A Spectroscopic and NMR Reinvestigation of the Hydrolysis of the Tetrathiovanadate Ion

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Received August 19, 1985

Abstract

The pH-dependent hydrolysis of the tetrathiovanadate ion VS_4^{3-} to vanadate VO_4^{3-} has been studied. Identification of the species present in reacting solutions has been established by electronic and vanadium-51 NMR spectra. Some VOS_3^{3-} intermediate has been demonstrated at higher pH. Severe decrease in rate as the reaction proceeds is due to participation of a back reaction involving HS^-. Mechanistic models are discussed for this complicated reaction. Copper(II) which has a high affinity for sulphide, catalyses the hydrolysis.

Introduction

Solid $(NH_4)_3VS_4$ has been studied by Raman and X-ray spectroscopy [1, 2]. The anion VS_4^{3-} which has a strong absorption at 545 nm hydrolyzes slowly in base [1, 3, 4]. A few hydrolysis rates plus activation parameters have been reported [5]; the dissociative mechanism proposed is not, however, consistent with the large negative $\Delta S^{\ddagger}$ values found and the species suggested [5] do not match the assignment of the 545 nm band to VS_4^{3-}.

The kinetics of the hydrolysis have now been reinvestigated and a companion study of aqueous thiovanadate species by ^{51}V NMR has been carried out. The previous inconsistencies are resolved and a better understanding of thiovanadate solution chemistry is obtained.

Experimental

$(NH_4)_3VS_4$ was prepared by the method of Kruss and Ohnmais [6]. Starting materials NH_4VO_3, NH_3, and H_2S were used without purification. The dark purple needlelike product was identified by its electronic spectrum [1, 2, 4]. NaOH (ACS grade) was used without purification; concentra-

tion of base stock solution (made with boiled distilled water) was determined with potassium acid phthalate.

The hydrolysis reaction was initiated by dissolving a weighed amount of $(NH_4)_3VS_4$ in base solution. Reaction was followed by absorption (545 nm) change with time in a Cary 15 instrument and occasionally by ^{51}V NMR.

NMR spectra were obtained on a Bruker WM-250 FT instrument using 10 mm diameter tubes. D_2O was employed as lock solvent; where necessary NaOH solutions were prepared in D_2O.

Results

Vanadium NMR

Before treatment of rate data, it is useful to discuss the ^{51}V NMR results on thiovanadates in alkaline solutions. NMR lines for four species have been identified although not all four were seen in every solution.

On dissolving $(NH_4)_3VS_4$, a strong line with a chemical shift of +1400 ppm (relative to external $VOCl_3$) is seen. In 0.5 M base, this slowly decreases in intensity. Two lines appear, a new one at +750 ppm and the expected one at −540 ppm assigned to VO_4^{3-} [7]. Roughly the percentage rate of decrease at +1400 ppm is the same as the percentage rate of increase at −540 ppm; on the other hand the absolute intensity at +740 ppm is always significantly lower and changes relatively little with time as expected for an intermediate.

A solution designed to contain significant amounts of VOS_3^{3-} was prepared by bubbling H_2S into cold saturated $NaVO_3$ [8]. The electronic spectrum of this solution (Fig. 1) showed a peak at 445 nm which has been assigned to VOS_3^{3-} [4, 8, 9], and the NMR spectrum of this solution presented in Fig. 2 shows + 740 ppm as the strongest line other than VO_4^{3-}. There is a small amount of VS_4^{3-} plus lines at +180 ppm and −250 ppm which we assign to $VO_2S_2^{3-}$ and VO_3S^{3-}, respectively. A tiny amount of pyrovanadate is seen at −561 ppm. All four thiovanadate lines can be assigned with confidence;

