Protonation Equilibria of Mononuclear Vanadate: Thermodynamic Evidence for the Expansion of the Coordination Number in VO_2^+

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A spectrophotometric investigation of the protonation of HVO_4^{2-} has been conducted at vanadium(V) concentrations low enough (5×10^{-5} mol dm^{-3}) to prevent the formation of polynuclear ions. Equilibrium constants as well as enthalpy and entropy changes for the formation of $H_2VO_4^-$ and VO_2^+ have been determined in ionic medium: 1.0 mol dm^{-3} NaCl and $NaClO_4$, respectively. The percentage concentration of the neutral species, H_3VO_4, is so low (apparently <1%) that the protonation of $H_2VO_4^-$ to form VO_2^+ occurs virtually in a single step. The disproportionately great stability of VO_2^+ relative to H_3VO_4 is explained in terms of an increase in the coordination number of vanadium when the cationic species is formed. This explanation is based on a comparison of the thermodynamic quantities of the vanadium(V) species with those of various other oxyacids reported in the literature.

Introduction

When the pH of a highly diluted solution of vanadate is lowered from 14 to 1, successive protonation of the tetrahedral VO_4^{3-} ion ultimately leads to the formation of a cationic species, usually formulated as VO_2^+ and believed to be six-coordinated. Recently, Harnung *et al*.[1] suggested that an increase in coordination number of vanadium from four to five takes place in the second protonation step, *i.e*., when HVO_4^{2-} is protonated to form $H_2VO_4^-$. These authors prepared a series of dinuclear complexes of vanadium(V) with α-hydroxy acids (previously studied by Lay and co-workers[2]) and found vanadium to be five-coordinated with respect to oxygen. The similarity between some spectral properties (UV−vis, MCD, and ^{51}V NMR) of the complexes and $H_2VO_4^-$ led to the above suggestion.

In the case of molybdenum(VI), an increase in the coordination number from four to six in the second protonation step, *i.e*., in the protonation of $HMoO_4^-$ to form $MoO_2(OH)_2(H_2O)_2$, has been proposed on the basis of thermodynamic evidence,[3] *viz*. equilibrium constants and enthalpy and entropy changes for the reactions concerned. This expansion of the coordination in the second protonation, previously thought to occur during the first protonation, is now generally accepted.[4−6]

In the case of vanadium(V), thermodynamic quantities have been determined only for the first protonation of VO_4^{3-}.[7] Equilibrium constants for subsequent protonation reactions at various ionic strengths have been reported,[8] but there is uncertainty about the value of the third protonation constant which has been determined by solvent extraction[8a] to have the value $\log K_3 = 3.8$; potentiometric and NMR measurements,[8d] besides casting some doubt on the existence of H_3VO_4, were consistent only with $K_3 < 3.08$ and $K_4 > 3.88$.

In view of these uncertainties and the importance of thermodynamic quantities to provide a better understanding of the relative stabilities of the various species in solution, the present spectrophotometric investigation of the successive protonations of HVO_4^{2-} has been undertaken. The enthalpy and entropy changes for the reactions have been determined. These results show that the formation of the cationic acid, VO_2^+, involves an expansion of the coordination sphere of vanadium(V).

Experimental Section

Reagents and Solutions. All reagents were of analytical grade (Merck and BDH), and solutions were prepared with water obtained from a Millipore Milli-Q system. A vanadate stock solution was prepared by dissolving $NaVO_3$ (Merck p.a.) in hot water. The cooled solution was filtered through a porosity four sintered-glass filter. The concentration of this solution was determined by titration with ammonium ferrous sulfate which had been standardized with potassium dichromate. Solutions were prepared from the vanadium stock solution by appropriate dilution and addition of recrystallized sodium chloride or sodium perchlorate to obtain a constant sodium ion concentration of 1.0 mol dm^{-3}. Hydrochloric acid and perchloric acid were standardized indirectly against potassium hydrogen phthalate by titration with sodium hydroxide.

