Aquated Cations in Aqueous Solution and the Kinetics of Proton Transfer

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Abstract: It has been previously discovered in this laboratory that the rate constant for the transfer to the solution bulk of protons from the primary hydration spheres of several hydrated cations in aqueous solution is of the form $k_M = k_1 + k_{2A}[HA]$, where HA indicates any of several general acids. In previous papers k_{2A} has been studied as a function of temperature for a number of acids, and a mechanism for the general acid catalysis has been suggested. In the present investigation an intensive study of k_{2A} is reported with Cr^{3+}, Ni^{2+}, VO^{2+}, and $CrCl^{2+}$ as the cations and with several acids covering a broad range of acid strengths. The results of this study are used to deduce the existence of two previously undetected features of the role of coordinated water in proton-transfer mechanisms in aqueous solution.

In previous papers[2] it has been established through the use of ^1H nmr that the pseudo-first-order rate constant for the transfer of protons from the primary hydration sphere of chromium(III), nickel(II), and vanadyl ions to bulk water in aqueous solution is of the form $k_M = k_1 + k_2[H^+]$. A mechanism was proposed for the acid-catalyzed process involving direct protonation of the aquated cations as the rate-determining step. Further work with aquated chromium(III) and vanadyl ions[2b] indicated that the reaction was also general acid catalyzed.

By analysis of the catalysis data, the following detailed mechanism for the acid-catalyzed reaction was postulated.[2b]

$$M(H_2O)_x{}^{n+} + HA^m \underset{}{\overset{K}{\rightleftharpoons}} \text{encounter complex (EC)}$$

$$EC \xrightarrow{k_a} \text{hydrogen-bonded complex (HBC)} \qquad (1)$$

$$HBC \longrightarrow M(H_2O)_xH^{(n+1)+} + A^{m-1}$$

where $M(H_2O)_x{}^{n+}$ is either $Cr(H_2O)_6{}^{3+}$ or $VO(H_2O)_5{}^{2+}$ and HA^m represents H_3O^+, HSO_4^-, acetic acid, or phosphoric acid.

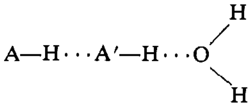
It was proposed that the rate-determining substep for all reactions studied other than VO^{2+}–acetic acid is the rearrangement of the encounter complex to form a hydrogen bond involving the transferring proton and the lone pair of a coordinated water molecule. This interpretation was based on the lack of correlation between the magnitude of the observed rate constant and the acid strength of the proton donor, the distinct correlation between the order and ratios of rate constants and the order and ratios of stability constants for the encounter complexes as estimated from diffusion theory,[3] and the large negative entropies of activation which characterize these rate constants, consistent with the protonation of a rather inaccessible lone pair.

The rate constant for VO^{2+}–acetic acid, however, was an order of magnitude smaller than expected for the above rate-determining step, and the activation parameters differed considerably from those of the other reactions studied.

Reevaluation of the kinetic data for reactions with HSO_4^- (*vide infra*) reveals the likelihood that no strong correlation exists between reaction rate and charge type as was previously thought.[2b] Detailed examination of mechanism 1 with H_3O^+ as the acid, certainly a representative strong acid, reveals that one of the proton-transfer reactions following the formation of the hydrogen-bonded complex must be rate determining if microscopic reversibility is to be satisfied. Indeed this is the case with catalysis by any general acid. Thus, mechanism 1 as previously formulated[2b] contains at least one vital flaw and must be examined further.

A more general view of the reaction under consideration is useful. Thus far the added acid has been viewed as the catalyst for proton transfer from the metal ion to the bulk solvent. An equally valid view has the metal ion catalyzing proton transfer from the acid to the bulk solvent. Since the metal ion is itself an acid, the most general formulation of the reaction is the catalysis by one acid of the transfer of a proton from another acid to the solvent.

Many features of mechanism 1 must be retained in a more general formulation of such catalyzed proton transfer. Formation of an encounter complex and rearrangement of the encounter complex to form a hydrogen-bonded complex must precede the rate-limiting proton transfer(s) which may be stepwise or concerted. Several possible mechanisms can operate within these limits, and these possibilities are best seen in relation to the schematic representation of the possible hydrogen-bonded complexes Ia–c.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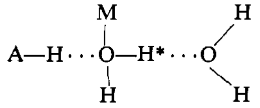
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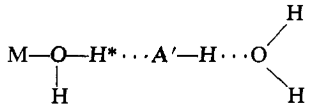
Ic

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[2] (a) T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, **5**, 1100 (1966); (b) T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Am. Chem. Soc.*, **89**, 1611 (1967).

[3] M. Eigen, W. Kruse, G. Maas, and L. DeMaeyer, *Progr. Reaction Kinetics*, 2, 285 (1964).

