487 (1937).

[8] E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

[9] R. W. Kingerley and V. R. LaMer, *ibid.*, **63**, 3256 (1941).

[10] J. Bigeleisen, private communication.

rationalization of the H–D isotope effect on K_{diss}, since $K_{\text{diss}} = K_{\text{w}} \cdot K_2$ (it being assumed that the isotope effect on K_{w} is understood).

Sutin and Dodson[11] have found that the association quotient for $FeCl^{++}$ $(\equiv K_3)$ increases by a factor of 2.6 when the solvent change from H_2O to D_2O is made. The large difference between the $(NH_3)_5CoCl^{++}$ and $FeCl^{++}$ systems is surprising, although it must be admitted that there is no substantial basis for preconceived ideas as to the magnitudes of the effects which are to be expected when differences in the nature of the reactants are introduced. It has been pointed out[12] that the differences between the Co(III) and Fe(III) systems are caused largely by differences in the aquo ions. This can be seen by comparing the H–D isotope effects for the reactions

$$(NH_3)_5CoCl^{++} + OH^- \underset{(k_4)}{=} (NH_3)_5CoOH^{++} + Cl^-$$

$$FeCl^{++} + OH^- \underset{(k_5)}{=} FeOH^{++} + Cl^-$$

$K_4^{D_2O}/K_4^{H_2O} \times K_5^{H_2O}/K_5^{D_2O}$ is calculated as 1.2; *i.e.*, the difference between the systems almost disappears for a comparison not involving the aquo ions.

From the variation of K_1 with temperature, ΔH_1 for the interval 25 to 51° is calculated as 3.4 kcal., and for the interval 51 to 80° as 3.9 kcal. Using the mean of these values as ΔH_1, ΔS_1, at 25° and $\mu = 0.31$ is calculated as 13 e.u. This value can be compared with those reported by Gates and King[13] for the association of Cr^{+++} with Cl^-: 10.6 e.u. at 4.4 M Cl^- and 17.2 e.u. at 0 M Cl^-, both with total anion normality at 4.44. From the data reported by Rabinowitch and Stockmayer for the association of Fe^{+++} with Cl^-, ΔS at $\mu = 0.61$ and 25° is calculated as 32 e.u. The reliability of the latter value, which depends on the assumption that ϵ for $FeCl^{++}$ does not change with temperature, is questioned by Gates and King.[13]

Some rough observations were made during the course of the present work on the rate of hydrogen exchange between $Co(NH_3)_5OH_2^{+++}$ and the solvent H_2O. The differences in ϵ for the isotopically different species can be used as a measure of the rate of exchange but they are hardly an accurate or sensitive measure. Infrared analysis of the ion, after precipitation as a salt, provides a better measure. The results we obtained using this method suggest that the rate of exchange is inverse in concentration of acid,[14] even when this is present at the 0.1 M level; they are not accurate enough however to exclude some contribution by an acid independent term. Under the conditions of the equilibrium measurements it was not possible to measure the association constant for $(NH_3)_5CoOD_2^{+++} + Cl^-$ in D_2O. At 1 M acid, however, such measurements may be possible, and are of interest in assessing the magnitude of the effect caused by hydrogen isotopic substitution in the first sphere of coördination.

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NEW YORK, N. Y.
CHICAGO, ILLINOIS

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[11] N. Sutin and R. W. Dodson, private communication.

[12] N. Sutin, private communication.

[13] H. S. Gates and E. L. King, THIS JOURNAL, **80**, 5011 (1958).

[14] J. S. Anderson, H. V. A. Briscoe and N. L. Spoor, *ibid.*, 361 (1943).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO, CHICAGO, ILL.]

The Transfer of Oxygen in Some Oxidation–Reduction Reactions of Aquo Complexes

BY WALTER KRUSE AND HENRY TAUBE

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Oxygen tracer experiments have been done which show that transfer of oxygen from $(NH_3)_5CoOH_2^{+++}$ to Cr^{++} in the oxidation–reduction reaction is quantitative. The reaction media included solutions acidic enough so that at least 50% of the reaction proceeds by the aquo path. Thus a bridged activated complex is demonstrated also for the aquo path. When *cis*-$(NH_3)_4Co(H_2O)_2^{+++}$ or *cis*-$en_2Co(H_2O)_2^{+++}$ is the oxidizing agent, also one and only one oxygen is transferred to the reducing agent. Thus there is no evidence in these systems for a double oxygen bridge in the activated complexes for electron transfer.

In an earlier paper,[1] the results of some tracer experiments bearing on the question of oxygen transfer from $(NH_3)_5CoOH_2^{++}$ to Cr^{++} aq. were reported. These experiments showed that the transfer is essentially complete by the path for the oxidation–reduction reaction which makes use of the activated complex implied by the rate function $((NH_3)_5CoOH_2^{+++})(Cr^{++})/(H^+)$. The work indicated that at least some transfer takes place by the path having the activated complex of composition $(NH_3)_5CoOH_2^{+++}.Cr^{++}$, but the evidence was weakened by a later revision of the kinetic data.[2]

With the development of the subject of the mechanism of oxidation–reduction reactions of complex ions, the question of oxygen transfer from an aquo ion oxidizing agent to the reducing agent has taken on increasing importance—obviously the views concerning the mechanisms of these reactions would be greatly affected if in a system in which a definitive test of this feature of mechanism can be made, no evidence for water transfer is found. Accordingly we have returned to the problem, taking advantage of the experience gained since the early results were obtained, and applying a new analytical technique, in the hope of obtaining a definite answer to the question posed. The experiments have also been extended to oxidizing agents of the *cis*-

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[1] R. K. Murmann, H. Taube and F. A. Posey, THIS JOURNAL, **79**, 262 (1957).

[2] A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959).