Spectrophotometric Titrations. A Varian Cary 210 spectrophotometer in conjunction with an Apple IIe computer was used for absorption measurements and data collection. For the investigation of the protonation of HVO_4^{2-}, the vanadate solution (5×10^{-5} mol dm^{-3}) was titrated with dilute sodium hydroxide solution at the same vanadate concentration covering the pH$_c$ range 6.3−9.2. It is imperative to effect the desired pH$_c$ change by titrating with alkali because acidification results in the formation of decavanadates which depolymerize very slowly. The diluted solutions used in the various titrations were allowed to stand for at least 24 h before the experiments were started. Tris (tris(hydroxymethyl)aminomethane) at a concentration of 0.001 mol dm^{-3} was used as a buffering agent. At 0.001 mol dm^{-3} concentration of Tris and 5×10^{-5} mol dm^{-3} vanadate, negligible concentrations of

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complexes form,[9] and the effect of Tris on the protonation and oligomerization equilibria is also presumably insignificant.[10] Spectra measured against air were recorded from 300 to 226 nm and corrected by subtracting a blank spectrum also measured against air. The ionic medium was 1.0 mol dm^{-3} sodium chloride. To exclude carbon dioxide from the system, a stream of purified nitrogen was passed through 1.0 mol dm^{-3} NaCl and then bubbled slowly through the titration solution. The protonation constants were determined at temperatures of 15, 25, 30, and 35 °C.

To avoid possible complexation and/or redox reactions with chloride in the investigation of the protonation of $H_2VO_4^-$, sodium perchlorate (1.0 mol dm^{-3}) was used as ionic medium. For this titration the vanadate solution, acidified to 0.50 mol dm^{-3} with $HClO_4$, was titrated with 0.5 mol dm^{-3} NaOH covering the pH$_c$ range 1.8−6.0. No buffer was needed in this pH range, and a wider wavelength range could be covered, namely, 325−200 nm. Spectra were recorded at pH$_c$ intervals of ∼0.25.

The free hydrogen concentration, *h*, was determined by measuring the potential, *E*°, to ±0.2 mV using a Ross combination electrode (Orion) with a 3.0 mol dm^{-3} $NaClO_4$ bridge solution. Equation 1 was used to calculate *h* from the measured potential at each titration point:

$$E = E^\circ + 59.16 \log h + E_j \tag{1}$$

Values for E° and E_j were determined from titrations of 1.0 mol dm^{-3} $NaClO_4$ with $HClO_4$ as described by Rossotti.[11] For brevity −log *h* is denoted by pH$_c$.

Results and Discussion

For the purpose of this discussion, the successive protonations of vanadate are represented by the following four equilibria, of which the first has been characterized in a previous investigation:[12]

$$VO_4^{3-} + H^+ \overset{K_1}{\rightleftharpoons} HVO_4^{2-} \tag{2}$$

$$HVO_4^{2-} + H^+ \overset{K_2}{\rightleftharpoons} H_2VO_4^{-} \tag{3}$$

$$H_2VO_4^{-} + H^+ \overset{K_3}{\rightleftharpoons} H_3VO_4 \tag{4}$$

$$H_3VO_4 + H^+ \overset{K_4}{\rightleftharpoons} VO_2^{+} + 2H_2O \tag{5}$$

Protonation of HVO_4^{2-}. The change in the UV spectrum, wavelength range 226−300 nm, brought about by increasing the pH$_c$ from 6.6 to 9.1 is shown in Figure 1. It is seen that protonation of HVO_4^{2-} results in a decrease in absorption; the peak at 266 nm associated with HVO_4^{2-} changes to a much weaker maximum at ∼260 nm when $H_2VO_4^-$ is completely formed at pH$_c$ = 6.

The program SPECFIT[13] was used to treat the data. The value calculated for the protonation constant, log K_2 = 7.92, can be compared with values reported for ionic strength 0.6 mol dm^{-3}, namely, log K_2 = 7.92 and 7.95 determined by NMR and potentiometry[8d,h] and log K_2 = 7.98 determined by spectrophotometry.[8g]

The enthalpy and entropy changes for the protonation reaction were determined from the change of the equilibrium constant with temperature. From the straight line plot of log *K* vs 1/*T* shown in Figure 2, values for ΔH° and ΔS° were derived by application of the well-known Gibbs equation:

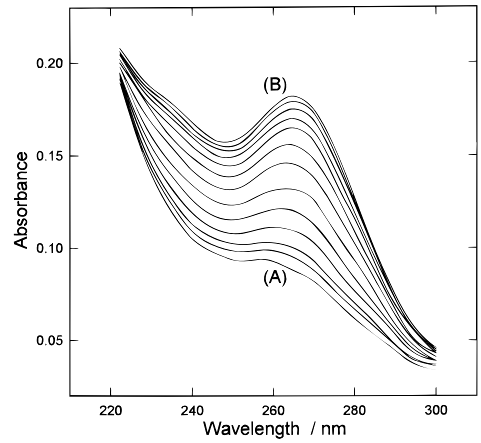

Figure 1. Change in absorption spectra with change in pH$_c$ from 6.634 (A) to 9.142 (B) of a 5 × 10^{-5} mol dm^{-3} vanadium(V) solution (1.0 mol dm^{-3} NaCl medium at 25 °C).

