The Kinetics of Protonation of Aquated Vanadyl Ions in Aqueous Solution

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Abstract: Studies of the kinetics of protonation of aquated cations in solution were extended to the vanadyl ion. As with chromium(III) and nickel(II) ions the rate constant for the transfer of protons from the aquated ion to the bulk is given by $k_M = k_1 + k_2[H^+]$. The values of the activation parameters for the k_2 process are such as to indicate that the mechanism previously proposed is a general one for aquated ions. Catalysis of proton transfer from aquated VO^{2+} was also found for HSO_4^-, phosphoric acid, and acetic acid, and the conclusion reached is that the reaction is general acid catalyzed. General acid catalysis was also found for the proton transfer from $Cr(H_2O)_6^{3+}$ to the solution bulk. Values of the rate constants and activation parameters for each reaction were obtained, and further information was deduced concerning the detailed mechanism of the acid-catalyzed proton-transfer reaction.

It has been previously shown[1] through proton magnetic resonance studies of aqueous solutions containing chromium(III) and nickel(II) ions that the pseudo-first-order rate constant for the transfer of protons from each of the two aquated ions to bulk water is of the form $k = k_1 + k_2[H^+]$. The acid-independent step in the case of the chromium(III) ion is acid dissociation, whereas that for nickel(II) ion is water-molecule exchange. A mechanism was proposed for the acid-catalyzed process involving the protonation of the aquated cations as the rate-determining step.

A number of questions are raised as a result of this study and among these are the following.

(1) As with any proton-transfer reaction, the rate-determining step above may be formulated in terms of discrete elementary substeps such as: (a) The formation of a hydrogen bond involving the transferring proton and a lone pair on a first coordination sphere water molecule. (b) The actual proton transfer across (or through) an energy barrier. The question arises as to which (if either) of these substeps is rate determining for a given cation.

(2) Is the proton exchange studied subject to general acid catalysis and if so what information can this yield concerning the more detailed mechanism?

It will be shown that these questions could be answered satisfactorily through a study of vanadyl ion. Vanadyl ion was chosen because it appeared to meet the requirements previously stated for observation by means of proton nmr of an acid-catalyzed proton-transfer reaction. The relaxation of protons by VO^{2+} had been studied by Hausser and Laukien.[2] The temperature dependence of the spin–spin relaxation time measured by the authors[2] gave a clear indication of a sizable temperature region of chemical-exchange controlled relaxation; *i.e.*, the relationship between line width and exchange rate is expressed by either eq 10a or 10c given in the treatment of Swift and Connick.[3] In addition, the large change in the relaxational behavior produced through the addition of H_2SO_4 was an indication of the operation of an acid-catalyzed mechanism.

Experimental Section

A stock solution of $VO(ClO_4)_2$ was prepared by the addition of a calculated amount of $Ba(ClO_4)_2$ to a solution of $VOSO_4$. The colloidal $BaSO_4$ was removed by centrifugation, and the resulting blue solution was filtered twice. The stock solution was then analyzed for VO^{2+} by titration with $KMnO_4$. From this solution, solutions of various acid concentrations were prepared by addition of standardized $HClO_4$, acetic acid, or orthophosphoric acid. To suppress the formation of the dihydrogen phosphate anion, *ca.* 0.5 *M* $HClO_4$ was added to each of the phosphoric acid solutions. A stock solution of $VOSO_4$ was also prepared and analyzed, and solutions of various acid strengths were prepared by addition of standardized H_2SO_4.

A $Cr(NO_3)_3$ stock solution was prepared from the reagent grade salt and the solution was analyzed for Cr^{3+}. Acidified solutions were prepared from this by addition of standardized $HClO_4$, H_2SO_4, acetic acid, or orthophosphoric acid.

Spectra were recorded on a Varian A-60A spectrometer and values of T_2 were obtained from line widths.

Results

Proton relaxation times, T_2, as a function of temperature for three $VO[ClO_4]_2$–$HClO_4$ solutions are shown in Figure 1. A hydration number of 5[4] has been assumed for VO^{2+} in the calculation of the concentration factor, P, where $P = 10[VO^{2+}]/(2[H_2O] + [H^+])$. The proton relaxation appears to be chemical-exchange controlled[3] over the entire temperature range employed and the acid dependence indicates an acid-catalyzed step.

