Rapid Acidification of Orthovanadate

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The reaction of orthovanadate, VO_4^{3-}, with excess of acid had been shown to follow at least two pathways. Very rapid reactions lead to the formation of an unknown intermediate together with a small and non-reproducible amount of decavanadate. Both the intermediate and the decavanadate are then degraded to the final product, VO_2^{+}.

EQUILIBRIUM studies [1] on vanadate solutions have shown that above pH 13·0, the major species in equilibrated solutions is orthovanadate, VO_4^{3-}. Between pH 6 and pH 2, and at concentrations greater than 10^{-3} g-atom dm^{-3}, the stable species is one of the protonated decavanadates $H_xV_{10}O_{28}^{(6-x)-}$ ($x = 0$—2) in which the vanadium atoms are octahedrally co-ordinated by oxygen atoms. A number of less well defined species exist between pH 6 and pH 13, including the divanadates $V_2O_7^{4-}$ and $HV_2O_7^{3-}$ and the metavanadates $(VO_3,xH_2O^-)_3$ and $(VO_3,xH_2O^-)_4$. At higher acid concentrations, VO_2^{+} is formed.

Schwarzenbach and Geier [2] have reported a continuous flow potentiometric study of the acidification of orthovanadate, in which they detected HVO_4^{2-}, $H_2VO_4^{-}$, and H_3VO_4. These species rapidly polymerise, to give the above products.

As part of a programme on the study of the equilibrium between, and rates of reaction of, polymeric hydroxo-bridged cations and oxo-bridged anions, we report a kinetic study of the reaction between orthovanadate and excess acid.

RESULTS AND DISCUSSION

A solution of Na_3VO_4 (0·1 mol dm^{-3}) was mixed with nitric acid of the same concentration by injection into a stopped-flow spectrophotometer. Reaction was complete within the mixing time, giving a transmittance which was greater the faster the mixing (that is, the harder the handle of the stopped flow apparatus was pulled). No further change was observed on keeping the mixed solutions for 1 h at room temperature. Transmittances obtained varied from 0·12 to 0·55. The absorbing species had a spectrum corresponding to that of decavanadate, $V_{10}O_{28}^{6-}$. The extinction coefficient corresponded to conversion of only 0·12—0·42% of the original orthovanadate into decavanadate under these conditions. The more rapid the mixing, the less decavanadate was formed.

When a large excess of acid was added to a solution of orthovanadate, and the reaction was observed at 450 or 500 nm, where orthovanadate does not absorb, three distinct steps were seen. (i) A very rapid fall in transmittance, which was complete within the mixing time; (ii) a rapid increase in transmittance to an intermediate value. This reaction was complete in *ca.* 100 ms; and (iii) finally, during *ca.* 50 s, the transmittance increased to 1·0 (100% transmission).

The first stage was too rapid to study on the stopped-flow apparatus. The second stage was studied in detail. The traces obtained were not reproducible. Subsequent injections from the same samples in the reservoir syringes did not give reproducible results. The trace showed no regular variation with the age of the orthovanadate solutions, with the order of the runs, with the interval between runs, or with deliberately different technique of injection from the drive syringes. Some typical results are shown in Figure 1. Any one set of curves, obtained from the same solutions and under the same conditions, yielded good first-order rate plots and moderately reproducible first-order rate constants (Table 1). The transmittance at the end of this second stage, however, was variable from one run to another. The trend in the pseudo-first order rate constants was to increase with increasing acid concentration, although the data was badly scattered (Figure 2). The effect of varying the initial vanadate concentration was extraordinary, in that an increase in vanadate concentration slowed the reaction (Figure 3). The rate plots from three of the curves are displayed in Figure 4.

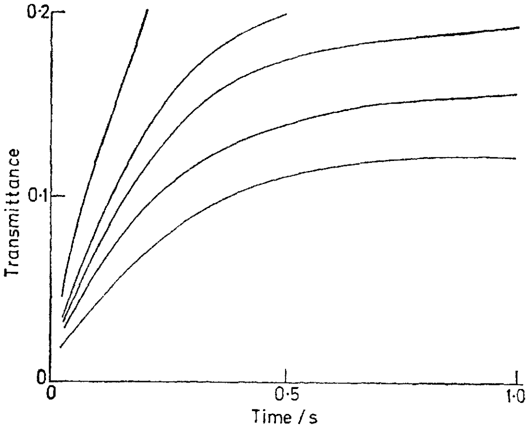

FIGURE 1 Traces obtained by mixing Na_3VO_4 (0·1 mol dm^{-3}) with HNO_3 (0·7 mol dm^{-3}), observing at 500 nm, at 25 °C and 1 s full-scale time-base. The transmittance scale was 0—20%. Successive runs under the same conditions gave widely different curves

The third stage showed more understandable behaviour. In spite of the differences in initial transmittance, good first-order rate plots and reproducible

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[1] D. L. Kepert, 'The Early Transition Metals,' Academic Press, London, 1972; M. T. Pope and B. W. Dale, *Quart. Rev.*, 1968, **22**, 527.