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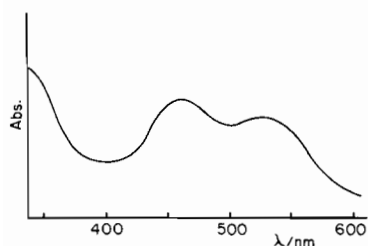
Fig. 1. The electronic spectrum of a solution designed to contain significant amounts of VOS_3^{3-}. The major peak at 450 nm has been assigned to this anion. The total vanadium concentration (in concentrated ammonia solution) is approximately 1×10^{-4} M (after a ten-fold dilution).
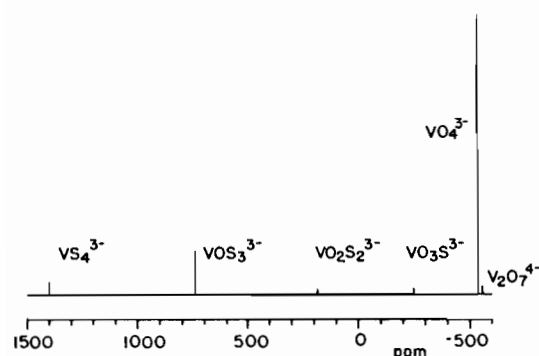

Fig. 2. The ^{51}V NMR spectrum of the solution described in Fig. 1. The vanadium concentration is approximately 1×10^{-3} M. See text for basis of assignments.

TABLE I. ^{51}V and ^{95}Mo Chemical Shifts for Thiometallate Anions

Anion[a]	^{51}V[b]	^{51}V[c]	^{95}Mo[d]
MS_4^{x-}	+1400	+1940	+2259
MOS_3^{x-}	+740	+1280	+1654
$MO_2S_2^{x-}$	+180	+720	+1067
MO_3S^{x-}	−250	+290	+497
MO_4^{x-}	−540	(0.0)	(0.0)

[a]M stands for metal; $x = 2$ for Mo and 3 for V.   [b] ^{51}V chemical shift (ppm) relative to $VOCl_3$.   [c] ^{51}V chemical shift (ppm) relative to VO_4^{3-}.   [d] ^{95}Mo chemical shift (ppm) relative to MoO_4^{2-}.

these assignments show a clear parallelism with the analogous ^{95}Mo lines of the thiomolybdates [10] as may be seen in Table I. Not only do the relative chemical shifts for these d^0 thioanions match well, but the changes in intensity reflect what we have seen in the thiomolybdate NMR spectra during hydrolysis [11] where it was found that the interconversions are more rapid as the number of thioligands decreases [11–13]. The absence of the lines at +180 and −250 ppm in spectra taken during

a hydrolysis run indicate that $VO_2S_2^{3-}$ and VO_3S^{3-} hydrolyze very rapidly to VO_4^{3-} and no significant buildup of either of these two intermediates occurs during hydrolysis.

Two other observations warrant mention. The NMR line for VOS_3^{3-} was seen to build up significantly when hydrolysis was carried out in strong base; on the other hand, near pH 12 this intermediate was not detected. The chemical shift for VS_4^{3-} is, we believe, the largest yet reported for vanadium.

An NMR intensity problem arose during this study. The final intensity of the VO_4^{3-} line was three times as large as the initial intensity of VS_4^{3-} and this intensity ratio was maintained during hydrolysis when VOS_4^{3-} did not build up. Given that no spectral (either NMR or electronic) survey brought forth any indication of a new vanadium species in large equilibrium with VS_4^{3-} we ascribe the intensity defect to instrument effects related to the huge spectral span and long 90° pulse width [14]. We found no evidence to suggest that our chemical results are in error due to the intensity difference.

Electronic Spectra

The spectrum of VS_4^{3-} has been reported [1,3,4] to have bands at 350, 395 and 545 nm and our fresh solutions confirm these (see below). The NMR data above also show that the reactant species is VS_4^{3-}.

The hydrolysis, although slower in strong base, still proceeds in 5 M NaOH. For this reason and in order to obtain an extinction coefficient for the band at 545 nm, the absorptions obtained were extrapolated to zero time (the dissolving time). Then making a Beer's law plot, we calculated the molar extinction coefficient to be 8600 M^{-1} cm^{-1}; this is larger than the literature values 5800 [3] and 7000 [4]. It may be assumed that the earlier lower coefficients reflect some hydrolysis, here found to be contributing even in short times at high base concentrations.

