Kinetics of the Dissociation of Decavanadate(6—) in Neutral and Weakly Basic Solutions

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The kinetics of decomposition of $[V_{10}O_{28}]^{6-}$ (2×10^{-3}—9×10^{-5} mol dm^{-3}) have been studied spectrophotometrically and pH-metrically within the range pH 6—12.5 at 25 °C, $I = 0.1$ mol dm^{-3}, and 0.1 mol dm^{-3} Na^+ cationic medium. A treatment of the pH dependence of the observed rate constants demonstrates the presence of fast acid–base pre-equilibria involving the reactive species $[V_{10}O_{28}]^{6-}$. Protonation leads to the well known and stable species $[HV_{10}O_{28}]^{5-}$ and decreases the overall decomposition rate. Deprotonation gives rise to an unknown and more reactive $[HV_{10}O_{29}]^{7-}$ species, increasing the rate. The equilibrium constant for formation of the $[HV_{10}O_{29}]^{7-}$ species from hydrated $[V_{10}O_{28}]^{6-}$ and hydroxide is 1.06×10^{5} dm^3 mol^{-1}. The rate of decomposition of decavanadate is given by the contributions from two first-order paths, $k_1[V_{10}O_{28}{}^{6-}] + k_1'[HV_{10}O_{29}{}^{7-}]$, where $k_1 = 1.6 \times 10^{-5}$ and $k_1' = 1.02 \times 10^{-4}$ s^{-1}.

IN a strongly basic medium (pH $\geqslant 12.5$) the rate of base decomposition of decavanadate is known to occur through two different paths; both follow first-order dependences on the concentration of decavanadate, and one of them is also first-order in hydroxide-ion and alkali-metal counter-ion concentrations.[1,2] In the range pH 8—10 the rate follows a first-order dependence on decavanadate concentration; a lower-order dependence on $[OH^-]$ has been observed, but not discussed.[1] The observed rate constant is significantly lower than that for the path of the same order occurring in strongly basic solutions. Thus, it has been suggested[1] that the mechanism of this pH-independent path changes on going from one to the other pH range.

In order to obtain further insight into this reaction we have extended the kinetic studies to the whole of the instability range of decavanadate. Slow hydrolysis of decavanadate is known to begin at an $[OH]^-$ content per vanadium atom (z) of >5.50,[3] which corresponds to the deprotonation range of $[HV_{10}O_{28}]^{5-}$ and under our experimental conditions occurs at pH $\geqslant 6.0$. We have only omitted the strongly basic range (pH >12.5), where the kinetic behaviour has been clarified.[1,2] The measurements have been made at 25 ± 0.2 °C, at 0.1 mol dm^{-3} ionic strength (I), and with sodium as the cationic medium, both in buffered and unbuffered solutions. Unbuffered solutions were used to obtain more details of the equilibria influencing the reactive species in the system, buffered solutions to simplify the interpretation of the kinetics.

Observed first-order rate constants for decomposition of decavanadate ion in buffered solutions at $I = 0.1$ mol dm^{-3} and 25 °C

10^3[Buffer]/mol dm^{-3}						10^3[Decavanadate]/ mol dm^{-3}	pH	$10^5k_{obs.}$/s^{-1}
$Hdmg^-$	23.3	dmg^{2-}	10.0	NaCl	46.7	0.100	6.0	0.17
	21.5		11.6		43.7	0.100	6.1	0.20
	19.7		13.6		39.5	0.100	6.2	0.25
	18.0		15.5		35.5	0.200	6.3	0.30
	14.8		18.0		31.2	0.200	6.45	0.40
	10.0		21.5		25.5	0.090	6.7	0.60
	6.4		27.0		13.0	0.090	7.0	0.91
Hdeb	35.0	deb^-	8.75		91.25	0.090	7.3	1.2
	20.0		12.5		87.5	0.100	7.7	1.7
	10.0		12.5		87.5	0.100	8.0	2.2
	20.0		50.0		50.0	0.100	8.3	3.0
	16.0		100.0			0.100	8.7	4.5
	8.0		100.0			0.090	9.0	6.0
$[HCO_3]^-$	62.0	$[CO_3]^{2-}$	12.6			0.100	9.3	7.4
	39.0		20.3			0.200	9.7	8.8
	24.6		25.1			0.200	10.0	9.4
	14.1		28.6			0.090	10.3	9.8
	2.9		32.3			0.090	11.0	10.0
		$[OH]^-$	31.5		68.5	0.090	12.5	10.5