Table I. Values of Rate Constants and Activation Parameters at 25° for Aqueous Solutions of Cr^{3+}, VO^{2+}, Ni^{2+}, and $CrCl^{2+}$ and Several Acid Catalysts

				$Cr(H_2O)_6^{3+}$					
Acid	H_3O^+ [b]	HSO_4^- [b]	H_3PO_4	CH_2ClCO_2H	HF	HCO_2H	CH_3CO_2H [c]	$C_2H_5CO_2H$	
Rate constant[a]	4.0×10^4	8.3×10^4	1.2×10^5	$7 + 10^4$	4.2×10^4	3.7×10^4	1.7×10^5	1.5×10^5	
ΔH^*, kcal	0	−1	2	0.5	0	4	3	3	
ΔS^*, eu	−38	−40	−29	−38	−38	−27	−25	−25	
Ref	2b	2b	2b	*c*	*d*	*c*	*c*	*c*	
				$VO(H_2O)_5^{2+}$					
Acid	H_3O^+ [b]	$CHCl_2CO_2H$	HSO_4^- [b]	H_3PO_4	CH_2ClCO_2H	HF	HCO_2H	CH_3CO_2H	$C_2H_5CO_2H$
Rate constant[a]	1.6×10^5	1.1×10^5	3.0×10^5	3.2×10^5	4.8×10^4	8.0×10^4	3.3×10^4	4.8×10^4	2.7×10^4
ΔH^*, kcal	3	5	2	2	5	5	6	8	9
ΔS^*, eu	−30	−20	−28	−26	−21	−19	−19	−11	−8
Ref	2b	*c*	2b	2b	*c*	*c*	*c*	2b	*c*
				$Ni(H_2O)_6^{2+}$					
Acid	H_3O^+	$CHCl_2CO_2H$	CH_2Cl-CO_2H	CH_3CO_2H	$C_2H_5CO_2H$				
Rate constant[a]	1.3×10^6	$\sim 2 \times 10^6$	(1×10^5)[e]	4.2×10^4	4.4×10^4				
ΔH^*, kcal	0.5	Small	Small	8	7				
ΔS^*, eu	−30	Large, negative	Large, negative	−12	−14				
Ref	2a	*d*	*d*	*d*	*d*				
				$[Cr(H_2O)_5Cl]^{2+}$					
Acid	H_3O^+	$CHCl_2CO_2H$	H_3PO_4	CH_3CO_2H	$C_2H_5CO_2H$				
Rate constant[a]	1.3×10^5	8.6×10^4	2.4×10^5	2.3×10^4	2.8×10^4				
ΔH^*, kcal	1	1	3	6.5	3				
ΔS^*, eu	−30	−33	−24	−17	−28				
Ref	*d*	*d*	*d*	*d*	*d*				

[a] Units of M^{-1} sec^{-1}. [b] From ref 2b without activity coefficient corrections. [c] Redetermined value in 10^{-2} *M* $HClO_4$. [d] This work. [e] Value at 273°K.

In drawing Ia, HA and HA′ are the two general acids involved in the catalyzed proton transfer to the bulk. Drawings Ib and Ic depict the metal ion, M, in each of the possible acid roles. H* is the proton to be transferred from the primary hydration sphere of the metal ion to the bulk water either directly (Ib) or after initial transfer to the acid HA (Ic). The hydrogen-bonded complexes Ia–c then just represent a proton transfer from HA to a bulk water molecule through an intervening bridge, and mechanism 1 represents a special case of Ib above.

The rate-limiting proton transfer may be the transfer of a proton to a bulk water molecule, or it may be the protonation of the intervening acid as was proposed for mechanism 1 in certain cases.[2b] As another alternative the two proton transfers could be concerted.

No conclusions concerning these alternatives or other aspects of the catalysis of proton transfer between weak acids could be reached on the basis of only a single measurement, namely that made with the VO^{2+}–acetic acid system[2b]. As a consequence the measurements were extended to Cr^{3+}, Ni^{2+}, and $CrCl^{2+}$ with a number of acid catalysts covering a relatively wide range of acid strengths.

In previous papers the kinetic data were treated with[2b] and without[2a] consideration of activity corrections. Because of major difficulties in treating the available activity data to give realistic and meaningful activity coefficients for HSO_4^-, the data in this paper are given without activity coefficient corrections, and the conclusions presented do not depend critically on activity coefficients.