Hydrolysis Rates

The change in absorbance at 545 nm is rapid at the beginning and subsequently slows down dramatically. A typical first-order plot is shown in Fig. 3; the change in rate (seen in all runs) is very obvious and large. Although it is possible to divide up the rate plot into sections (of lower constant at longer time), there is no evidence for distinct parts of the curve (as would be expected for a biphasic process). There is neither a definite point of slope change nor any sign of distortion in the 545 nm peak being followed. Nevertheless for the convenience of initial data treatment, the plots were divided into two sections; a separation of the rate constants for the initial rapid (k_{1obs}) and the following slow (k_{2obs}) decomposition was made.
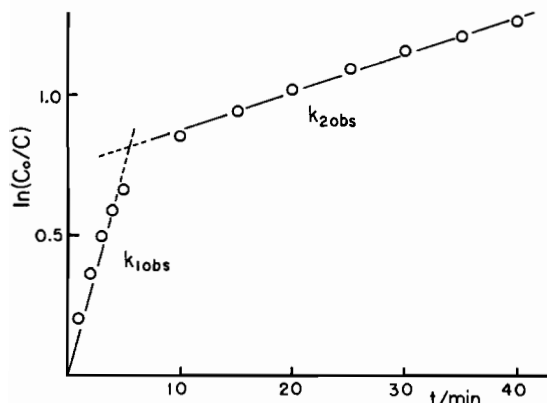
Fig. 3. A plot of hydrolysis rate data treated as biphasic first order in VS_4^{3-}. Conditions are $[NaOH] = 0.1$ M, $[VS_4^{3-}] = 1.0 \times 10^{-4}$ M, and at 22 °C.
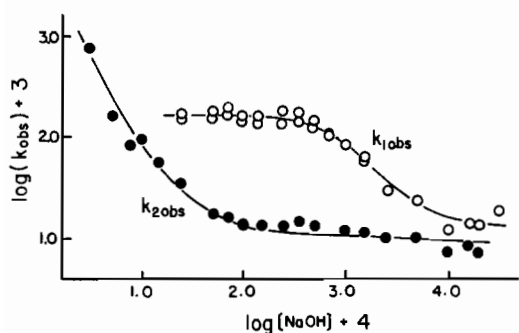

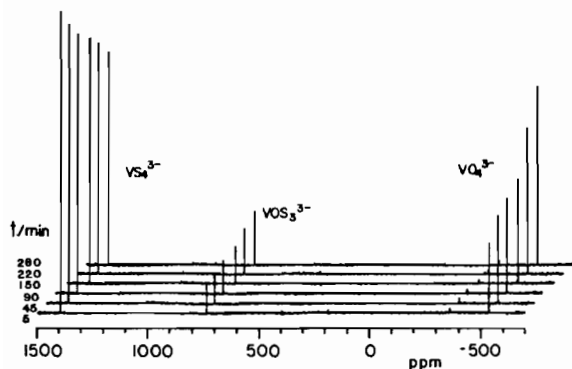
Fig. 4. Dependence of biphasic treatment rate constants on $[OH^-]$ at 22 °C.

Fig. 5. Repeated ^{51}V NMR scans at designated times, showing decrease in $[VS_4^{3-}]$, increase in $[VO_4^{3-}]$, and presence of VOS_3^{3-} intermediate. The $[NaOH] = 0.5$ M, $[VS_4^{3-}]_o \sim 1 \times 10^{-3}$ M and temperature = 22 °C.

The dependence of these constants on base was studied in the range from 1×10^{-4} M to 3 M $[OH^-]$ and the results are presented in Fig. 4. An inverse dependence which will be treated in the 'Discussion' can be seen.

In Fig. 5, the results of one kinetics experiment are presented. It will be seen that the reactant VS_4^{3-}

concentration is decreasing with time, the product VO_4^{3-} is increasing in amount, and there are significant amounts of VOS_3^{3-} and VO_4^{3-} already at five minutes even though much VS_4^{3-} remains after 280 minutes. The NMR intensity problem mentioned above shows up if the changes in peak heights for VS_4^{3-} and VO_4^{3-} are compared. The importance of this intensity problem on the height of the VOS_3^{3-} line is not subject to experimental evaluation. The tiny line near −360 ppm is a fold-over peak and does not represent another vanadium species.