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

rate constants were obtained. These rate constants depended on acid concentration, but not on initial orthovanadate concentration. They were identical with rate constants obtained for mixing a decavanadate solution with acid of the same concentration and ionic strength.[3]

TABLE 1

Rate constants calculated for two sets of rate data

1 $[VO_4^{3-}] = 0{\cdot}05$ mol dm^{-3}, $[H^+] = 1{\cdot}25$ mol dm^{-3} 23·0 °C, four runs

Run	Rate constant/s^{-1}	Std. devn.
a	114	0·016
b	115	0·017
c	132	0·030
d	108	0·019

2 $[VO_4^{3-}] = 0{\cdot}05$ mol dm^{-3}, $[H^+] = 1{\cdot}0$ mol dm^{-3} 25·0 °C, four runs

Run	Rate constant/s^{-1}	Std. devn.
a	63	0·0065
b	65	0·010
c	61	0·0093
d	54	0·021

If the kinetic results for the second stage are plotted as absorbance against time, the absorbance due to the decavanadate can be subtracted from the total absorbance for each curve, to give a rate plot for the decomposition of the intermediate. The resulting rates are identical for a given set of conditions (Figure 5). The amount of intermediate formed is thus reproducible, and presumably accounts for the bulk of the vanadium compared with the much smaller quantity of decavanadate formed. The decomposition of the intermediate follows first-order kinetics, with rate constants ranging from 23 to 126 s^{-1}, depending on the initial vanadate concentration and on the acid concentration.

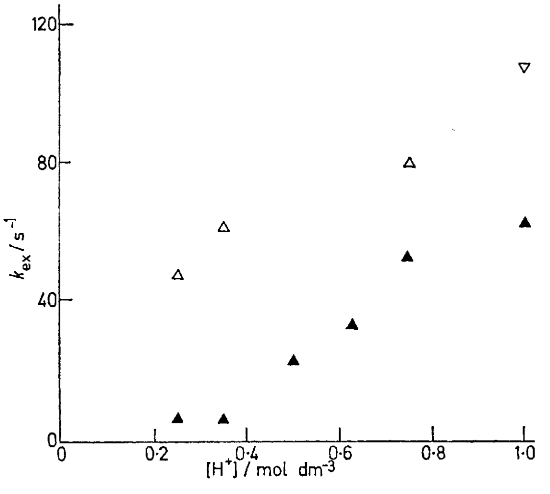

FIGURE 2 Hydrogen-ion concentration dependence of the experimental rate constant for decomposition of the intermediate, formed by reaction of orthovanadate with excess of acid, at two initial orthovanadate concentrations: ▲ 0·05 mol dm^{-3} VO_4^{3-}; △, 0·005 mol dm^{-3} VO_4^{3-}

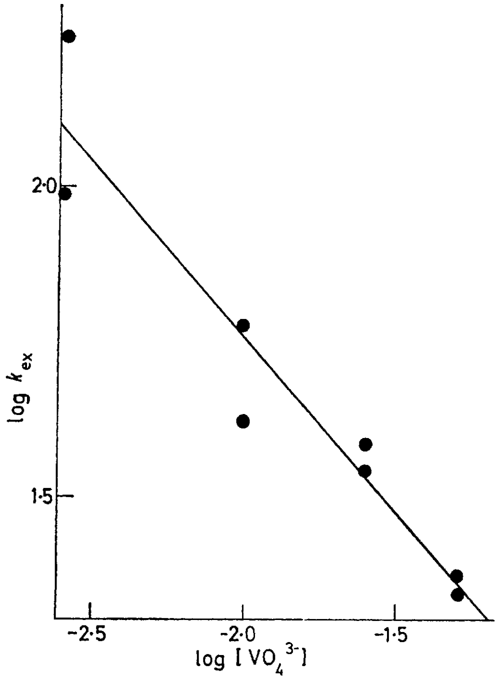

FIGURE 3 Dependence of the rate constant for the decomposition of the intermediate on the initial orthovanadate concentration, at acid concentration 0·5 mol dm^{-3} and ionic strength 1·3 mol dm^{-3}