Experimental Section

A stock solution of $VO(ClO_4)_2$ was prepared and analyzed for VO^{2+} as in the previous study.[2b] A stock solution of $Cr(NO_3)_3$ was prepared from the reagent grade salt and the solution was analyzed spectrophotometrically.[4] A stock solution of $Ni(NO_3)_2$ was prepared from the reagent grade salt and the solution was analyzed for nickel gravimetrically using dimethylglyoxime.[5]

Chloropentaaquochromium(III) perchlorate was prepared by the method of Ogard and Taube.[6] The chromium concentration was determined spectrophotometrically as chromate ion after treatment with alkaline H_2O_2.[7]

From these stock solutions of chromium(III), nickel(II), vanadyl, and chlorochromium(III) ions, solutions of various acid concentrations were prepared by addition of standardized formic, acetic, propionic, monochloroacetic, dichloroacetic, hydrofluoric, phosphoric, and perchloric acids. To avoid possible complications from acid dissociation products (*cf.* ref 2) strong acid was added to solutions containing acids with $pK_a > 3$.

Concentrations of water in all of the solutions were calculated from the densities which were measured with a Westphal balance.

Results

The methods used to evaluate rate constants for the acid-catalyzed reaction are analogous to those employed in ref 2b, but without activity coefficient corrections. A brief outline of the method used for each acid is given for the reactions of aquated chromium(III), nickel(II), and vanadyl ions. A more detailed description of the previously unreported protonation kinetics of $[CrCl(H_2O)_5]^{2+}$ is given.

Rate constants and activation parameters at 298°K for all the acid-catalyzed reactions, including those in ref 2, are given in Table I.

In the following discussion, k_2 refers to the rate constant for acid catalysis by H_3O^+, k_p to the rate constant for acid catalysis by any other proton donor, k_M to the measured rate constant, and k_1 to the acid-independent step whether it is acid dissociation or whole water exchange.

(4) P. J. Elving and B. Zemel, *J. Am. Chem. Soc.*, **79**, 1281 (1957).

(5) L. Erdey, "Gravimetric Analysis," Vol. 7, Part II, Pergamon Press, London, 1965, p 386.

(6) A. E. Ogard and H. Taube, *J. Am. Chem. Soc.*, **80**, 1084 (1958).

(7) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

A. Hexaaquochromium(III) Ion. In previous work,[2] rate constants for the acid-catalyzed proton-transfer reaction have been reported for HNO_3, $HClO_4$, HSO_4^-, H_3PO_4, and acetic acid. Rate data have now been obtained for propionic, formic, and monochloroacetic acids; the value for acetic acid has been redetermined in the presence of added $HClO_4$.

a. **Acetic Acid.** Values of $k_M = (PT_2)^{-1}$ for $Cr(NO_3)_3$–acetic acid solutions containing 10^{-2} *M* $HClO_4$ were determined at several temperatures. Then from a plot of k_M *vs.* $[CH_3CO_2H]$, values of k_p were obtained from the slope and k_1 from the intercept. The small contribution to k_M from catalysis by H_3O^+ was ignored and no correction was made for the dissociation of acetic acid. Values of k_1 are in good agreement with those obtained previously.[2b]

The significant difference in the value of k_p and its activation parameters from that reported in ref 2b is ascribed to the presence of varying amounts of acid dissociation products in the solutions used in the initial determination.

b. **Propionic Acid, Formic Acid, and Hydrofluoric Acid.** The treatment was the same as for acetic acid, with 10^{-2} *M* $HClO_4$ added to prevent complications from acid. Significant differences in the rate constants and activation parameters were also found when the experiment was repeated in the absence of strong acid.

c. **Monochloroacetic Acid.** Values of k_M for $Cr(NO_3)_3$–CH_2ClCO_2H solutions containing *ca.* 10^{-2} *M* $HClO_4$ were determined at several temperatures. A correction was then made for the dissociation of monochloroacetic acid using readily obtainable[8] values of the thermodynamic equilibrium constant at several temperatures. The postulated rate expression for this system is

$$k_M = k_1 + k_2[H^+] + k_p[CH_2ClCO_2H] \qquad (2)$$

Thus with values of k_2 from ref 2b ($Cr(NO_3)_3$–$HClO_4$ solutions), a plot of $k_M' = k_M - k_2[H^+]$ *vs.* $[CH_2ClCO_2H]$ is linear with slope k_p.

d. **Sulfuric Acid.** Previous results reported for HSO_4^- [2b] were obtained using values for the HSO_4^- single-ion activity coefficient estimated by converting values for the mean ionic activity coefficient of sulfuric acid as a 2:1 electrolyte to values for a 1:1 electrolyte. The mean ionic activity coefficients so obtained were considerably smaller than those for equimolar hydrochloric acid or perchloric acid solutions and these low values were attributed to a low value for the HSO_4^- activity coefficient. These low values for HSO_4^- in comparsion with ClO_4^- which it should resemble to a first approximation led us to reconsider the method used for obtaining the HSO_4^- activity coefficient. Reexamination of the original H_2SO_4 activity data[9] leads us to conclude that the mean ionic activity coefficient for H_2SO_4 as a 2:1 electrolyte cannot be satisfactorily converted to that for a 1:1 electrolyte because of difficulty in the necessary extrapolation to infinite dilution for the 1:1 electrolyte case.