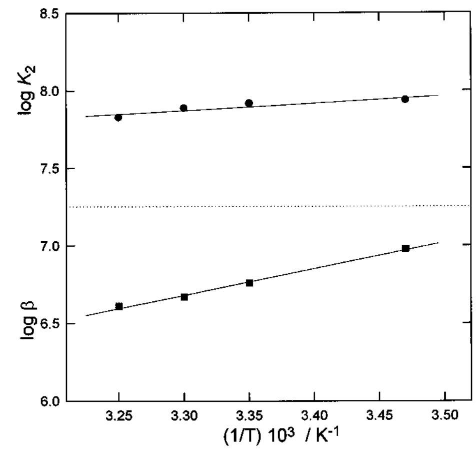

Figure 2. Protonation constants log K_2 and log β as a function of reciprocal temperature (K).

$$-2.303RT \log K = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

These values (Table 1) are very similar to those reported for the second protonation of phosphate and arsenate[14] and therefore do not suggest a change in the coordination of vanadium in this step. The comparable decrease of these thermodynamic quantities from the first to the second protonation step also indicates normal behavior. A deviation from these trends would certainly have been a strong indication of a change in coordination number.

Protonation of $H_2VO_4^-$. The spectral change observed on further protonation of $H_2VO_4^-$ in the pH$_c$ range 6.0−2.6 is similar to that observed during the previous protonation, namely, a gradual decrease in absorption which occurs until complete protonation to the cationic species, VO_2^+, has taken place. The characteristic band at ∼260 nm has disappeared, and the spectrum exhibits only two very weak bands at ∼275 and ∼205 nm. When the change in absorption with pH$_c$ at a suitable wavelength, *e.g.*, 247 nm, is considered (Figure 3), it is seen that the slope of the curve pertaining to the protonation of $H_2VO_4^-$ is much steeper than that for the protonation of HVO_4^{2-} which clearly indicates that more than one proton is involved in the former reaction. Moreover, this curve (and those at various other wavelengths) shows no sign of an inflexion which would have indicated the presence of significant amounts of the intermediate neutral acid H_3VO_4. Treatment of the data,

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Table 1. Equilibrium Constants and Thermodynamic Quantities for the Protonation of Various Oxyanions at 25 °C[a]

protonation reaction	log K	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/K mol)	I	ref
VO_4^{3-}/HVO_4^{2-}	13.27	−24	174	1.0[b]	7
$HVO_4^{2-}/H_2VO_4^-$	7.92 ± 0.02	−9 ± 2	122 ± 9	1.0[b]	*d*
$H_2VO_4^-/H_3VO_4$	(2.6)	(6)	(71)	1.0	*d*
H_3VO_4/VO_2^+	[4.2]	[−39]	[−51]	1.0	*d*
$H_2VO_4^-/VO_2^+$	6.76 ± 0.02	−33 ± 2	20 ± 7	1.0[c]	*d*
PO_4^{3-}/HPO_4^{2-}	12.38	−15.9	184	0	14
$HPO_4^{2-}/H_2PO_4^-$	7.20	−3.8	125	0	14
$H_2PO_4^-/H_3PO_4$	2.15	7.9	68	0	14
$AsO_4^{3-}/HAsO_4^{2-}$	11.50	−18.4	159	0	14
$HAsO_4^{2-}/H_2AsO_4^-$	6.96	−3.3	121	0	14
$H_2AsO_4^-/H_3AsO_4$	2.24	7.1	67	0	14
$CrO_4^{2-}/HCrO_4^-$	5.74	4.6	134	0.0	14
$HCrO_4^-/H_2CrO_4$	−0.7	38	113	1.0	14
$MoO_4^{2-}/HMoO_4^-$	3.47	22	143	1.0[b]	3
$HMoO_4^-/MoO_3(H_2O)_3$	3.74	−47	−85	1.0[b]	3
$MoO_3(H_2O)_3/MoO_2(OH)(H_2O)_3^+$	1.05	6	40	3.0[c]	16

[a] Numbers in parentheses are extrapolated values, and those in brackets were obtained from these values and the experimental values (cf. text). [b] Medium = NaCl. [c] Medium = $NaClO_4$ (mol dm^{-3}). [d] This work.