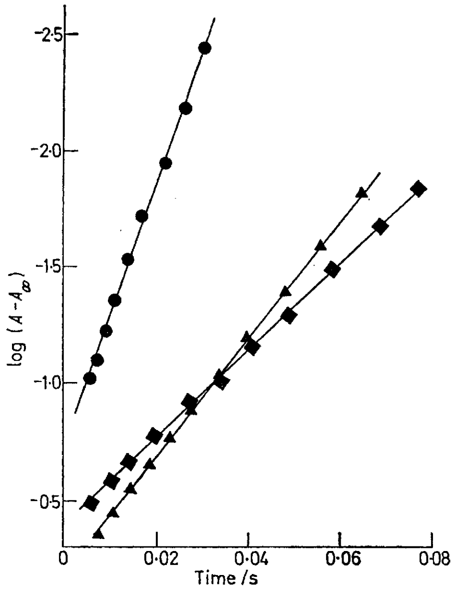

FIGURE 4 Typical rate plots for the decomposition of the intermediate in 0·5 mol dm^{-3} acid at ionic strength 1·3 for three initial orthovanadate concentrations: ●, 0·0025 mol dm^{-3} VO_4^{3-}; ▲, 0·1 mol dm^{-3} VO_4^{3-}; and ◆, 0·025 mol dm^{-3} VO_4^{3-}

The spectrum of the intermediate can be obtained from a series of runs at different wavelengths, after correction for the absorbance of decavanadate and dioxovanadium(v) (Table 2).

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[3] B. W. Clare, D. L. Kepert, and D. W. Watts, following paper.

The intermediate has not been identified. It behaves reproducibly at any one initial vanadate concentration, but apparently is not a single species, as its rate of decomposition depends on the initial orthovanadate concentration. This implies that at least two species are present, their relative amounts varying. Possibly, the higher initial vanadate concentrations favour a more polymerised species, which then decomposes more slowly. If this is so, it is hard to see how the mixture can follow first order kinetics.

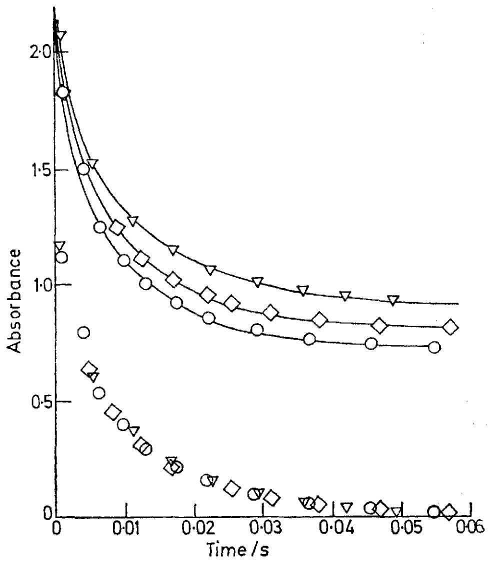

FIGURE 5 Analysis of three of the curves shown in Figure 1. The three upper traces are plots of optical density against time for three of the curves. The lower curve is obtained by subtracting the absorbance due to the decavanadate from the total absorbance for each of the three upper traces

TABLE 2

Spectrum of the intermediate

Wavelength/nm	Extinction coeff.
400	30
450	15
500	6
550	0·6

It may be thought that the intermediate is a mixture of metavanadates of formula $(VO_3)_n^{n-}$ where n is 3 or 4. Such a solution can be prepared by acidifying a hot solution of orthovanadate so that when cooled it has pH 7·5. The spectrum, however, does not correspond to our intermediate, showing that it is not metavanadate.

When this metavanadate solution is mixed with acid in the stopped-flow apparatus, the same three stages are observed as with orthovanadate, and the same rate constants are obtained. It therefore appears that the formation of the intermediate requires more than the 2 mol of hydrogen ion per mole of orthovanadate necessary to form the metavanadates.

EXPERIMENTAL

The ceramic plungers of the standard Durrum–Gibson stopped-flow spectrophotometer were found to be attacked by strong acids, and became liable to jam in the syringe barrels. They were replaced with stainless steel plungers greased with Apiezon L grease. The stainless steel cell block supplied was replaced with a standard Kel-F block. Perchloric acid proved unsatisfactory as a source of hydrogen ions, as it evolved gas in contact with the stainless steel of the apparatus. Nitric acid was chosen for its passivating effect.

The stock orthovanadate solution was prepared from ammonium metavanadate (M and B reagent grade: Found: V, 43·5. Calc. for NH_4VO_3: V, 43·5%) (0·1M) and sodium hydroxide (0·32 mol of standardised solution), with boiling until all ammonia had been expelled. It was then cooled and diluted to 1 dm^{-3}. Nitric acid was A.R. grade.

Treatment of the Rate Data.—For a first-order reaction where only the reactants, and not the products, absorb light, the rate constant k and absorbance A are related by equation (1). In this work, reactions were followed for 3—4 half-lives. Thus log A has a range of *ca.* unity. The standard deviations quoted are obtained by taking the square root of the mean square of the deviation of the experimental log A from the line of best fit.

$$\log A = \log A_0 - kt/2{\cdot}303 \qquad (1)$$

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