As reported in Table I, the values for HSO_4^- with chromium(III) and vanadyl ions have been recalculated from the data used in ref 2b, making no activity coefficient corrections and neglecting the small correction for further dissociation of HSO_4^-. Comparison of the values in Table I with those in ref 2b indicates that, although the present value for the rate constant is considerably smaller than that reported previously (1×10^6 *vs.* 8×10^4 M^{-1} sec^{-1}), the more significant enthalpy of activation (0 *vs.* −1 kcal/mole) and entropy of activation (−31 *vs.* −40 eu) remain similar to the activation parameters obtained for other strong acids with chromium(III).

e. **Perchloric Acid.** For consistency in comparing results for the different acids, the kinetic parameters reported for H_3O^+ in Table I are those calculated without activity coefficient corrections and differ only slightly from those reported previously[2b] since the corrections were small.

B. Aquated Vanadyl Ion. In previous work[2b] rate constants for the acid-catalyzed proton-transfer reaction have been reported for $HClO_4$, HSO_4^-, H_3PO_4, and acetic acid. Rate data have now been obtained for hydrofluoric, propionic, formic, and mono- and dichloroacetic acids. A hydration number of 5 has been assumed for VO^{2+} in the calculation of the previously defined[2] concentration factor, *P*, though recent work[10] suggests that 4 may be more realistic.

a. **Hydrofluoric, Propionic, Formic, and Monochloroacetic acids.** The treatment in each case was the same as for the corresponding chromium(III) systems.

b. **Dichloroacetic Acid.** Values of k_M for $VO(ClO_4)_2$–$CHCl_2CO_2H$ solutions were determined at several temperatures. A correction was then made for the dissociation of $CHCl_2CO_2H$ using the concentration equilibrium quotient at 25° given in the literature.[11] No correction was made for the temperature variation of this equilibrium constant. Then k_p was evaluated by plotting $k_M' = k_M - k_2[H^+]$ *vs.* $[CHCl_2CO_2H]$ using values of k_2 from ref 2b ($VO(ClO_4)_2$–$HClO_4$ solutions).

c. **Perchloric and Sulfuric Acids.** The recalculation of previous results[2b] was the same as for the corresponding chromium(III) systems. For HSO_4^- the rate constant in Table I is smaller than previously reported (4×10^6 *vs.* 3×10^5 M^{-1} sec^{-1}), while the activation parameters are now closer to those found for other strong acids ($\Delta H^* = 2$ kcal/mole compared with 4 kcal/mole; $\Delta S^* = -28$ eu compared with −14 eu).

The values reported for H_3O^+ in Table I are only slightly different from those calculated previously[2b] using activity coefficients.

C. Hexaaquonickel(II) Ion. In the previous work[2a] rate constants for the acid-catalyzed proton-transfer reaction have been reported for HNO_3 solutions. Rate data have now been obtained for acetic, propionic, and mono- and dichloroacetic acids. In this regard it may be mentioned that k_1, the rate constant for the uncatalyzed transfer, has been precisely determined[12] from a pmr line-width study of an unacidified Ni^{2+} solution over a temperature range extending to −30°. The rate constant is $3 \pm 1 \times 10^4$ sec^{-1} in excellent agreement with the ^{17}O result.[13] The previously reported value was somewhat high because of two fac-

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[8] "Handbook of Chemistry and Physics," 47th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1966.

[9] H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **57**, 27 (1935).

[10] J. Reuben and D. Fiat, *Inorg. Chem.*, **6**, 579 (1967).

[11] G. Kortum, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworth and Co., Ltd London, 1961, p 295.

[12] T. J. Swift and G. P. Weinberger, *J. Am. Chem. Soc.*, **90**, 2023 (1968).

[13] R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).

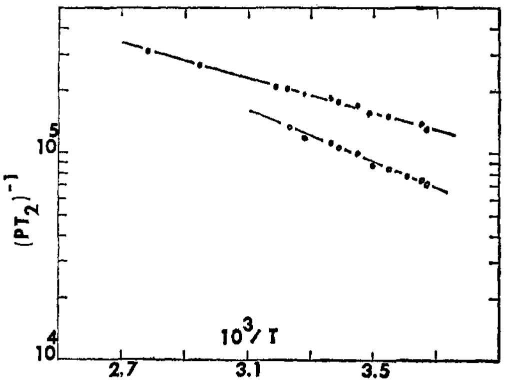

Figure 1. Graph of $-\log PT_2$ *vs.* $10^3/T$ for $[Cr(H_2O)_5Cl](ClO_4)_2$ solutions at the following concentrations of $HClO_4$: ○, 0.42 *M;* ●, 1.00 *M.*

tors. First there was a sizable contribution from $k_2[H^+]$ even at the relatively low concentration of $[H^+]$ employed in the "unacidified" solution, and, second, there is a quite sizable second coordination sphere relaxation of protons by Ni^{2+} and this was not detected in the earlier study. These errors strongly affect the calculated k_1, but they play no role in the calculation of k_2 or k_p.