EXPERIMENTAL

Common buffers suitable for maintaining pseudo-first-order conditions within the selected pH range cannot be used because they react with decavanadate to give heteropolyvanadates. Other buffers, in which the acid species is cationic, have been avoided to keep the cationic medium unchanged. Sodium 3,3′-dimethylglutarate (dmg^{2-})–$Hdmg^-$, 5,5′-diethylbarbiturate (deb^-)–Hdeb, and carbonate–hydrogencarbonate buffers were found to be without interference and able to cover nearly all the pH range. Thus, working buffers were prepared as in the Table from

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[1] J. B. Goddard and A. M. Gonas, *Inorg. Chem.*, 1973, **12**, 574.

[2] D. M. Druskovich and D. L. Kepert, *J.C.S. Dalton*, 1975, 947.

[3] F. Corigliano and S. Di Pasquale, *Inorg. Chim. Acta*, 1975, **12**, 102.

high grade H_2dmg, Na[deb], Hdeb, $Na_2[CO_3]$, and $Na[HCO_3]$ at $I = 0.1$ mol dm^{-3} and the pH was checked against standard buffers. Stock solutions of HCl and Na[OH] were standardized against high-purity $Tl_2[CO_3]$. Standard solutions of vanadium(V) at $z = 5.50$, *i.e.* predominantly in the form $[HV_{10}O_{28}]^{5-}$, were prepared by dissolving a weighed amount of high purity V_2O_5 ($\geqslant 99.8\%$) in (*i*) H_2O_2 in order to obtain a fresh solution of $H_6V_{10}O_{28}$ and, on completion of oxygen evolution, neutralizing with standard Na[OH],[4] (*ii*) a standard Na[OH] solution (molar ratio $6:1$ [NaOH] : $[V_2O_5]$) and neutralizing with a standard HCl solution ([HCl] : $[V_2O_5] = 5:1$). The concentrations of $[HV_{10}O_{28}]^{5-}$ were adjusted to 6.67×10^{-3} and 2.5×10^{-3} mol dm^{-3} respectively to give $I = 0.1$ mol dm^{-3} in both solutions. The vanadium titre was checked by the methods in ref. 3.

To an aliquot portion of one of these solutions was added a suitable buffer to give a pH value at a decavanadate concentration ranging between 2×10^{-4} and 0.9×10^{-4} mol dm^{-3}, or suitable volumes of standard 0.1 mol dm^{-3} Na[OH] and NaCl solutions to obtain $[OH^-] : [HV_{10}O_{28}{}^{5-}]$ molar ratios of 1, 2, 3, 5, 6, 8, 10, and 15 : 1 (corresponding to mean z values of 5.60, 5.70, 5.80, 6.00, 6.10, 6.30, 6.50, or 7.00) at a decavanadate concentration ranging between 2×10^{-3} and 2×10^{-4} mol dm^{-3}. In the unbuffered solutions precautions were taken against CO_2 absorption from the atmosphere. The concentration of hydroxide ion in the unbuffered experiments and the concentration of decavanadate in both series were followed throughout the course of reaction by recording the pH and the visible spectrum between 420 and 520 nm [only the decavanadates absorb (as in Figure 1), the products being colourless].

Spectral and kinetic measurements were carried out on a Perkin-Elmer 124 double-beam spectrophotometer. The pH measurements were made with glass (Radiometer G202B) and calomel (bridged with 0.1 mol dm^{-3} NaCl solution) electrodes connected to an Amel model 333 digital potentiometer.