There was no evidence from either the electronic or NMR spectra for protonation of VS_4^{3-} in the pH range of our studies.

Slowdown in Rate

Two reasons for the decrease in rate with time must be considered. One is that the kinetic order in VS_4^{3-} is larger than one; experimental evidence that this is not a correct basis will be given below. The other basis (and much more probable) is that there is a rapid reversible step which generates HS^- and that this product acts as an inhibitor. This possibility was tested by carrying out several hydrolysis rate experiments in a medium containing H_2S; the rates were indeed slower, sometimes by more than a powder of ten, indicating that the decrease in rate constant is not due to a higher order. Further evidence that it is a consequence of HS^- inhibition may be seen in Fig. 6, wherein the dependence of k_{2obs} on initial
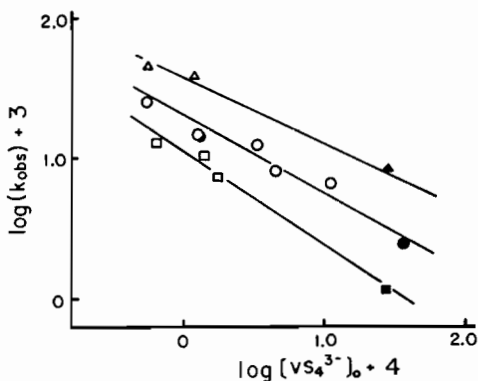

Fig. 6. Dependence of apparent first-order hydrolysis constant on initial VS_4^{3-} concentration. The slopes are about one half. Closed points are from NMR experiments and open points from spectrophotometric runs. The symbols □, ○ and △ indicate the runs at NaOH concentrations of 0.50, 0.025 and 0.0015 M, respectively.

$[VS_4^{3-}]$ is presented. The apparent rate constants from 5.5×10^{-5} to 1.1×10^{-3} M VS_4^{3-} were obtained from the electronic spectrum while the constants near 4×10^{-3} M were derived from NMR experiments. There is a marked decrease in rate as the initial

reactant concentration increases; were the order in [VS_4^{3-}] greater than one, the change would be in the opposite direction. The rates shown in Figure 6 do agree with HS^- inhibition, however, because the build-up of product is greater when the initial reactant concentration increases.

Activation Parameters

From rate studies over the temperature range 10.1 to 34.0 °C, values of k_{1obs} and k_{2obs} were calculated and from these activation quantities determined. For k_{1obs}, the value for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were 24.8 kJ mol^{-1} and -233 J mol K^{-1} respectively; for k_{2obs} the analogous quantities were 31.3 kJ mol^{-1} and -213 J mol^{-1} K^{-1}. These numbers are in general agreement with those reported by Yatsimirskii and Zakharova [5]. Under one set of conditions, they give $\Delta H^{\ddagger} = 38.9$ kJ mol^{-1} and $\Delta S^{\ddagger} = -188$ J mol^{-1} K^{-1}; for an experiment at a slightly slower rate, they give $\Delta H^{\ddagger} = 32.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -213$ J mol^{-1} K^{-1}. All of their experiments were carried out after extensive hydrolysis had already occurred and a large fraction of total sulfide had been converted to HS^-.