a. Acetic Acid. Values of k_M for $Ni(NO_3)_2$–acetic acid solutions containing *ca.* 5×10^{-2} *M* HNO_3 were obtained by the method outlined in ref 2a. A correction was then made for the dissociation of acetic acid through use of the concentration equilibrium quotient,[14] K_1'. Then as for the $Cr(NO_3)_3$–CH_2ClCO_2H system, a plot of $k_M' = (k_M - k_2[H^+])$ *vs.* $[CH_3CO_2H]$ was made, where k_2 values were obtained from ref 2a.

b. Propionic Acid. The treatment was exactly as for acetic acid with the value of K_1 at 0° obtained from the literature.[8] Approximations to the activity coefficients used to calculate K_1' were made as for acetic acid.

c. Monochloroacetic Acid. Values of k_M were obtained as in ref 2a. A correction was made for the dissociation of CH_2ClCO_2H using K_1 from ref 8 and the values of activity coefficients used to calculate K_1' as for acetic and propionic acids; then k_p was calculated from eq 2 with use of values of k_1 and k_2 from ref 2a. However, because of the large contribution to k_M from k_2, the uncertainties in the value of K_1' and in particular the small accessible region of chemical-exchange-controlled proton relaxation, Arrhenius plots exhibited considerable scatter, and consequently it was impossible to estimate reliable activation parameters.

d. Dichloroacetic Acid. The treatment was the same as for monochloroacetic acid with the concentration equilibrium quotient obtained from ref 11. Activation parameters were not estimated because of the considerable scatter in the Arrhenius plots.

An attempt to obtain k_p for HSO_4^- was unsuccessful because, at the low concentrations of H_2SO_4 used, the main anionic species is SO_4^{2-}. No attempt was made to determine k_p for H_3PO_4 because of the impossibility of suppressing the formation of $H_2PO_4^{2-}$ and still preserving the chemical-exchange-controlled region.

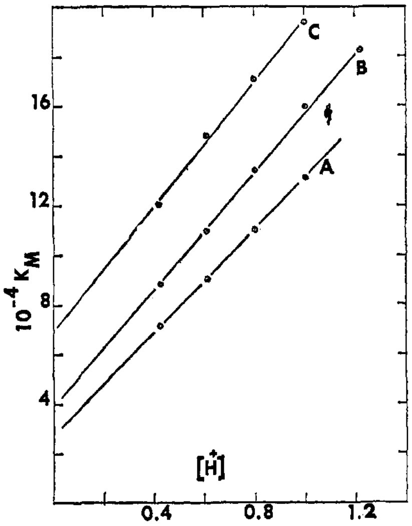

Figure 2. Graph of k_M (sec^{-1}) *vs.* hydrogen ion concentration for a 7.1×10^{-3} *M* $[Cr(H_2O)_5Cl](ClO_4)_2$ solution at the following temperatures: (A) 272.5°K, (B) 286°K, (C) 304.5°K.

D. Chloropentaaquochromium(III) Ion. This ion was studied to provide a comparison with Cr(III) in order to determine the effect of a change in the formal charge of the cation on the kinetics of the acid-catalyzed proton exchange.

Proton relaxation times of $CrCl_3$ in aqueous solution have been examined previously,[15] but the temperature-dependent equilibria greatly increased the complexity of the system, and a complete study was not attempted. In this work $CrCl^{2+}$ was separated by an ion-exchange technique[8] from *cis*- and *trans*-$[Cr(H_2O)_4Cl_2]^+$ and $Cr(H_2O)_6^{3+}$. The monochloro complex was chosen for study because of its slow rate of aquation to the hexaaquo complex and because of the inverse hydrogen ion dependence of this rate[16] (*ca.* 0.03%/hr compared to *ca.* 16%/hr for the dichloro complex[17] at 25°, in solution containing 0.05 *M* chromium(III) and 0.5 *M* $HClO_4$). The solutions were maintained at 0° throughout the separation and between kinetic measurements to minimize the aquation rate.[16] Reproducibility of relaxation times for freshly prepared solutions and the same solutions stored at 0° for 2 weeks confirms the effectiveness of this procedure.