RESULTS AND DISCUSSION

Stoicheiometry.—The stoicheiometry of the possible reactions is given (omitting water) by (1) followed by

$$[HV_{10}O_{28}]^{5-} + [OH]^- \xrightleftharpoons{\text{fast}} [V_{10}O_{28}]^{6-} \qquad (1)$$

(2) where only the step from unprotonated decavanadate to trioxovanadate (and not the reverse) is slow.[5-7]

$$[V_{10}O_{28}]^{6-} \xrightleftharpoons{+4\,[OH]^-} \left\{\begin{matrix} 2.5\,[V_4O_{12}]^{4-} \\ \text{or} \\ 3.33\,[V_3O_9]^{3-} \end{matrix}\right\} \xrightleftharpoons{+5\,[OH]^-} 5\,[HV_2O_7]^{3-} \xrightleftharpoons{+5\,[OH]^-} \left\{\begin{matrix} 5\,[V_2O_7]^{4-} \\ \text{or} \\ 10\,[HVO_4]^{2-} \end{matrix}\right\} \xrightleftharpoons{+10\,[OH]^-} 10\,[VO_4]^{3-} \qquad (2)$$

Unbuffered Solutions.—The spectrum of these solutions was found to be somewhat different from that of the starting $[HV_{10}O_{28}]^{5-}$ species (Figure 1), and the pH measurements showed that a fast deprotonation of decavanadate preceded its slow decomposition. This is in agreement with previous findings.[3,6] Subsequently, when the absorbances tended to zero, the spectrum remained qualitatively unchanged, except when the pH decreased to <8. In this case the spectrum returned to the shape of that of $[HV_{10}O_{28}]^{5-}$, more obviously the lower the pH, and the decomposition of decavanadate was not complete at equilibrium. Values of the ratio of the reaction rate to the actual decavanadate concentration, $d[(A_0 - A_t)/A_t]dt$, where A_0 and A_t are absorbances at time zero and t, respectively, have been determined from values of $A_0 - A_t$ and the time, at a suitable wavelength within the 420—520 nm range, by setting small finite differences, $\Delta(A_0 - A_t)/\Delta t$, equal to $d(A_0 - A_t)/dt$ assuming that A_t is the midpoint of the absorbance interval. Thus, values of the rate constants ($k_{obs.}$) have been obtained and are reported at pH_t, assuming the latter to be the mean of the pH values at the extremes of the same time interval, Δt, in the plot of pH against t (Figure 2). Change of the initial concentration of decavanadate from 2×10^{-3} to 2×10^{-4} mol dm^{-3} appears to have little influence. At pH <8 the calculation of $k_{obs.}$ as above was no longer correct since increasing quantities of the undecomposed reactant changed into the protonated form, which is stable and less absorbing. Nevertheless, the function $\ln(A_t - A_\infty)$ (which has been shown to be proportional to $\ln[V_{10}O_{28}{}^{6-}]_t$; A_∞ is the absorbance on completion of reaction) was linear with time in this pH range, and the gradient gave a first-order, pH-independent, rate constant of $k = 1.6 \times 10^{-4}\ s^{-1}$.