The possibility of general acid catalysis was first investigated with $VOSO_4$–H_2SO_4 solutions. Considerably greater line broadening was obtained for these solutions as compared with equimolar solutions of $VO(ClO_4)_2$–$HClO_4$ solution. Since the bisulfate ion is the main anionic species present at these concentrations (0.2–1 *M*), the increased broadening was tentatively attributed to general acid catalysis by HSO_4^-. Further studies involving $VO(ClO_4)_2$–acetic acid solutions and $VO(ClO_4)_2$–phosphoric acid solutions also gave additional broadening, indicative of catalysis by the undissociated acid. Similar studies were carried out with Cr^{3+}, all showing evidence for general acid catalyzed behavior.

In order to elucidate the detailed mechanism of these acid-catalyzed reactions, the individual rate constants

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[1] T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, **5**, 1100 (1966).

[2] R. Hausser and G. Laukien, *Z. Physik*, **153**, 394 (1959).

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

[4] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

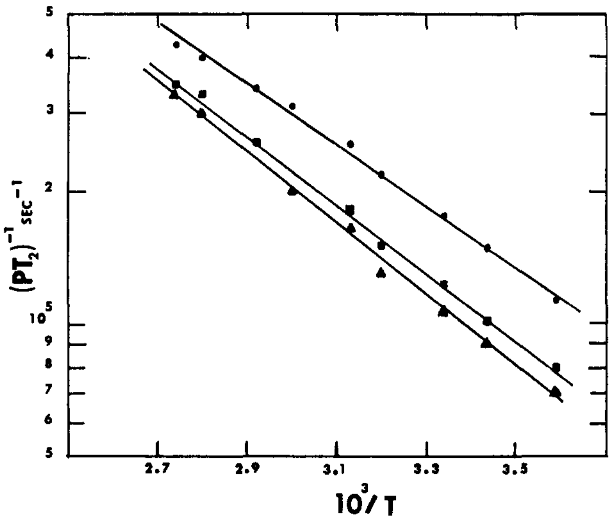

Figure 1. Graph of log $(PT_2)^{-1}$ *vs.* $10^3/T$ for 0.0349 M $VO(ClO_4)_2$ solutions at the following concentrations (M) of $HClO_4$: ●, 1.00; ■, 0.70; ▲, 0.60.

for both general and specific acid catalysis of proton transfer from aquated VO^{2+} and Cr^{3+} ions must be evaluated and their *relative* magnitudes compared.

The postulated rate expressions are as follows

$$k_M = k_1 + k_2[H^+] \tag{1}$$

$$k_M = k_1 + k_2[H^+] + k_3[HSO_4^-] \tag{2}$$

$$k_M = k_1 + k_4[AcOH] \tag{3}$$

$$k_M = k_1 + k_2[H^+] + k_5[H_3PO_4] \tag{4}$$

where $k_M = (PT_2)^{-1}$ for the various solutions, and k_2, k_3, k_4, and k_5 are the rate constants for acid catalysis by hydronium ion, bisulfate ion, acetic acid, and orthophosphoric acid, respectively. P for bisulfate ion, acetic acid, and orthophosphoric acid is given by $2n[M]/(2[H_2O] + \Sigma H_i)$, where n is the primary hydration number of the paramagnetic cation, [M] is the cation concentration, and ΣH_i is the total concentration of protons in the system which can exchange rapidly with the solvent.

The relative magnitudes of these rate constants are such that, in order to make a meaningful comparison, it is necessary to make a correction for activity coefficients. This is especially important in comparing rates in perchloric and sulfuric acids where the mean activity coefficients differ considerably for equimolar solutions.

Using absolute rate theory[5] one can write

$$k = \frac{k^0\gamma_A\gamma_B}{\gamma_*} \tag{5}$$

where k = measured rate constant in solution at ionic strength C, k^0 = rate constant at infinite dilution for that solvent, γ_A and γ_B = activity coefficients of reactants at ionic strength C, and γ_* = activity coefficient of activated complex at ionic strength C. Substitution of (5) into rate expressions 1–4 gives

$$k_M = k_1{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H_2O})}{\gamma_{M^{n+}\cdots H_2O}} + k_2{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H^+})}{\gamma_{M^{n+}\cdots H^+}}m_{H^+} \tag{1a}$$

$$k_M = k_1{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H_2O})}{\gamma_{M^{n+}\cdots H_2O}} + k_2{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H^+})}{\gamma_{M^{n+}\cdots H^+}}m_{H^+} + k_3{}^0\frac{(\gamma_{M^{n+}})(\gamma_{HSO_4^-})}{\gamma_{M^{n+}\cdots HSO_4^-}}m_{HSO_4^-} \tag{2a}$$