Proton relaxation rates as a function of temperature for two $[Cr(H_2O)_5Cl](ClO_4)_2$–$HClO_4$ solutions are shown in Figure 1. The term *P* is the concentration factor, $10[CrCl^{2+}]/(2[H_2O] + [H^+])$ where $[H_2O]$ is the concentration of bulk water. The proton relaxation appears to be chemical exchange controlled[18] over the entire temperature range employed (0–80°), and the acid dependence indicates an acid-catalyzed step.

Figure 2 is a plot of k_M at three temperatures for $[Cr(H_2O)_5Cl](ClO_4)_2$–$HClO_4$ solutions as a function of hydrogen ion concentration. From this plot and eq 1b of ref 2b, values of k_1(intercept) and k_2(slope) were obtained, and hence values of k_2 averaged at each

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(14) Values of K_1, the thermodynamic equilibrium constant, were obtained from ref 8, and the activity coefficients for the calculation of K_1' were estimated by the method given in ref 2b for the dissociation of phosphoric acid.

(15) T. H. Brown, R. A. Bernheim, and H. S. Gutowsky, *J. Chem. Phys.*, 33, 1593 (1960).

(16) T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965).

(17) C. W. Meridith, W. D. Matthews, and E. F. Orlemann, *ibid.*, 3, 320 (1964).

(18) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

Table II. Values of k_1 and k_2 as Functions of Temperature and Values of ΔH^* and ΔS^* at 25° for $[Cr(H_2O)_5Cl]^{2+}$ in Aqueous Solution[a]

Temp, °K	$10^{-4}k_1$, sec^{-1}	ΔH^*, kcal	ΔS^*, eu	$10^{-5}k_2$, M^{-1} sec^{-1}	ΔH^*, kcal	ΔS^*, eu
272.5	2.9	4 ± 1	-23 ± 4	1.0	1 ± 1	-30 ± 4
277	3.4			1.1		
286	3.9			1.2		
295	5.2			1.3		
304.5	6.9			1.3		

[a] See ref 2b, Table II, for a discussion of experimental error limits.

temperature over several concentrations were computed. Values of k_1, k_2, and the appropriate activation parameters are given in Table II.

A comparison of the relative deprotonation rates for chromium(III) and chlorochromium(III) is of some interest. Although literature data for the acid dissociation constant of $CrCl^{2+}$ are not available, $pK_a(Cr^{3+}) = 4.0 < pK_a(CrCl_2^+) = 5.4$[19] suggests an intermediate value for $CrCl^{2+}$. Then, the smaller value of k_1 for $CrCl_2^+$ (6.2×10^4 at 298°K compared to 11.0×10^4 for Cr^{3+})[2] is consistent with the value anticipated for an acid dissociation reaction.

Another feature of this comparison is that proton relaxation in $CrCl^{2+}$ solutions is chemical exchange controlled between at least 0 and 80°, whereas relaxation control becomes predominant at temperatures >60° for Cr^{3+} solutions. The additional fact that the overall exchange rate k_M for a 1 M $HClO_4$ solution is slightly faster for $CrCl^{2+}$ than for Cr^{3+} at 60° indicates that the relaxation process involved is more efficient for the former.

After the existence of a chemical-exchange-controlled relaxation region had been established, as well as the presence of an acid-catalyzed step for $CrCl^{2+}$, catalysis rate constants were determined for acetic, propionic, phosphoric, and dichloroacetic acids.

a. Acetic and Propionic Acids. The procedure was the same as with the corresponding Cr^{3+} solutions. The acetic acid solution was made 0.1 M in $HClO_4$ and the propionic acid solution was made 5×10^{-2} M in $HClO_4$ to avoid complications from acid dissociation products.

b. Dichloroacetic Acid. Values of k_M for $[Cr(H_2O)_5Cl](ClO_4)_2$–$CHCl_2CO_2H$ solutions containing *ca.* 10^{-1} M $HClO_4$ were determined at several temperatures. A correction was made for the dissociation of $CHCl_2CO_2H$ using the value of the concentration equilibrium quotient given in ref 11. Then k_p was evaluated from eq 2 with values of k_1 and k_2 from Table II.

c. Phosphoric Acid. Values of k_M for $[Cr(H_2O)_5Cl](ClO_4)_2$–H_3PO_4 solutions containing 0.5 M $HClO_4$ were determined at several temperatures. Values of $k_p (\equiv k_5)$ were calculated using eq 4b of ref 2b and values of k_1 and k_2 from Table II. A small correction was also made for the first dissociation step of H_3PO_4 using the concentration equilibrium quotient K_1'.[14]

Discussion

In Table I the acids are arranged from left to right for each cation in the order of decreasing acid strength.