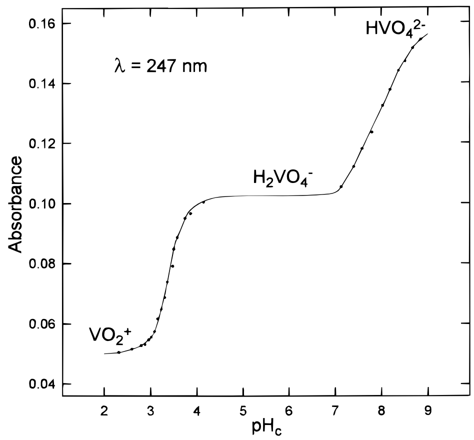

Figure 3. Change in absorbance of a 5×10^{-5} mol dm^{-3} vanadium(V) solution at wavelength 247 nm as a function of pH_c at 35 °C.

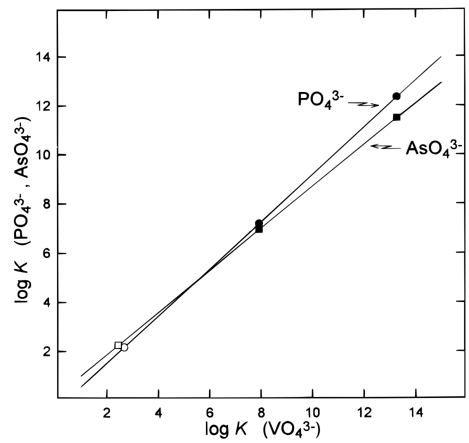

Figure 4. Plots of log values of successive protonation constants of PO_4^{3-} and AsO_4^{3-} vs those of VO_4^{3-}. Solid symbols represent experimental values; log K_3 values (PO_4^{3-}, AsO_4^{3-}) are plotted as open symbols on the extrapolated lines.

assuming that the protonation of $H_2VO_4^-$ takes place in two distinct steps (eqs 4 and 5), resulted in a value for log K_3 (1.5) which is too small relative to log K_4 (5.36) to be meaningful; for $K_3/K_4 < 10^{-4}$, the maximum percentage concentration of H_3VO_4 would be <0.5%. (As is to be expected, the calculated spectrum for H_3VO_4 was very irregular, illustrating that it was composed of absorbances which were much smaller than the experimental uncertainties.) The first protonation step was therefore neglected, and the data were treated in terms of only the following equilibrium:

$$H_2VO_4^- + 2H^+ \overset{\beta}{\rightleftharpoons} VO_2^+ + 2H_2O \qquad (6)$$

where $\beta = K_3K_4$.

An excellent fit between calculated and measured absorbances at all wavelengths was obtained with log $\beta = 6.76$. This value can be compared with log $\beta = 6.92$ determined in 0.6 mol dm^{-3} NaCl medium by Pettersson *et al.*[8h] In an earlier paper, Pettersson and co-workers[8d] also found that their NMR and potentiometric data were best described when the neutral acid H_3VO_4 was excluded from the calculations. These authors concluded that H_3VO_4, should it really exist, would only be a very minor species for which log $K_3 < 3.08$ and log $K_4 > 3.88$, which is consistent with the results now obtained.

These findings show that the literature value for log K_3 (3.8) which had been determined by solvent extraction[8a] in 0.5 mol dm^{-3} $NaClO_4$ medium could be too high by *at least* 1 log unit. As the experimental work and data treatment do not seem to be at fault, this high value might be the result of some interaction between vanadium(V) and the particular extractant (methyl isobutyl carbinol) used in the study. Complexation or esterification of vanadium(V) with various alcohols has been reported recently.[15]

The absorbance data pertaining to the other temperatures were treated in the same way as described above to determine values for log β at 25 °C. In each case the value calculated for log K_3 (~1) implied such a small amount of H_3VO_4 in solution as to render K_3 meaningless. In fact, neglecting this reaction (eq 4) in the computations resulted in an insignificant increase in σ_A.

The plot of log β vs $1/T$ shown in Figure 2 gives a straight line with a slope somewhat steeper than that for K_2, inferring a more favorable enthalpy change for this reaction compared to the previous protonation step. The thermodynamic quantities are listed in Table 1.

Thermodynamic Quantities and Expansion of the Coordination Sphere. A graphical comparison of the log values (pertaining to 25 °C) of the successive protonation constants of VO_4^{3-} with those of PO_4^{3-} and AsO_4^{3-} is shown in Figure 4. These linear free-energy plots lead to extrapolated values for

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the third protonation constant, log $K_3 = 2.6$ and 2.4 when related to phosphate and arsenate, respectively. If, for example, K_3 is fixed at the value 2.6 in the computer treatment of the data (at 25 °C), a value of log $\beta = 6.93$ is calculated which is only a little higher than that obtained as described above (6.76), but the fit is not as good as when K_3 is omitted. This result shows that K_3 is smaller than 2.6, but even for these values of the constants the maximum percentage concentration for H_3VO_4 would only be about 6%. It is therefore clear that the experimental characterization of this equilibrium would not be feasible. The problem is caused by the excessive overlap of the third and fourth protonation equilibria resulting from the abnormally high value of K_4.