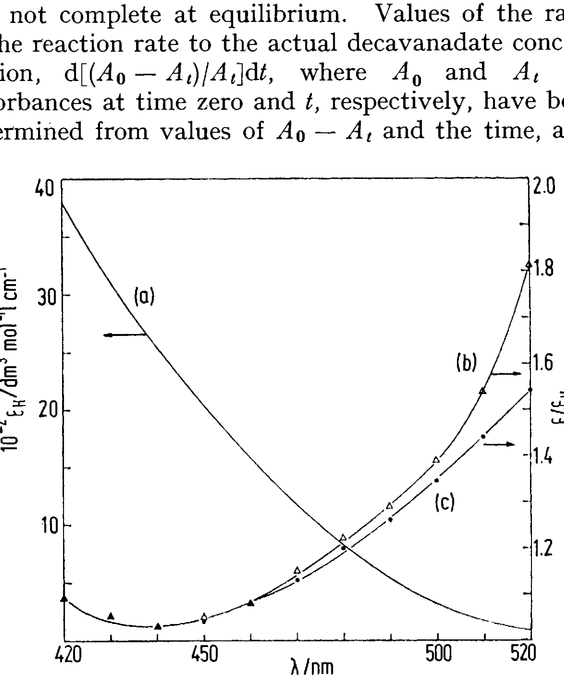

FIGURE 1 (*a*) Spectrum (420—520 nm) of a vanadium(V) solution at $z = 5.50$ ($[HV_{10}O_{28}]^{5-}$ is the predominant species). (*b*) and (*c*) ratio of molar absorption coefficients extrapolated to $t = 0$ of vanadium(V) solutions buffered at pH 8.0 and 12.0 respectively to those of curve (*a*)

Figure 3 shows the decrease of pH with time for the

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[4] K. F. Jahr, J. Fuchs, and F. Preuss, *Chem. Ber.*, 1963, **96**, 556.

[5] N. Ingri and F. Brito, *Acta Chem. Scand.*, 1959, **13**, 1971.

[6] G. Schwarzenbach and G. Geier, *Helv. Chim. Acta*, 1963, **46**, 906.

[7] M. T. Pope and B. W. Dale, *Quart. Rev.*, 1968, **22**, 527.

same initial decavanadate concentration (2×10^{-3} mol dm^{-3}) and different reagent ratios. It appears as though there is a slow 'titration' of $[OH]^-$ by decavanadate on its way to decomposition.