Table III. Acid Dissociation Constants for the Various Acids Used[a]

Acid	K_A	Acid	K_A
H_3O^+	55.5	CH_2ClCO_2H	1.4×10^{-3}
$CHCl_2CO_2H$	3.3×10^{-2}	HF	6.7×10^{-4}
HSO_4^-	1.2×10^{-2}	HCO_2H	1.8×10^{-4}
H_3PO_4	7.5×10^{-3}	CH_3CO_2H	1.8×10^{-5}
		$C_2H_5CO_2H$	1.3×10^{-5}

[a] Thermodynamic dissociation constants at 25° taken from ref 11.

In Table III are listed the acid dissociation constants at 25° for each of the acids employed. Two very useful observations can be made immediately from these data.

A. With a given metal ion, catalysis by weak acids such as acetic acid is characterized with few exceptions by a much less negative ΔS^* than catalysis by strong acids. In addition the ΔH^* values are generally larger for the weak acids (although this is considerably less marked with $Cr(H_2O)_6^{3+}$ than with the other metal ions) than for the strong acids. These differences between the two types of catalysts undoubtedly reflect a significant difference in the catalysis mechanisms.

B. For a typical weak acid such as acetic acid, the rate constants given in Table I are larger than the rate constant at the same temperature for the dissociation of acetic acid converted to a bimolecular rate constant for the purpose of comparison (1.4×10^4 l./(mole sec)).[3] The significance of this fact rests in the very high likelihood that in catalyzing a proton transfer from a hydrated metal ion to the bulk the acid proton of the acetic acid is also exchanged a very significant fraction of the time. In fact, it is difficult to envision a mechanism for catalysis by acetic acid where this would not be true.

Hence in addition to acetic acid serving as a catalyst for the hydrated ion, the hydrated ion serves as a catalyst for the weak acid.

Such an occurrence is similar to the cyclic internal proton exchange for acetic acid studied by Luz and Meiboom[20] in which acetic acid catalyzes proton transfer from water to water, and bridging waters catalyze proton exchange from acetic acid to water. The bimolecular rate constant at 25° for this cyclic process (k is 8.7×10^5 l./(mole sec), $\Delta H^* = 3.1$ kcal/mole, and $\Delta S^* = 13.0$ eu) as well as the activation parameter values lead to the suggestion that the process observed with metal ions and weak acids is a cyclic mutual catalysis.

It was this possibility which prompted the use of hydrofluoric acid as one of the weak acid catalysts. While the cyclic mechanism could possibly operate with HF, it is unlikely that it could be as effective as for acetic acid because of difficulty in forming the cyclic transition state.

However, as is seen in Table I, hydrofluoric acid is a quite effective catalyst, and hence a cyclic mechanism is unlikely as the source of the catalysis reported in Table I.

However, a mechanism does not have to involve a cyclic transition state in order to involve mutual catalysis as is shown in mechanism 3, the mechanism proposed for the mutual catalysis. In this scheme the

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(19) "Stability Constants," Special Publication No. 7, part II, The Chemical Society, London, 1958, p 7.

(20) Z. Luz and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 3923 (1963).

$$\mathrm{M(^{*}HO)}_x{}^{n+} + \mathrm{HA}^m \underset{k_{-\mathrm{E}}}{\overset{k_\mathrm{E}}{\rightleftharpoons}} \text{encounter complex (*EC)} \qquad (3a)$$

$$\text{*EC} \underset{k_{-\mathrm{a}}}{\overset{k_\mathrm{a}}{\rightleftharpoons}} \text{hydrogen-bonded complex (*HBC)} \qquad (3b)$$

$$\text{*HBC} \xrightarrow{k_\mathrm{b}} \mathrm{M(H_2O)}_{x-1}\mathrm{(OH)}^{(n-1)+} + {}^{*}\mathrm{HA}^m + \mathrm{H_3O^+} \qquad (3c)$$

asterisk indicates the presence of the proton transferred from the aquated metal ion in the over-all process. HA^m represents the added acid plus any water molecules involved, and k_b is assumed to be rate determining. The hydrogen-bonded complex indicated here is proposed to be Ic given in the introductory section. In this mechanism the hydrated metal ion catalyzes the ionization of the weak acid, and the acid dissociation of the hydrated metal ion is promoted by the incipient conjugate base of the weak acid. This process contains the essentials that made the cyclic mechanism effective without being cyclic, although a contribution from a cyclic mechanism in the case of carboxylic acid catalysts is not precluded.