Copper Catalysis

The hydrolysis rate for VS_4^{3-} should be influenced by metal ions which have an affinity for sulfide ligands. Indeed it was found that the hydrolysis rate was accelerated by added copper salts, and dark brown precipitates were observed. A similar situation was observed for copper-influenced thiomolybdate hydrolysis [15]. The rate of copper catalysis (prior to precipitation) was studied as function of base and copper(II) concentrations and the results are presented in Figs. 7 and 8.
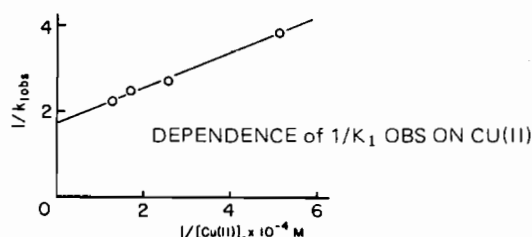

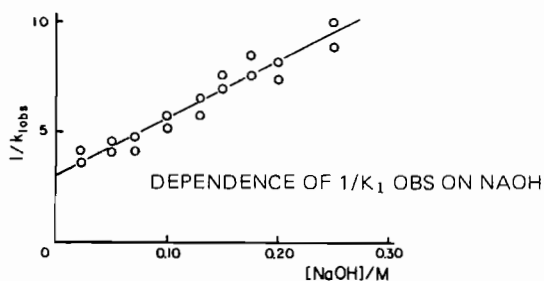Fig. 7. Double reciprocal plot showing derived dependence on copper concentration.

Fig. 8. Reciprocal plot showing derived dependence on sodium hydroxide concentration.

Worthy of note is the observation that autoinhibition was not observed when the copper(II) was present.

Discussion

Analysis of Observations

In order to arrive at a reasonable mechanism for the tetrathiovanadate hydrolysis, we must rely on observations and arguments aside from the usual rate law correlations. This stems from the fact that the kinetics of the hydrolysis are not amenable to ready interpretation; for example, the order in VS_4^{3-} can not be obtained from normal integrated rate plots. Because of the autoinhibitory effect of small amounts of HS^- (even seen in a few percent reaction), initial rates also are not helpful in order determination. The ^{51}V NMR was excellent for showing the presence of VOS_3^{3-} but not convenient for determination of instantaneous concentrations, thus attempts to solve the conservation equation

$$[HS^-] = 4[VS_4^{3-}]_o - 3[VOS_3^{3-}] - 4[VS_4^{3-}]$$

were not successful.

Interpretation of mechanism had to rely on salient facts from the present and previous studies, on conclusions from the related thiomolybdate systems, and on models fitted by computer analysis.

The following seven observations were considered in our mechanism evaluation:

(i) The rate that was being followed was disappearance of VS_4^{3-}; this was indicated by electronic spectra and by NMR. Appearance of VO_4^{3-} was also followed by NMR and its rate matched that of VS_4^{3-} loss. Therewore we can write

$$-\frac{d[VS_4^{3-}]}{dt} \sim +\frac{d[VO_4^{3-}]}{dt}$$

(ii) The dominant stoichiometry is $VS_4^{3-} + 4HO^- \rightarrow VO_4^{3-} + 4HS^-$.

(iii) Near pH 14 the presence of the intermediate VOS_3^{3-} was indicated by NMR in amounts ($\sim 10\%$) such that the steady-state approximation is not applicable. At lower pH (near 12) little or no VOS_3^{3-} was found during hydrolysis.

(iv) The rate of hydrolysis slows down dramatically with percent reaction. This has been shown to be an involvement of HS^- in a back reaction.

(v) The order in VS_4^{3-} can be extracted from an integrated plot provided the concentration of HS^- is constant. Although never exactly true, it is approximately valid near the end of the reaction when little VS_4^{3-} remains and most of the HS^- is formed. Under these conditions, a first-order plot is nearly linear [5]. Therefore the reaction is first order in VS_4^{3-}.

(vi) The activation parameters indicate that association is an essential characteristic of the reaction mechanism. The six values of $\Delta H^{\ddagger}$ ranging from 22 to 39 kJ mol^{-1} are low (indicative of bond formation); the values of $\Delta S^{\ddagger}$ from -190 to -240 J mol^{-1} K^{-1} also point to significant bonding in the transition state.

(vii) The rate increases as base concentration decreases, however the variation appears to be more closely related to an equilibrium protonation than to a kinetic order. A tentative treatment is given below.