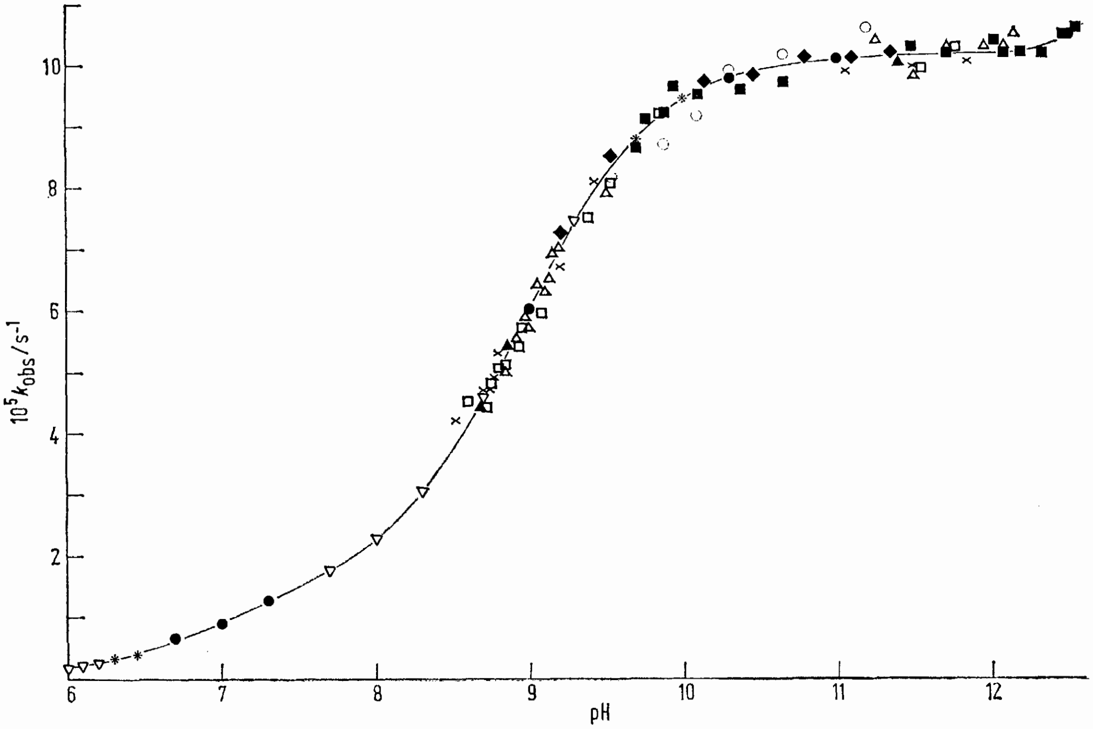


FIGURE 2 pH Dependence of $k_{obs.}$ in buffered (●, ▽, ✱) and unbuffered [z = 5.80 (▲), 6.00 (×), 6.10 (□), 6.30 (△), 6.50 (○), and 7.00 (♦, ■)] solutions at initial concentrations (10^{-3} mol dm^{-3}) of decavanadate = 0.09 (●), 0.10 (▽), 0.20 (✱, ♦), and 2.0 (▲, ×, □, △, ○, ■), I = 0.1 mol dm^{-3}, and 25 °C

The 'break' occurs cleanly before the equilibrium conditions are achieved. This means that free $[OH]^-$ is taken up by the newly formed products more quickly than by the slowly decomposing reagent.

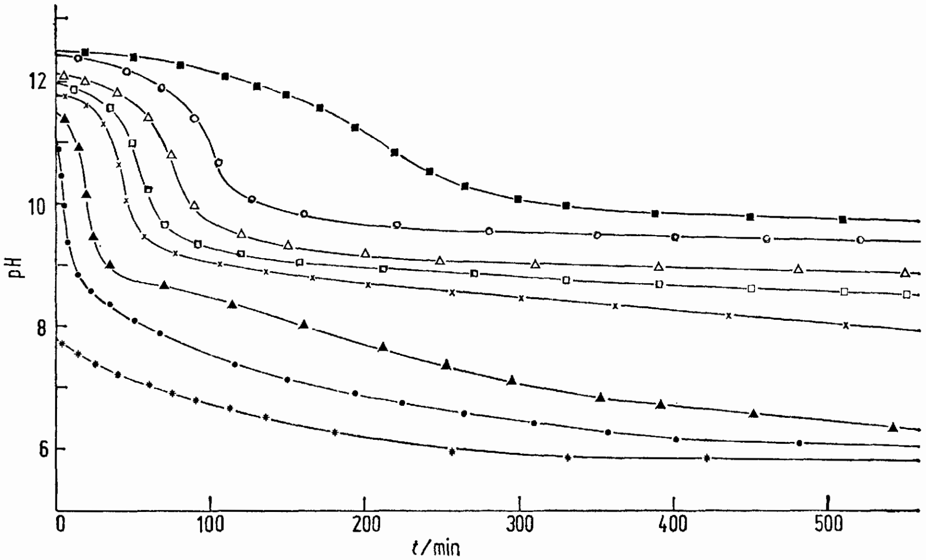


FIGURE 3 Plots of pH against time for solutions containing the same initial concentration of decavanadate (2×10^{-3} mol dm^{-3}), molar ratios $[OH^-] : [HV_{10}O_{28}{}^{5-}]$ = 1 (✱), 2 (●), 3 (▲), 5 (×), 6 (□), 8 (△), 10 (○), and 15 (■), I = 0.1 mol dm^{-3}, and 25 °C

Subsequently, in order to explain the fact that the decomposition of decavanadate continues and the pH decreases much more slowly than before, we assumed a slow back donation of $[OH]^-$ from the products to the decavanadate. This was, indeed, the expected behaviour on the basis of the known speed of the equilibria between meta- and ortho-vanadate and *vice versa.*[5] In the absence of free $[OH]^-$, the H^+-producing decomposition of decavanadate can continue only if a parallel H^+-consuming protonation takes place. This may occur either with a decrease, if possible, of the z value of the products, or, even, by protonation of the same reagent. The last event takes place at pH <8, according to the Scheme, and shows that the reacting species behaves as an ampholyte. If a is the initial concentration of unprotonated decavanadate and x the portion transformed into hydrolysed products in time t, it follows that $dx/dt = k_1[a - (n + 1)x]$ and, after integration, the rate constant observed, k, will be first order and $(n + 1)$ times the true rate constant, k_1, of the slow path. This means that k depends on the nature of the products, n being 4 for vanadate, 9 for $[HV_2O_7]^{3-}$, 14 for $[V_2O_7]^{4-}$ or $[HVO_4]^{2-}$, *etc.*, or intermediate values for mixtures of two or more of these species.