This mechanism for weak acids immediately leads to a complementary mechanism for strong acids such as $\mathrm{H_3O^+}$. Since such acids are much more likely to serve as proton donors rather than proton acceptors, mechanism 3 is most unlikely. However, if hydrogen-bonded complex Ib is substituted for Ic and the following rate-determining step is substituted for (3c), a highly plausible mechanism is obtained for catalysis by strong acids.

$$\text{*HBC} \xrightarrow{k_\mathrm{b}'} \mathrm{M(H_2O)}_x{}^{n+} + \mathrm{A}^{m-1} + {}^{*}\mathrm{H_3O^+} \qquad (3c')$$

The particularly attractive feature of this mechanism is that it leads to a simple explanation of the large difference in activation parameter values between strong acids and weak acids.

Now experimentally $\mathrm{d[M(H_2O)}_x{}^{n+}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{M(H_2O)}_x{}^{n+}][\mathrm{HA}^m]$, and from mechanism 3 or 3′, $\mathrm{d[M(H_2O)}_x{}^{n+}]/\mathrm{d}t = k_\mathrm{b}[\mathrm{HBC}]$. From these two equations

$$k_\mathrm{p} = k_\mathrm{b}[\mathrm{HBC}]/[\mathrm{M(H_2O)}_x{}^{n+}][\mathrm{HA}^m] \qquad (4)$$

It is then assumed that the encounter complex is in rapid equilibrium with the reactants and that $k_{-\mathrm{a}} \gg k_\mathrm{b}$ or k_b' so that

$$K_\mathrm{E} = k_\mathrm{E}/k_{-\mathrm{E}} = [\mathrm{EC}]/[\mathrm{M(H_2O)}_x{}^{n+}][\mathrm{HA}^m] \qquad (5)$$

$$K_\mathrm{A} = k_\mathrm{a}/k_{-\mathrm{a}} = [\mathrm{HBC}]/[\mathrm{EC}] \qquad (6)$$

With the combination of eq 4, 5, and 6, the expression for k_p is

$$k_\mathrm{p} = K_\mathrm{E}K_\mathrm{A}k_\mathrm{b} \qquad (7)$$

or

$$k_\mathrm{p} = K_\mathrm{E}K_\mathrm{A}'k_\mathrm{b}' \qquad (7')$$

Both mechanisms 3 and 3′ involve the same sort of encounter complex, and hence this does not provide the differentiation. However, the value of K_A is expected to be much smaller for mechanism 3′ than for mechanism 3 because of the differences in structures Ib and Ic. Structure Ib requires the formation of a hydrogen bond between the acidic proton of HA^m and the relatively inaccessible lone pair on a primary sphere water. Although the enthalpy change associated with rearrangement of the encounter complex should be small, the entropy change is expected to be large. The acid and metal ion are in a more restricted arrangement in the hydrogen-bonded complex than in the more loosely defined encounter complex, and the hydrogen bonding of the associated water molecules is markedly changed, indicating a large negative entropy change associated with formation of the complex.

By comparison, the formation of hydrogen-bonded complex Ic requires much less alteration of the acid and metal ion environments since the hydrogen bonds are more "natural" ones. With this formation of a hydrogen bond between one of the primary sphere water protons and one of the lone pairs available on the acid, the spatial requirements for the complex are less stringent than for Ib, and the necessary solvent rearrangement should also be less. Hence, the entropy change associated with forming complex Ic should be considerably less than that for complex Ib. Again, the enthalpy change for the process should be small.

The activation barrier in (3c) and (3c′) should be primarily enthalpic in nature since only proton transfer is involved, and ΔH^* should be significantly larger for weak acids than for strong acid catalysts. Thus the ΔS^* difference between strong and weak acid catalysts should arise from K_A and K_A' and the ΔH^* difference from k_b and k_b'.

This interpretation of the source of the large negative entropies observed for strong acid catalysis is further supported by an additional observation which can be made from the data of Table I.

A comparison of the relative magnitudes of activation entropies for different metal ions with the same acid indicates that for the strongest acids studied ($\mathrm{H_3O^+}$, $\mathrm{CHCl_2CO_2H}$, $\mathrm{HSO_4^-}$, $\mathrm{H_3PO_4}$), ΔS^* becomes more negative as the acid strength of the aquated metal ion increases,[19] *i.e.*, $\mathrm{Ni^{2+}} > \mathrm{VO^{2+}} > \mathrm{CrCl^{2+}} > \mathrm{Cr^{3+}}$.

It is rather surprising that the strongest acid ($\mathrm{Cr(H_2O)_6{}^{3+}}$) is the most difficult to catalyze, but since an increase in acid strength of the hydrated cation is undoubtedly accompanied by a decreased probability of formation of a structure such as Ib, this observation is quite consistent with mechanism 3′.

In summary it appears very likely that coordinated water can and does play two previously undetected roles in proton transfer in aqueous solution. It can catalyze the transfer of protons between other weak acids and bulk water (mechanism 3), and it can serve as a bridge for the transfer of protons between strong acids and bulk water (mechanism 3′).

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