$$k_M = k_1{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H_2O})}{\gamma_{M^{n+}\cdots H_2O}} + k_4{}^0\frac{(\gamma_{M^{n+}})(\gamma_{AcOH})}{\gamma_{M^{n+}\cdots AcOH}}m_{AcOH} \tag{3a}$$

$$k_M = k_1{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H_2O})}{\gamma_{M^{n+}\cdots H_2O}} + k_2{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H^+})}{\gamma_{M^{n+}\cdots H^+}}m_{H^+} + k_5{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H_3PO_4})m_{H_3PO_4}}{\gamma_{M^{n+}\cdots H_3PO_4}} \tag{4a}$$

where for VO^{2+}, $n = 2$; for Cr^{3+}, $n = 3$.

Concentrations are written in terms of molalities since most of the literature data on activity coefficients are expressed in molal units. However, rate constants will be reported in the normal molar units since the concentrations used are small enough to permit the equating of molarity and molality within experimental error.

To a first approximation $\gamma_{H_2O} = \gamma_{AcOH} = \gamma_{H_3PO_4} = 1$ and $\gamma_{M^{n+}} = \gamma_{M^{n+}\cdots H_2O} = \gamma_{M^{n+}\cdots AcOH} = \gamma_{M^{n+}\cdots H_3PO_4}$ since the total charge is constant. The approximation to the other activated complexes is taken to be a metallic cation with a charge equal to the sum of charges on the reactants. Hence $M^{n+}\cdots H^+ \simeq M^{(n+1)+}$; $M^{n+}\cdots HSO_4^- \simeq M^{(n-1)+}$. Therefore the rate expressions reduce to

$$k_M = k_1{}^0 + k_2{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H^+})}{\gamma_{M^{(n+1)+}}}m_{H^+} \tag{1b}$$

$$k_M = k_1{}^0 + k_2{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H^+})}{\gamma_{M^{(n+1)+}}}m_{H^+} + k_3{}^0\frac{(\gamma_{M^{n+}})(\gamma_{HSO_4^-})}{\gamma_{M^{(n-1)+}}}m_{HSO_4^-} \tag{2b}$$

$$k_M = k_1{}^0 + k_4{}^0m_{AcOH} \tag{3b}$$

$$k_M = k_1{}^0 + k_2{}^0\frac{(\gamma_{M^{n+}})(\gamma_{H^+})}{\gamma_{M^{(n+1)+}}}m_{H^+} + k_5{}^0m_{H_3PO_4} \tag{4b}$$

Further Estimations of Activity Coefficients. Estimates must be made of the following values: (a) ratios of cation activity coefficients such as $\gamma_{M^{n+}}/\gamma_{M^{(n+1)+}}$ for cations present in relatively low concentrations in perchloric or sulfuric acid solutions; (b) activity coefficients for hydrogen ion and bisulfate ion in these same solutions.

A "constant ionic strength" approximation was made for all ratios in approximation a; *i.e.*, the ratios were taken as being independent of the concentration of acid in the range studied, independent of temperature, and having a value of unity. Detailed calculations using data[6] on the variation of $\gamma_\pm$(HCl) (0.01M) in varying

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[5] *Cf.* A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 7.

concentrations of excess mono-, bi-, and trivalent metal chlorides coupled with the conclusions of a detailed discussion by Robinson and Stokes[7] on mixed 1:1 electrolyte–HCl solutions indicated a maximum probable error of ±20% in the above approximation.

The application of approximation a makes little difference in the interpretation of the results reported in the present work since the correction is relatively small. Approximation b is relatively important, however, and involves single ion activity coefficients rather than ratios as in (a). The high values of $\gamma_\pm$ for HCl, $HClO_4$, HBr, and HNO_3[6] at concentrations employed in this work in conjunction with the high values of $\gamma_\pm$ for various 1:1 electrolytes containing these anions[6] suggest that the value of γ_{H^+} is close to unity. In addition a striking similarity was noted between the mean ionic activity coefficients of equimolal aqueous perchloric and hydrochloric acids as shown in Table I.[8]

Table I. Comparison of Mean Activity Coefficients for Aqueous Solutions of Perchloric and Hydrochloric Acids

Acid, m	$\gamma_\pm(HCl)$	$\gamma_\pm(HClO_4)$
0.1	0.796	0.803
0.2	0.767	0.778
0.3	0.756	0.768
0.4	0.755	0.766
0.5	0.757	0.769
0.6	0.763	0.776
0.7	0.772	0.785
0.8	0.783	0.795
0.9	0.795	0.808
1.0	0.809	0.823

As a consequence of these considerations and of the fact that mean ionic activity coefficients for perchloric acid solutions have been determined only at 25°, while $\gamma_\pm(HCl)$ values are available[6] over a temperature range, γ_{H^+} was approximated in this work by $\gamma_\pm(HCl)$. In view of the values of $\gamma_\pm(HCl)$ and suggested close to unity values of γ_{H^+}, it seems likely that $\gamma_\pm(HCl)$ values represent probable lower limits for γ_{H^+}. It will be shown in the Discussion section that the use of values of γ_{H^+} larger than $\gamma_\pm(HCl)$ leads only to a strengthening of the conclusions presented.