$$[V_{10}O_{28}]^{6-} + n\,H_2O \xrightarrow{\text{slow}} \text{hydrolysed products} + n\,H^+$$

$$n\,[V_{10}O_{28}]^{6-} + n\,H^+ \overset{\text{fast}}{\rightleftharpoons} n\,[HV_{10}O_{28}]^{5-}$$

$$(n + 1)\,[V_{10}O_{28}]^{6-} + n\,H_2O \xrightarrow{\text{slow}} \text{hydrolysed products} + n\,[HV_{10}O_{28}]^{5-}$$

SCHEME

The true value of k_1 could be found by treatment of the data obtained in buffered solutions (see below). Its value is ten times lower than the k value found under these conditions, suggesting that $n = 9$ and, consequently, that the mean z value of the hydrolysed products is 6.50. In the kinetic studies with $z = 5.60$, the ratio of the final and the initial concentration of decavanadate, found to be equal to $0.90 \pm 0.01 : 1$, leads to the same conclusion. In spite of such evidence, this is quite a surprising result, since only the species with the lowest z value of 6.0, *i.e.* $[VO_3]^-$, was expected to be present in equilibrium with $[HV_{10}O_{28}]^{5-}$ at these low pH values.[6,7] For this reason, and in order to identify the true co-product of hydrogendecavanadate, an additional experiment was carried out in which solutions having $z = 6.0$, 6.5, 7.0, or 8.0 were separately prepared and mixed with $[HV_{10}O_{28}]^{5-}$ ($z = 5.50$) in the ratios required to give on average the same z value of 5.60. As in the previous experiments, the spectrum at 420—520 nm remained invariant only for the $z = 5.50$–$z = 6.50$ (9 : 1) mixture, while the $z = 5.50$–$z = 6.0$ (4 : 1) mixture led to an immediate equilibrium and an increase in absorbance (fast reaction from trioxovanadate to decavanadate) and those with $z = 5.50$–$z = 7.0$ (93 : 7) and $z = 5.50$–$z = 8.0$ (19 : 1) gave an immediate increase in absorbance (due to deprotonation of $[HV_{10}O_{28}]^{5-}$) followed by a slow decrease (decavanadate decomposition). These results are considered as confirmation that trioxovanadate is not a primary product of the decomposition of decavanadate, as was believed previously,[6,7] or, to be more exact, it is not the only one. Studies on the mechanism will be necessary to understand the reason for this.

Buffered Solutions.—The observed rate constants were all first order in decavanadate concentration but independent of its initial concentration. They were dependent on the pH (Figure 2 and Table).

Assuming that $K_w = 1.0 \times 10^{-14}$ dm^6 mol^{-2} under our conditions, plots of $k_{obs.}^{-1}$ against $[OH^-]^{-1}$ (Figure 4) are linear at the highest values of $[OH^-]^{-1}$ (pH 6—7). This means that, within this interval, the expression (3)

$$k_{obs.}^{-1} = k_1^{-1} + k_1^{-1}K_{IP}^{-1}[OH^-]^{-1} \qquad (3)$$

is obeyed, where k_1 is the rate constant and K_{IP} the constant of a fast pre-equilibrium. The intercept and gradient of the above plots yield 1.6×10^{-5} s^{-1} and 1.15×10^7 dm^3 mol^{-1} for k_1 and K_{IP} respectively. The last value is identical to that obtained at the same temperature, ionic strength, and medium (0.1 mol dm^{-3} Na^+) by Schwarzenbach and Geier for equilibrium (1).[6] Discussion of k_1 has been anticipated in the preceding section.