Although the extrapolated value(s) for log K_3 might be too high by 0.5−1.0 log unit, the results show that similar plots of $\Delta H°$ and $\Delta S°$ values should provide quite reasonable estimates for these thermodynamic quantities for the third protonation step (eq 4). If these extrapolated values for reaction 4 (listed in parentheses in Table 1) are subtracted from those determined experimentally for reaction 6, the following thermodynamic quantities are obtained for the fourth protonation step: $\Delta H° = -39$ kJ mol^{-1} and $\Delta S° = -51$ J K^{-1} mol^{-1}

$$H_3VO_4 + H^+ \rightleftharpoons VO_2^+ + 2H_2O$$

These values are not typical of a simple protonation reaction for which the entropy change is normally a positive quantity ($\Delta S°$ often amounting to 100 ± 50 J K^{-1} mol^{-1}) and the enthalpy change either a small positive or negative value, especially if the negative charge on the base is 2 or smaller (cf. Table 1). These anomalous thermodynamic quantities for the fourth protonation step of vanadate can be explained in terms of an increase in the coordination number of vanadium(V) as represented by the following equation:

$$H_3VO_4 + H^+ + 2H_2O \rightleftharpoons VO_2(H_2O)_4^+$$

The very favorable enthalpy change is accounted for by the extra bond energy in the six-coordinated cation and the unfavorable entropy change by the uptake of two molecules of water.

These results can be compared with those obtained for the protonation of molybdate for which an expansion of tetrahedral to octahedral coordination occurs in the second protonation step.[3] In the case of molybdate the enthalpy and entropy changes for the first protonation are normal, but a very favorable $\Delta H°$ coupled with an unfavorable $\Delta S°$ is observed when $HMoO_4^-$ is protonated to form the neutral acid $MoO_2(OH)_2(H_2O)_2$ (or $MoO_3(H_2O)_3$ as it is sometimes formulated). Further protonation leads to the formation of the singly charged cation $MoO_2(OH)(H_2O)_3^+$, a reaction for which the thermodynamic quantities are normal again[16] (Table 1).

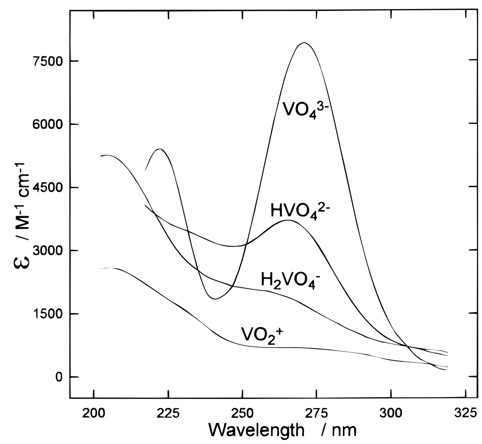

Figure 5. Absorption spectra of the various mononuclear vanadium(V) species.

It is therefore concluded that an increase in coordination number of vanadate occurs when the cation is formed; the thermodynamic evidence presented here clearly does not tally with an increase in coordination number from four to five when $H_2VO_4^-$ is formed, as suggested by Harnung *et al.*[1]

The individual spectra for each of the mononuclear vanadate ions are shown in Figure 5. The change in absorption caused by successive protonations of vanadate is clearly not in conflict with an expansion of coordination number of vanadium with the formation of VO_2^+. The tetrahedral VO_4^{3-} ion shows two very prominent absorption peaks in the UV at wavelengths of 224 and 271 nm. Upon protonation the absorption decreases resulting in a spectrum for HVO_4^{2-} with an absorption band at 266 nm. Further protonation to $H_2VO_4^-$ results in very much the same change in that the latter band again shifts a few nanometers to shorter wavelengths showing a very weak band at ∼260 nm. These rather systematic changes do not seem to be consistent with an abrupt change in the coordination sphere of vanadium. The change in spectrum when $H_2VO_4^-$ is protonated to VO_2^+ is also not very different from the previous changes insofar as a decrease in absorption has occurred. What appears to be significant, however, is that the strong absorption band of VO_4^{3-}, which has decreased on successive protonations, is absent in VO_2^+. If this band is associated with a four-coordinated structure, its disappearance would be consistent with the formation of the octahedrally coordinated VO_2^+ ion.

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