Mean ionic activity coefficients for sulfuric acid[9] in the concentration range employed here are considerably smaller than those for equimolal hydrochloric acid solutions. This is true even after the values of $\gamma_\pm(H_2SO_4)$ are converted to those of a 1:1 electrolyte (the authors[9] treated H_2SO_4 formally as a 2:1 electrolyte). No data are available on the activity coefficients of bisulfate salts, but it appears reasonable to assume that the low values of $\gamma_\pm(H_2SO_4)$ result from low values of $\gamma_{HSO_4^-}$ rather than from any significant change in γ_{H^+}. Consequently, values of $\gamma_{HSO_4^-}$ were approximated by

$$\gamma_\pm{}^2(H_2SO_4)/\gamma_{H^+} \simeq \gamma_\pm{}^2(H_2SO_4)/\gamma_\pm(HCl)$$

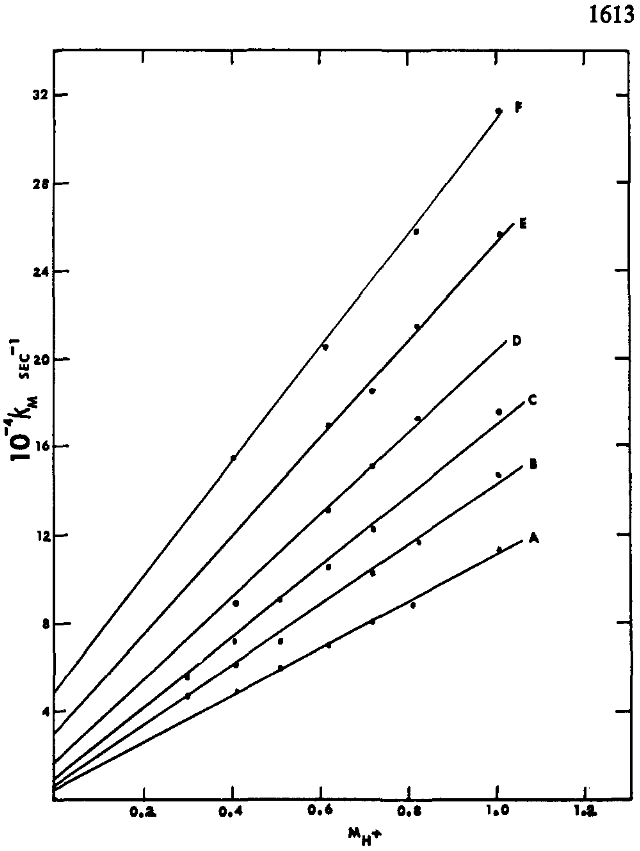

Figure 2. Graph of k_M *vs.* hydrogen ion molality for a 0.0349 M $VO(ClO_4)_2$ solution at the following temperatures: A, 278.5°K; B, 291°K; C, 300°K; D, 312.5°K; E, 319.5°K; F, 333°K.

where $\gamma_\pm(H_2SO_4)$ is the 1:1 electrolyte value.

Evaluation of Rate Constants. The various rate constants were now determined as follows.

A. Calculation of $k_1{}^0$ and $k_2{}^0$. Figure 2 is a plot of k_M at six temperatures for $VO(ClO_4)_2$–$HClO_4$ solutions as a function of hydrogen ion concentration (expressed in molal units). From this plot and eq 1b, values of $k_1{}^0$ (intercept) and $k_2{}^0\gamma_{M^{2+}}\gamma_{H^+}/\gamma_{M^{3+}} \simeq k_2{}^0\gamma_{H^+}$ (slope) were obtained, and hence values of $k_2{}^0$, averaged

Table II. Values of $k_1{}^0$, $k_2{}^0\gamma_{H^+}$, and $k_2{}^0(\mathrm{av})$[a] as Functions of Temperature and Values of ΔH^* and ΔS^* for $VO(H_2O)_5{}^{2+}$ in Aqueous Solution