A companion study [11, 13] of thiomolybdate replacement mechanisms led to the following conclusions which are believed relevant to the tetrathiovanadate hydrolysis mechanism. The increase in hydrolysis rate follows the order

$$MoS_4{}^{2-} < MoOS_3{}^{2-} < MoO_2S_2{}^{2-} < MoO_3S^{2-}$$

The activation parameters (again low $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$) and the influence of pH (general acid catalysis) suggest an increase in coordination number on going from ground state to transition state. Turnover of ligands in the state of higher coordination number is more rapid than change in coordination number to and from ground state. In every case studied, the reaction was first order in molybdate.

Proposed Mechanism

We devised several model mechanisms each involving a number of steps along with combinations of equilibrium and steady-state approximations. These models considered the identified $VOS_3{}^{3-}$ and intermediates of higher coordination number such as $VS_2(SH)_2(OH)_2{}^{3-}$. No single model fitted all the results — partly because the sulfur mass conservation equation could not be solved exactly and partly because none of the approximation methods could have been valid under all of our conditions.

One simple model led to an interesting result. The three-rate-constant sequence was fitted to our

$$VS_4{}^{3-} \underset{k_2'}{\overset{k_1'}{\rightleftarrows}} VOS_3{}^{3-} + HS^-$$

$$VOS_3{}^{3-} \xrightarrow{k_3'} \text{products}$$
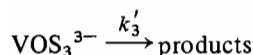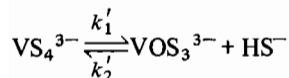
initial rate data for runs at different base concentrations. The calculated constants are given in Table II. It was found that k_1' depends strongly on base in a manner reminiscent of a tiration curve (with $pK \simeq 13.15$), whereas neither k_2' nor k_3' is base dependent. This suggested that an equilibrium proton change prior to the first slow step should be considered.

TABLE II. Rate Constant for Model I by Computer Calculation[a]

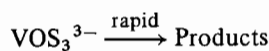| [NaOH] (M)	k_1' (s^{-1})	k_2' (s^{-1} M^{-1})	k_3' (s^{-1})
3.0	0.022	0.05	0.06
2.0	0.017	0.19	0.25
1.5	0.015	0.07	0.25
1.0	0.036	0.17	0.10
0.7	0.046	0.19	0.10
0.5	0.068	0.61	0.15
0.3	0.075	0.62	0.10
0.25	0.083	0.22	0.10
0.20	0.051	0.11	0.10
0.15	0.08	0.09	0.10
0.10	0.156	0.32	0.11
0.07	0.157	0.10	0.09
0.05	0.173	0.11	0.09
0.035	0.260	0.18	0.09
0.025	0.230	0.13	0.07
0.015	0.250	0.20	0.09
0.010	0.190	0.13	0.08
0.0072	0.350	0.20	0.08
0.0050	0.220	0.10	0.08
0.0025	0.330	0.16	0.17

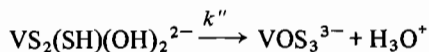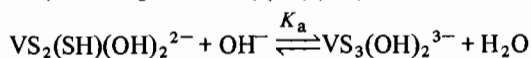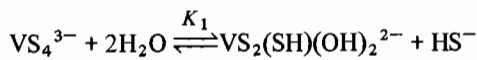[a] $[VS_4{}^{3-}] \sim 1 \times 10^{-4}$ M, temperature = 22 °C.

The possibility that either $VS_4{}^{3-}$ or HS^- could be involved in this ionization had to be considered. No protonation of $VS_4{}^{3-}$ was expected near pH 13 and no spectral (NMR or electronic) variation was found. The ionization was considered, however

$$HS^- \rightleftharpoons S^{2-} + H^+$$
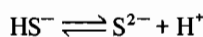
recent studies [16] indicate that the relevant pK_a is $\simeq 17$, far too high to be important here. We therefore assign this ionization curve to an intermediate prior to the first rate step.

