Kinetic Study of the Acid Decomposition of Decavanadate

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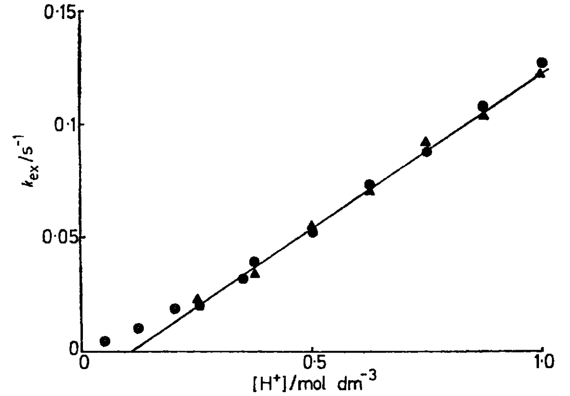
The reaction of decavanadate at concentration of 0·5 × 10^{-2} and 0·5 × 10^{-3} mol dm^{-3} with acid was followed by use of a stopped-flow spectrophotometer, ionic strength being maintained with sodium nitrate. A plot of pseudo-first-order rate constant against hydrogen ion concentration showed that at high acid concentrations (>0·2M) the rate constant increased linearly with acid concentration, but that the line obtained had a finite positive intercept on the acid concentration axis. The suggested mechanism involves equilibria between $H_2V_{10}O_{28}^{4-}$, $H_3V_{10}O_{28}^{3-}$, and $H_4V_{10}O_{28}^{2-}$, with decomposition occurring through $H_4V_{10}O_{28}^{2-}$.

As part of a programme on the study of the equilibria between and rates of reaction of polymeric hydroxo-bridged cations and oxo-bridged anions, we report the acid induced decomposition of decavanadate, $V_{10}O_{28}^{6-}$. As mentioned in the preceding paper, decavanadate is the predominating species in equilibrated solutions of vanadium(v) in aqueous solution at vanadium concentrations above 10^{-3} g-atom dm^{-3} and between pH 2 and pH 6. The equilibrium behaviour of vanadium in this range has been extensively studied, and this work has been extensively studied, and this work has been reviewed.[1,2] There has been no study to date, however, on the kinetics of formation or decomposition of this species in acid solution.

RESULTS

Solutions of decavanadate (10^{-2} and 10^{-3} mol dm^{-3}) were mixed with solutions of nitric acid and sodium nitrate in the stopped-flow apparatus at 25 °C. The ionic strength of the mixed solution was maintained at 1·3 mol dm^{-3} with sodium nitrate. The transmittance of the solution was observed at 485 nm.



The dependence of the rate constant for the acid-induced decomposition of decavanadate on acid concentration for two decavanadate concentrations. Ionic strength was maintained at 1·3 mol dm^{-3}; ●, 10^{-2} mol dm^{-3} decavanadate; ▲, 10^{-3} mol dm^{-3} decavanadate

The initial absorbance was that expected for this concentration of decavanadate alone. The absorbance then fell to zero during about 50 s, the rate depending on the acid concentration. The resulting data yielded good pseudo-first-order rate plots, the standard deviation (see previous paper) usually being in the range 5 × 10^{-3} to 20 × 10^{-3}. The reaction was followed over three to four half-lives. The rate constants obtained were the same for both concentrations of decavanadate used (Figure). At high acid concentrations, the rate constant increased linearly with acid concentration, but extrapolation of the line obtained had a finite positive intercept on the acid concentration axis (Figure).

DISCUSSION

A number of possible mechanisms were examined to explain the positive intercept on the acid axis. First, stoicheiometric removal of hydrogen ions can be discounted, as it would require one decavanadate ion to utilise approximately 200 hydrogen ions. Further, the intercept obtained was the same for both concentrations of decavanadate (see above, Figure).