Temp, °K	$10^{-4}\cdot k_1{}^0$, sec^{-1}	ΔH^*, kcal	ΔS^*, eu	$10^{-5}\cdot k_2{}^0\gamma_{H^+}$, M^{-1} sec^{-1}	$10^{-5}\cdot k_2{}^0(\mathrm{av})$, M^{-1} sec^{-1}	ΔH^*,[b] kcal	ΔS^*,[b] eu
278.5	0.4			1.1	1.3		
291	0.7			1.3	1.5		
300	1.1	8 ± 1	−14 ± 4	1.7	2.0	2 ± 1	−26 ± 4
312.5	1.8			1.9	2.3		
319.5	2.9			2.2	2.8		
333	5.0			2.5	3.2		

[a] The values of $k_2{}^0(\mathrm{av})$ contain a systematic uncertainty of *ca.* 40% due to approximations a and b in addition to the random error indicated by the significant figure in the table. This is also true for rate constants reported in subsequent tables where approximations a and b have been used. [b] The limits of error given were calculated from Arrhenius plots and do not contain the systematic uncertainty arising from the temperature dependence of the errors in the estimation of activity coefficients. Since the temperature dependence of the activity coefficients used is small,[6] this contribution to the uncertainty has been neglected in this and subsequent tables.

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(6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, Appendix A.

(7) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworth & Co. (Publishers) Ltd., London, 1965, p 432 ff.

(8) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, 45, 612 (1949).

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

Table III. Values of k_1^0, $k_2^0\gamma_{H^+}$, and k_2^0(av) as Functions of Temperature and Values of ΔH^* and ΔS^* for $Cr(H_2O)_6^{3+}$ in Aqueous Solution

Temp, °K	$10^{-4}k_1^0$, sec^{-1}	ΔH^*, kcal	ΔS^*, eu	$10^{-4}k_2^0\gamma_{H^+}$, M^{-1} sec^{-1}	$10^{-4}k_2^0$(av), M^{-1} sec^{-1}	ΔH^*, kcal	ΔS^*, eu
283	5.4	6 ± 1	−16 ± 3	4.0	4.9	−0.5 ± 1	−38 ± 3
295	9.4			4.0	5.0		
303.5	12.6			4.0	5.0		
311.5	15.7			4.0	5.1		

at each temperature over several concentrations, were computed. The small change in γ_{H^+} with concentration enabled this simple graphical method to be used successfully within the limits of experimental error. Values of k_1^0, $k_2^0\gamma_{H^+}$, and k_2^0(av) and the appropriate activation parameters are given in Table II.

The question arises concerning the nature of the acid-independent step characterized by k_1^0. Is it water exchange as in nickel(II) ion or acid dissociation as found for chromium(III) ion?[1] The kinetics of water exchange have recently been investigated by ^{17}O nmr methods[10] and the results are: $k(25°) = (1/n)2 \times 10^3$ sec^{-1}; $\Delta H^* = 13.7$ kcal; $\Delta S^* = (2.2\text{-}4.6 \log n)$ eu, where n is the hydration number of the vanadyl ion. This rate constant is only a few per cent of the value of k_1^0 at 25° given in Table II, and the k_1^0 process is clearly acid dissociation.

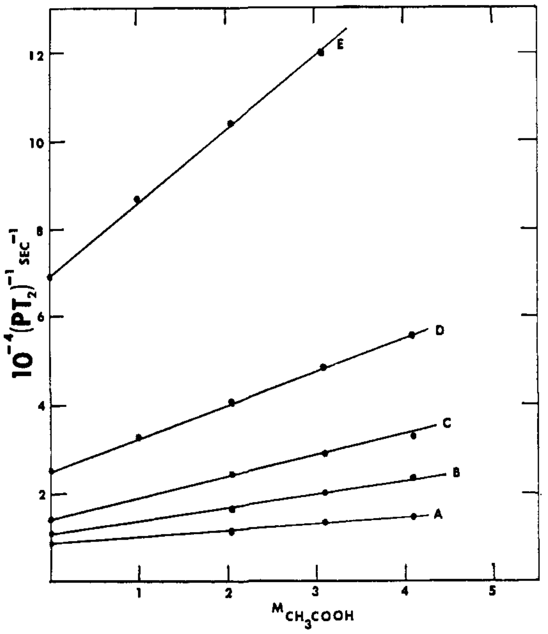

Figure 3. Graph of $(PT_2)^{-1}$ *vs.* acetic acid molality for a 0.0326 M $VO(ClO_4)_2$ solution at the following temperatures: A, 282°K; B, 294°K; C, 302°K; D, 313°K; E, 333°K.