The next model includes a high coordination intermediate and an ionization but avoids the use of the steady-state approximation for $VOS_3{}^{3-}$. The steps in this model are

$$VS_4{}^{3-} + 2H_2O \overset{K_1}{\rightleftharpoons} VS_2(SH)(OH)_2{}^{2-} + HS^-$$

$$VS_2(SH)(OH)_2{}^{2-} + OH^- \overset{K_a}{\rightleftharpoons} VS_3(OH)_2{}^{3-} + H_2O$$

$$VS_2(SH)(OH)_2{}^{2-} \xrightarrow{k''} VOS_3{}^{3-} + H_3O^+$$

$$VOS_3{}^{3-} \xrightarrow{\text{rapid}} \text{Products}$$

We can see if this mechanism will reproduce the titration type curve found in the model I derivation. The rate step differential equation would be

$$\text{Rate} = k''[VS_2(SH)(OH)_2{}^{2-}]$$

and we use the K_1 equilibrium

$$[VS_2(SH)(OH)_2{}^{2-}] = \frac{K_1[VS_4{}^{3-}]}{[HS^-]}$$

$$= \frac{K_1[VS_4{}^{3-}]}{4([VS_4{}^{3-}]_0 - [VS_4{}^{3-}])}$$

assuming there is not a serious buildup of $VOS_3{}^{3-}$. Inserting this into the rate expression, we obtain

$$\text{Rate} = -\frac{d[VS_4{}^{3-}]}{dt} = \frac{k''K_1[VS_4{}^{3-}]}{4([VS_4{}^{3-}]_0 - [VS_4{}^{3-}])}$$

for which an integration is possible. By taking $[VS_4{}^{3-}]_0$ and $[VS_4{}^{3-}]$ as a and x respectively, the equation becomes

$$-\frac{dx}{dt} = \frac{k''K_1 x}{4(a-x)}$$

Integrating and taking the boundary conditions $x = a$ at $t = 0$, we obtain

$$a\ln\left(\frac{a}{x}\right) - (a-x) = \left(\frac{k''K_1}{4}\right)t$$

A plot of the left hand side against time is presented (along with a typical first-order plot for the same experiment) in Fig. 9. As expected there is less
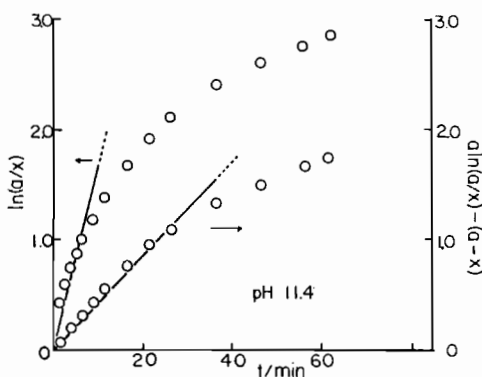

Fig. 9. Simple first order in $VS_4{}^{3-}$ plot (left axis) and first order plot in $VS_4{}^{3-}$ with attempted correction for HS^- inhibition.

curvature; nevertheless some remains and this may be related to the inability to correct for the amount of intermediate $VOS_3{}^{3-}$.

A plot of $k''K_1/4$ against pH (Fig. 10) shows the expected pattern for ionization of a solution species; in this case the pseudo-pK_a is 12.95. The presence of two horizontal portions of the curve proves that the rate step above pH 14 is different from that below pH 12.

It is nevertheless important to note that model II is the microscopic reverse of the mechanism found [13] for the reaction
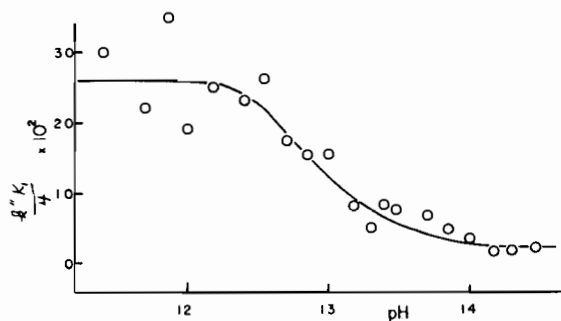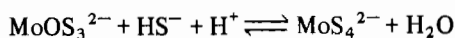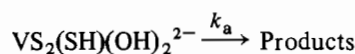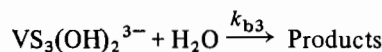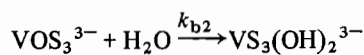

Fig. 10. Plot of rate constant $k''K_1/4$ against pH showing ionization of an intermediate near pH = 13.

$$MoOS_3{}^{2-} + HS^- + H^+ \rightleftharpoons MoS_4{}^{2-} + H_2O$$

Also this model is consistent with the observation that HS^- is an equilibrium autoinhibitor throughout the pH range we have covered.