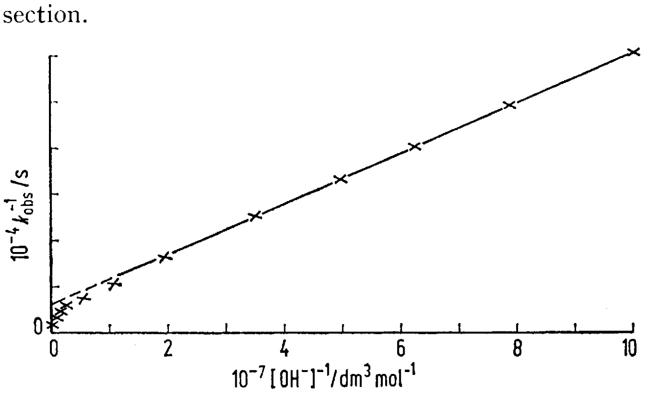


FIGURE 4 Linear dependence of $k_{obs.}^{-1}$ on $[OH^-]^{-3}$ at the highest values of $[OH^-]^{-1}$ (buffered solutions, $I = 0.1$ mol dm^{-3}, 25 °C)

Equation (3) cannot account for the trend on the basic side of the plot of $k_{obs.}$ against pH in Figure 2, because the limiting value of k_1 should have been observed for $k_{obs.}$ at pH $\simeq 8$. Thus, we suspected a further deprotonation for the hydrated $[V_{10}O_{28}]^{6-}$ species, which leads to something like a $[HV_{10}O_{29}]^{7-}$ species. Inconclusive evidence for this, from conductimetric and preparative work and from e.m.f. measurements in a rapid-flow apparatus, has been reported by Jahr *et al.*[4] and by Schwarzenbach and Geier,[6] respectively. The uncertainty is justified since it is difficult to ascertain to what extent alkali is taken up either for a further deprotonation, or for the incipient hydrolytic decomposition of decavanadate, or for hydrolysis of the cation present in solution (likely in some of Jahr's measurements). However, in the presence of alkali- or heavy alkaline-earth-metal cations, where the last event may be discarded, the first two processes could be differentiated on the basis of the probably very large difference in reaction rates. Consequently, on the basis of the present well known order of magnitude of the decomposition rate ($\leqslant 10^{-4}$ s^{-1}), Schwarzenbach and Geier's evidence, gained from titrations performed within a maximum time of 0.1 s from mixing, can be assumed as indicative of deprotonation.

With the support of this argument, we assumed that the species $[HV_{10}O_{29}]^{7-}$ is quickly formed on deprotonation of hydrated $[V_{10}O_{28}]^{6-}$ at pH >8 and that decavanadate could also decompose *via* this species, through a further, independent, first-order path. Therefore, the decomposition rate of decavanadate in neutral and weakly alkaline medium (pH 6—12.5) should obey expression (4), and the overall relation for $k_{obs.}$ becomes (5) where k_1' is the first-order rate constant *via*

$$-d[V_{10}O_{28}]_T/dt = k_1[V_{10}O_{28}{}^{6-}] + k_1'[HV_{10}O_{29}{}^{7-}] \qquad (4)$$

$$k_{obs.} = \frac{k_1K_{IP}[OH^-] + k_1'K_{IP}K_{IP}'[OH^-]^2}{1 + K_{IP}[OH^-] + K_{IP}K_{IP}'[OH^-]^2} \qquad (5)$$

$[HV_{10}O_{29}]^{7-}$ and $K_{IP}' = [HV_{10}O_{29}{}^{7-}][V_{10}O_{28}{}^{6-}]^{-1}[OH^-]^{-1}$. For high values of $[OH^-]$ (but lower than 0.05 mol dm^{-3}, where the higher-order path begins to operate) [1,2] the limiting value of $k_{obs.}$ is k_1'. Thus, the mean value of the limiting $k_{obs.}$ values within the range pH 10.5—12.5 has been calculated (1.02×10^{-4} s^{-1}) and attributed to k_1'. Hence, the only remaining unknown (K_{IP}') in equation (5) has been calculated from a number of sets of $k_{obs.}$ and $[OH^-]$ as 1.06×10^5 dm^3 mol^{-1} (mean).