Values of k_1^0 and k_2^0(av) for the $Cr(NO_3)_3$–$HClO_4$ system were calculated in the same manner as for $VO(ClO_4)_2$–$HClO_4$ and are given in Table III.

B. Calculation of k_4^0. Figure 3 is a plot of $(PT_2)^{-1} = k_M$ *vs.* acetic acid molality for $VO(ClO_4)_2$–acetic acid solutions at several temperatures. From eq 3b, the slope is k_4^0 and the intercept k_1^0. Values of k_4^0 for $Cr(NO_3)_3$–acetic acid solutions were obtained in the same way and the results are given in Table IV.

Table IV. Values of k_4^0 as Functions of Temperature and Values of ΔH^* and ΔS^* for $VO(H_2O)_5^{2+}$ and $Cr(H_2O)_6^{3+}$ in Aqueous Solution

VO^{2+}				Cr^{3+}			
Temp, °K	$10^{-4}\cdot k_4^0$, M^{-1} sec^{-1}	ΔH^*, kcal	ΔS^*, eu	Temp, °K	$10^{-4}\cdot k_4^0$, M^{-1} sec^{-1}	ΔH^*, kcal	ΔS^*, eu
282	1.6	8 ± 1	−11 ± 4	283	8.3	0 ± 1	−38 ± 5
294	3.1			303	9.1		
302	4.8			313	8.5		
313	7.7						
333	17.0						

The values obtained from the intercepts (k_1^0) are slightly larger than those given in Tables II and III, since at the pH employed (*ca.* 3), there is a small contribution to line width from the acid dissociation products (*cf.* the plot of line width *vs.* [H$^+$] for the chromium(III) ion[1]).

C. Calculation of k_3^0. Values of k_3^0 were calculated for the $VOSO_4$–H_2SO_4 system using eq 2b and values of k_1^0 and k_2^0(av) from Table II; γ_{H^+} and $\gamma_{HSO_4^-}$ were approximated as discussed earlier. A small correction was also made for the second dissociation step of H_2SO_4, using the concentration equilibrium quotient K_2'.[11] As can be seen in Table V, the value of k_3^0 obtained in this manner varies little over the range of acid concentrations studied.

Some comment must be made concerning sulfate complex formation with VO^{2+}. Evans[14] has found indications of such complex formation in contrast to $VO(ClO_4)_2$ which shows little if any ion–ion interaction in aqueous solution. Strehlow and Wendt[15] have determined the stability constant of the $VOSO_4$ complex to be 2.5. With this value it is calculated that only a few per cent of the VO^{2+} is present as the sulfate complex in the solutions of Table V. It is possible that this amount could contribute to the small observed variation of k_3^0 with concentration in the data

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(10) K. Wüthrich and R. E. Connick, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(11) The relationship between K_2' and the true equilibrium constant K_2 is $K_2' = K_2\gamma_{HSO_4^-}/\gamma_{H^+}\gamma_{SO_4^{2-}}$. Values of K_2 at various temperatures were obtained from the literature,[12] $\gamma_{HSO_4^-}$ and γ_{H^+} were approximated as before, and $\gamma_{SO_4^{2-}}$ was estimated from K_2SO_4 and KCl mean activity coefficient data using the MacInnes hypothesis.[13]

(12) C. W. Davies, H. W. Jones, and C. B. Monk, *Trans. Faraday Soc.*, **48**, 921 (1952).

(13) D. A. MacInnes, *J. Am. Chem. Soc.*, **41**, 1086 (1919).

(14) J. C. Evans, *Inorg. Chem.*, 2, 372 (1963).

(15) H. Strehlow and H. Wendt, *ibid.*, 2, 6 (1963).

Table V. Pseudo-First-Order Rate Constants and Calculated Values of k_3^0 for $VOSO_4$–H_2SO_4 Solutions as Functions of Temperature