Secondly, the effect of protonation of the main vanadate anion, A^{n-}, present in the solution was considered. With the acid in great excess, the predicted pseudo-first-order rate law can be stated as equation (1)

$$\frac{dP}{dt} = k_{ex}A^{TOT} = \frac{K^{V}_{1}k_{V}[H^+]}{1 + K^{V}_{1}[H^+]}A^{TOT} \qquad (1)$$

where k_{ex} is the experimental pseudo-order rate constant, A^{TOT} is the total concentration of decavanadate, K^{V}_{1} is the protonation constant of A^{n-}, and k_V is the true first-order rate constant for the decomposition of the protonated decavanadate. This equation leads to a curve which is always convex upwards, and therefore is incompatible with our results.

The third mechanism considered was the double protonation of the main vanadate species. The two successive protonation constants were denoted K^{V}_{1} and K^{V}_{2}. If the diprotonated species decomposes in a first-order process with rate constant k_V, and as before, k_{ex} and A^{TOT} are the experimental pseudo-first-order rate constant and the total decavanadate concentration

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[1] D. L. Kepert, in 'Comprehensive Inorganic Chemistry,' eds. A. F. Trotman Dickenson, J. C. Bailar, H. J. Emeléus, and (the late) R. S. Nyholm, vol. 4, Pergamon, Oxford, 1973, p. 1.

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

respectively, then we obtain equations (2)—(4). This

$$A^{n-} + H^{+} \xrightleftharpoons{K^{\mathrm{V}}_{1}} HA^{(n-1)-} \qquad (2)$$

$$HA^{(n-1)-} + H^{+} \xrightleftharpoons{K^{\mathrm{V}}_{2}} H_{2}A^{(n-2)-} \qquad (3)$$

$$H_{2}A^{(n-2)-} \xrightarrow{k_{\mathrm{V}}} \text{Products (P)} \qquad (4)$$

mechanism, in excess of acid, leads to the rate law (5).

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k_{\mathrm{ex}}A^{\mathrm{TOT}} = A^{\mathrm{TOT}}\left(\frac{K^{\mathrm{V}}_{1}K^{\mathrm{V}}_{2}k_{\mathrm{V}}[\mathrm{H}^{+}]^{2}}{1 + K^{\mathrm{V}}_{1}[\mathrm{H}^{+}] + K^{\mathrm{V}}_{1}K^{\mathrm{V}}_{2}[\mathrm{H}^{+}]^{2}}\right) \qquad (5)$$

Subsequent work (see later) suggests that $K^{\mathrm{V}}_{1}/K^{\mathrm{V}}_{2}$ is *ca.* 100, and thus that the term $K^{\mathrm{V}}_{1}K^{\mathrm{V}}_{2}[\mathrm{H}^{+}]^{2}$ can be neglected in the denominator of (5), yielding (6). This

$$k_{\mathrm{ex}} = \frac{K^{\mathrm{V}}_{1}K^{\mathrm{V}}_{2}k_{\mathrm{V}}[\mathrm{H}^{+}]^{2}}{1 + K^{\mathrm{V}}_{1}[\mathrm{H}^{+}]} \qquad (6)$$

indeed leads to a plot which consists of a straight line at high acid concentrations, of slope $K^{\mathrm{V}}_{2}k_{\mathrm{V}}$ and intercept $1/K^{\mathrm{V}}_{1}$ on the acid concentration axis. The values obtained for K^{V}_{1} and $K^{\mathrm{V}}_{2}k_{\mathrm{V}}$ are in the Table. It should be noted that data of this kind does not allow the separation of the term $K^{\mathrm{V}}_{2}k_{\mathrm{V}}$ into its components.