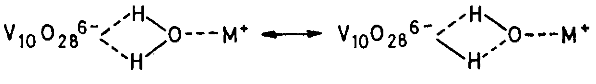
The values of the equilibrium and rate constants so determined have been introduced into equation (5) to generate the curve of $k_{obs.}$ against pH. This curve gives a good fit to the experimental points in Figure 2, confirming that the kinetic law assumed is obeyed.

The path having rate constant k_1' operates in strongly alkaline media (pH >12.5) as well, but here a further $[OH^-]$- and $[Na^+]$-dependent path exists.[1,2] However, since all the reactive forms of decavanadate (on the basis of our results) are present only as $[HV_{10}O_{29}]^{7-}$ under these conditions, the overall rate law may be represented by the extended form (4') of expression (4). The

$$-d[V_{10}O_{28}]_T/dt = k_1[V_{10}O_{28}{}^{6-}] + (k_1' + k_2[OH^-][Na^+])[HV_{10}O_{29}{}^{7-}] \qquad (4')$$

conclusion resulting from this work, that the k_2 path depends on the $[HV_{10}O_{29}]^{7-}$ species instead of $[V_{10}O_{28}]^{6-}$, may well account for the need to assume that more than two sodium ions are associated with the reactive decavanadate species in order to explain the observed $[Na^+]$ dependence at the high cation concentrations used by Goddard and Gonas.[1] Indeed, the conditions under which Schwarzenbach and Geier [6] found a maximum of two alkali-metal ions associated were such that only $[HV_{10}O_{28}]^{5-}$ and $[V_{10}O_{28}]^{6-}$ could be present.

In conclusion, the different values reported for the first-order rate constant of the base decomposition of decavanadate, found to be higher in a strongly basic medium than in the range pH 8—10,[1] can be explained in terms of a fast pH-dependent pre-equilibrium between two decavanadate species, the more basic of which is the more reactive. Little, if any, difference has been found in the different pH ranges when hydrophilic cations are absent (replaced by tetra-alkylammonium ions) or at temperatures ⩾45 °C.[1] This may occur for two different reasons: (*i*) the deprotonation of hydrated $[V_{10}O_{28}]^{6-}$ does not take place; (*ii*) the deprotonation is already complete in the weakly basic range. Statement (*i*) seems to be appropriate to explain the tetra-alkylammonium effect, on the basis of the observed weakening of the acidic properties of decavanadate species on going from alkali-metal to alkylammonium cationic media.[6] These phenomena have in turn been imputed to strong associations of decavanadate with hydrophilic cations. So, the consequent decrease in negative charge on the polyanion promotes the release of H^+. A release of H^+ even from the hydration sphere of $[V_{10}O_{28}]^{6-}$ is more difficult to explain, unless associations are assumed to take place in solution *via* water molecules interposed between decavanadate and other cations (as observed in the solid state [8]), so that the water hydrogens are bound to the external oxygens of the polyanion and the water oxygens to the cations. Such a situation is known to lead to the phenomenon called 'localized hydrolysis',[9] and to determine the weakening of the O–H bond of water and the reinforcement of the hydrogen bond to the terminal oxygens of the polyanion:



Since the polarizing power of the associated cations is essential to localized hydrolysis, it is not difficult to explain why tetra-alkylammonium ions (as far as they really associate with decavanadate [2]) fail to determine it. The effect of increasing temperature, which stimulates hydrolysis and the acidic properties of decavanadates,[10] can therefore be better explained by (*ii*).

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[8] H. T. Evans, jun., *Inorg. Chem.*, 1966, **5**, 967; A. G. Swallow, F. H. Ahmed, and W. H. Barnes, *Acta Cryst.*, 1966, **21**, 397; N. Pullman, *Diss. Abs.*, 1967, **B28**, 140.

[9] R. A. Robinson and H. S. Harned, *Chem. Rev.*, 1941, **28**, 419.

[10] F. Brito, *Anales Real Soc. Espan. Fis. Quim.*, 1966, **B62**, 123.