Temp, °K	K_2'	m_{H^+}	$m_{HSO_4^-}$	γ_{H^+}	$\gamma_{HSO_4^-}$	$10^{-5}k_M$, sec^{-1}	$10^{-6}k_3^0$, M^{-1} sec^{-1}	$10^{-6}k_3^0$(av), M^{-1} sec^{-1}
285	0.08	1.073	1.019	0.839	0.066	3.62	2.31	2.3 ± 0.3
	0.075	0.801	0.753	0.803	0.0764	2.82	2.47	
	0.07	0.531	0.493	0.775	0.0962	1.95	2.38	
	0.065	0.397	0.367	0.766	0.115	1.56	2.34	
	0.06	0.263	0.243	0.767	0.143	1.08	2.00	
295.5	0.06	1.056	1.036	0.826	0.054	4.19	3.13	3.3 ± 0.3
	0.055	0.785	0.770	0.788	0.0618	3.28	3.42	
	0.05	0.515	0.509	0.764	0.0772	2.36	3.49	
	0.045	0.381	0.383	0.757	0.0928	1.91	3.44	
	0.04	0.249	0.257	0.759	0.117	1.36	2.95	
308	0.044	1.042	1.051	0.804	0.0422	4.61	4.06	4.4 ± 0.3
	0.04	0.771	0.783	0.774	0.0485	3.70	4.57	
	0.037	0.504	0.520	0.753	0.0610	2.68	4.65	
	0.034	0.372	0.392	0.745	0.0741	2.18	4.54	
	0.03	0.241	0.265	0.748	0.0940	1.64	4.18	
317	0.03	0.762	0.792	0.763	0.0400	4.07	5.79	6.1 ± 0.3
	0.026	0.494	0.530	0.742	0.0506	3.11	6.34	
	0.022	0.361	0.403	0.738	0.0613	2.56	6.14	
321	0.026	0.758	0.796	0.757	0.0374	4.33	6.54	6.6 ± 0.1
	0.018	0.357	0.407	0.733	0.0581	2.67	6.70	

of Table V, but in any case the additional experimental uncertainty is included in the error limits for the average values of k_3^0. The calculated activation parameters for the k_3^0 process are $\Delta H^* = 4 \pm 1$ kcal; $\Delta S^* = -14 \pm 4$ eu.

The $Cr(NO_3)_3$–H_2SO_4 system was treated in exactly the same manner as the $VOSO_4$–H_2SO_4 system. Values of k_3^0(av) and the activation parameters are given in Table VI.

Table VI. Calculated Values of k_3^0(av) for $Cr(NO_3)_3$–H_2SO_4 Solutions as a Function of Temperature

Temp, °K	$10^{-6}k_3^0$(av), M^{-1} sec^{-1}	ΔH^*, kcal	ΔS^*, eu
283	1.1		
293	1.2	0 ± 1	−31 ± 4
303	1.3		

Sulfate complex formation can definitely be troublesome in this system since the blue solutions will turn green on standing because of formation of the complex. However, the reaction is relatively slow and reproducible data can be obtained if the experiments are performed at room temperature and below with freshly prepared solutions.

D. Calculation of k_5^0. Values of k_5^0 were calculated for the $VO(ClO_4)_2$–$HClO_4$–H_3PO_4 system using eq 4b and values of k_1^0 and k_2^0(av) from Table II. As for sulfuric acid, a small correction was made for the first dissociation step of phosphoric acid using the concentration equilibrium quotient K_1'.[16] Through the addition of *ca.* 0.5 M $HClO_4$, the formation of $H_2PO_4^-$ was suppressed considerably. Values of k_5^0 obtained from eq 4b are constant within experimental error as a function of phosphoric acid concentration indicating that the contribution to line broadening from the small amount of $H_2PO_4^-$ still present in the system is negligible. The $Cr(NO_3)_3$–H_3PO_4–$HClO_4$ system was treated analogously, and values of k_5^0(av) and the activation parameters are given in Table VII.

Table VII. Calculated Values of k_5^0(av) for VO^{2+} and Cr^{3+} Systems as Functions of Temperature

VO^{2+}				Cr^{3+}			
Temp, °K	$10^{-5}\cdot k_5^0$(av), M^{-1} sec^{-1}	ΔH^*, kcal	ΔS^*, eu	Temp, °K	$10^{-4}\cdot k_5^0$(av), M^{-1} sec^{-1}	ΔH^*, kcal	ΔS^*, eu
281	2.1			281	9		
294	2.8			290.5	11	2 ± 1	−29 ± 4
308	3.6	2 ± 1	−26 ± 4	300.5	13		
315	4.0						

No attempt was made to determine the rate for general acid catalysis by $H_2PO_4^-$ because of the substantial complex formation indicated by other workers for both chromium(III)[18] and vanadyl[19] ions.

Discussion

Two questions were raised in the introductory section. The second of these can be answered immediately on the basis of the data given above, since general acid catalysis was observed in the protonation of both aquated chromium(III) and vanadyl ions. The fact of general acid catalysis and the data obtained from it also provide the information necessary to answer the first question posed in the introduction.