Experimental values for the constants in equation (6)

Ionic strength	K^{V}_{1}/mol^{-1}	$K^{\mathrm{V}}_{2}k_{\mathrm{V}}$/mol^{-1} s^{-1}
1·3	10 ± 1	0·132 ± 0·005
4·9	10 ± 1	0·18 ± 0·01

The reciprocal of K^{V}_{1} will be an equilibrium constant for a reaction of type (7) where the equilibrium constant is given by equation (8) and pK_{6-x} = 1·0. Schwarzenbach and Geier [3] give values for both the acid dissociation constants, K_{6} and K_{5} (pK_{6} = 5·8, pK_{5} = 3·6).

$$H_{x+1}V_{10}O_{28}{}^{(5-x)-} \xrightleftharpoons{K_{6-x}} H^{+} + H_{x}V_{10}O_{28}{}^{(6-x)-} \qquad (7)$$

$$K_{6-x} = \frac{1}{K^{1}_{\mathrm{V}}} = 0{\cdot}10 \text{ mol} \qquad (8)$$

It is likely that pK_{4} is *ca.* 1·4, as successive pK values for polybasic acids are found to differ by similar increments, if there has been no change of structure.[4] Such a value agrees quite well with our experimental pK_{6-x} = 1·0, suggesting that $x = 2$ and K^{V}_{1} and K^{V}_{2} may be identified with $1/K_{4}$ and $1/K_{3}$ respectively.

$$H_{2}V_{10}O_{28}{}^{4-} + H^{+} \xrightleftharpoons{K^{\mathrm{V}}_{1}} H_{3}V_{10}O_{28}{}^{3-} \qquad (9)$$

$$H_{3}V_{10}O_{28}{}^{3-} + H^{+} \xrightleftharpoons{K^{\mathrm{V}}_{2}} H_{4}V_{10}O_{28}{}^{2-} \qquad (10)$$

Thus decavanadate can exist in solution as the stable ions $V_{10}O_{28}{}^{6-}$, $HV_{10}O_{28}{}^{5-}$, and $H_{2}V_{10}O_{28}{}^{4-}$. Once the solution contains mainly $H_{3}V_{10}O_{28}{}^{3-}$, however, enough of the unstable $H_{4}V_{10}O_{28}{}^{2-}$ is present to cause decomposition of the polyanion. The temperature-dependence of k_{ex} yields an experimental activation energy of 75 kJ mol^{-1}. This activation energy is a function of the temperature-dependence of both K^{V}_{1} and $K^{\mathrm{V}}_{2}k_{\mathrm{V}}$.

EXPERIMENTAL

The Durrum–Gibson stopped-flow spectrophotometer was modified as described earlier.[5] It was found that reproducible behaviour could be obtained only if the apparatus was freshly cleaned and the syringes well greased with Apiezon L grease, and the flow system carefully freed from bubbles. These precautions were much more critical with the decavanadate–acid system than they were with, for example, the ferric thiocyanate system recommended by the manufacturers to test their equipment.[6] When carried out, they enabled the superposition of several traces on the oscilloscope screen, with no observable discrepancy. Even with these precautions, and when superimposable traces were obtained, it was found that the rate constant obtained was not reproducible from day to day. This could not be related to freshness of the stock solution, to time elapsed since dilution of the stock solution, to room temperature, or to light level in the room. The error in the most extreme cases amounted to 10%, in the rate constant, but was generally less than 5%. No explanation of the effect can be put forward.

Materials.—The stock decavanadate was prepared by dissolving ammonium metavanadate (0·1 mol) in sodium hydroxide (0·32 mol) in aqueous solution. The solution was boiled to incipient crystallisation. Distilled water (700 ml) was added. To the cold solution, nitric acid (0·284 mol) was added. The solution was boiled for 45 min, then cooled and diluted to 1 dm^{-3}. The pH was then 4·8.

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

[4] C. S. G. Phillips and R. J. P. Williams, ' Inorganic Chemistry,' Oxford University Press, London, 1965.

[5] B. W. Clare, D. L. Kepert, and D. W. Watts, preceding paper.

[6] Manual for Stopped Flow Spectrophotometer, Durrum Corp.