The observations about $VOS_3{}^{3-}$ buildup (negligible at low pH but important in strong base) and two rate determining steps (also pH low and high) may be related and we so assume. This then leads to the following minimum mechanism for the hydrolysis between pH 11 and 3 M base.

$$VS_4{}^{3-} + 2H_2O \xrightleftharpoons{K_1} VS_2(SH)(OH)_2{}^{2-} + HS^-$$

$$VS_2(SH)(OH)_2{}^{2-} + HO^- \xrightleftharpoons{K_a'} VS_3(OH)_2{}^{3-} + H_2O$$

$$VS_3(OH)_2{}^{3-} \xrightarrow{k_{b1}} VOS_3{}^{3-} + H_2O$$

$$VOS_3{}^{3-} + H_2O \xrightarrow{k_{b2}} VS_3(OH)_2{}^{3-}$$

$$VS_3(OH)_2{}^{3-} + H_2O \xrightarrow{k_{b3}} \text{Products}$$

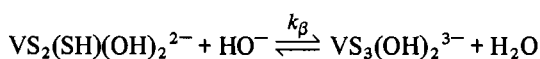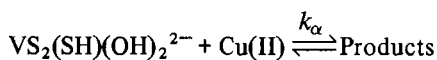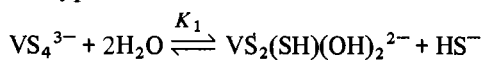$$VS_2(SH)(OH)_2{}^{2-} \xrightarrow{k_a} \text{Products}$$
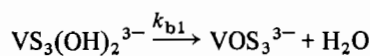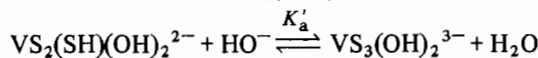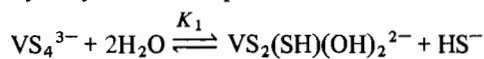
In principle it is possible to fit our experimental measurements to a mechanism made up of the above (or similar) two equilibria and four rate steps. In practice, however, all six constants are parameters and there is significant error because the simple conservation equations cannot be exactly solved and the integrated rate plots as in Fig. 9 do not permit precise evaluation of constants. Fitting six parameters is feasible, but convincing it would not be. Some discussion concerning the magnitudes of constants is to be found in the next section.

Other Points

Below pH 11, acid catalysis becomes more important. Because of the resultant rapid rates, it was not possible to obtain enough data to warrant evaluation of the rate law, etc.

The protonation-type curves of Figs. 4 and 10 indicate that the value of K_a' is 10, to about a factor of 2.

Figures 7 and 8 are explicable if copper(II) is trapping an intermediate and if base is competing with copper for the intermediate. This suggests steps of the type

$$VS_4{}^{3-} + 2H_2O \xrightleftharpoons{K_1} VS_2(SH)(OH)_2{}^{2-} + HS^-$$

$$VS_2(SH)(OH)_2{}^{2-} + Cu(II) \xrightleftharpoons{k_\alpha} Products$$

$$VS_2(SH)(OH)_2{}^{2-} + HO^- \xrightleftharpoons{k_\beta} VS_3(OH)_2{}^{3-} + H_2O$$

If k_α and k_β are large, then the intercepts on the Figures should provide evaluations of K_1. The values obtained are 0.34 and 0.58 s^{-1} respectively at 22 °C. It may be relevant that the observed pseudo-first-order constant for hydrolysis near pH 12 is 0.25 ± 0.05 s^{-1}; there is a consistency in these three values.

Acknowledgements

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