Before this question is discussed, however, a further point raised by the results of Rivkind[20] must be clarified. Rivkind has detected the acid-dependent step in the case of VO^{2+} and has proposed a spin-relaxation

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[16] $K_1' = K_1(\gamma_{H_3PO_4}/\gamma_{H^+}\gamma_{H_2PO_4^-})$ where the true equilibrium constant K_1 at various temperatures was obtained from the literature[17] and $\gamma_{H_2PO_4^-}$ was estimated from KCl and KH_2PO_4 mean activity coefficient data using the MacInnes hypothesis;[13] $\gamma_{H_3PO_4}$ was taken as 1 and $\gamma_{H^+} \simeq \gamma_\pm$ (HCl).

[17] See "Handbook of Chemistry and Physics," 47th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p 1758.

[18] R. F. Jameson and J. E. Salmon, *J. Chem. Soc.*, 360 (1955).

[19] J. E. Salmon and D. Whyman, *ibid., Sect. A*, 980 (1966).

[20] A. I. Rivkind, *J. Strukt. Chem.* (USSR), 4, 615 (1963).

mechanism involving the protonation of the vanadyl oxygen and scalar coupling between the added proton and the VO^{2+} paramagnetic electron.

The similarity in the values of the activation parameters of the k_2 step for chromium(III), nickel(II), and vanadyl ion suggests that the mechanism is essentially the same for all three ions, and this result is a strong argument against the Rivkind interpretation.

Some definite conclusions can be reached concerning the detailed mechanism of cation protonation. If the actual proton transfer across (or through) an energy barrier is the rate-determining substep in cation protonation, one would expect the rate constant k_3^0 to be considerably smaller than k_2^0 for the same cation. The transfer of a proton from H_3O^+ to noncoordinated water is known[21] to be close to diffusion controlled in aqueous solution. Proton transfer from HSO_4^- to noncoordinated water is significantly slower than this ($k = 1 \times 10^9$ sec^{-1} at 25°).[22] On the basis of this sort of reasoning one would expect the following order of rate constants: $k_2^0 > k_3^0 \simeq k_5^0 >> k_4^0$.

A reference to the results obtained here reveals that this does not even closely approximate the order found but that, with the single exception of k_4^0 for VO^{2+}, the actual order is $k_3^0 > k_5^0 \simeq k_4^0 > k_2^0$, and there is a distinct correlation between the value of a particular rate constant and the charge of the proton donor. The order and ratios of rate constant values are approximately the order and ratios of stability constants for the encounter complexes (ion pair in the case of HSO_4^-) involving the hydrated cations and the proton donors which are estimated from diffusion theory.[23]

Some comment must be made concerning the order of the rate constants observed in light of the approximations for activity coefficients made previously. These center around the values of k_2^0 and k_3^0 since no serious approximations were involved in the calculation of k_4^0 and k_5^0. As was stated in a previous section the principal approximation involved in the calculation of k_2^0 and k_3^0 was the estimation of γ_{H^+} and $\gamma_{HSO_4^-}$. The values used were a probable lower limit for γ_{H^+} and a probable upper limit for $\gamma_{HSO_4^-}$. The use of a larger value of γ_{H^+} or of a smaller value of $\gamma_{HSO_4^-}$ would result in a larger value of k_3^0/k_2^0 than that reported here and a strengthening of the conclusion reached.

As was mentioned above, the value of k_4^0 for vanadyl ion is about an order of magnitude smaller than that of k_5^0. In addition the values of both activation parameters differ considerably between the two processes. This may result from proton transfer being the rate-determining step for acetic acid–vanadyl ion solutions, but clearly the evidence is too scanty at present to support such a conclusion.

It is 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 a lone pair of a coordinated water molecule. The low probability of formation of a hydrogen bond involving this relatively inaccessible lone pair would account for the rather large negative ΔS^* values observed even in the case of the k_3^0 process.

On the basis of these considerations the k_2^0, k_3^0, k_4^0, and k_5^0 protonation steps can all be represented by the following proposed mechanism

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

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

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

where $M(H_2O)_x^{n+}$ is either $Cr(H_2O)_6^{3+}$ or $VO(H_2O)_5^{2+}$ and HX^m represents H_3O^+, HSO_4^-, acetic acid, or phosphoric acid. The substep characterized by k_a is proposed to be rate determining for all systems with the possible exception of VO^{2+}–acetic acid, and the variation of the over-all rate constant with the charge m is proposed to be due to the variation of the stability constant K.

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