967. *Peroxy-complexes of Inorganic Ions in Hydrogen Peroxide–Water Mixtures. Part V.* Decomposition by Vanadate Ions.*

By P. Flood, T. J. Lewis, and D. H. Richards.

Dissolution of vanadium pentoxide in hydrogen peroxide–water mixtures produces a single peroxy-complex. According to the pH of the system this complex exists in one of three forms: as a singly charged pervanadyl cation, as a singly charged pervanadate anion, or as a doubly charged pervanadate anion. The equilibrium constants relating these species have been measured over a range of hydrogen peroxide concentrations, and deductions concerning the degenerate activity coefficient of the hydrogen ion in hydrogen peroxide–water mixtures have been made therefrom. The rate of decomposition is proportional to the calculated concentration of pervanadyl ion, and its large variation with hydrogen peroxide concentration is due to corresponding variation in the equilibrium constant between this ion and the pervanadate ion.

The existence of pervanadates has long been recognized. Vanadium pentoxide, although sparingly soluble in water, dissolves readily in the presence of hydrogen peroxide. The pervanadic acid from which the resulting pervanadates are derived has been variously and inconclusively described as H_3VO_5 [1] and H_3VO_6.[2] A pervanadyl ion, VO_2^+, has also

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* Part IV, preceding paper.

[1] Meyer and Pawletta, *Z. phys. Chem.*, 1927, **125**, 49.

[2] Jahr, *Z. Elektrochem.*, 1941, **47**, 810.

been described.[1] In the present work, although we believe that the absence of more than one peroxy-complex suggests complete peroxidation to H_3VO_8, we obtained no direct evidence for this formula, and to avoid misunderstanding write the various peroxy-species as though derived from the pervanadic acid, H_3VO_5.

EXPERIMENTAL

The techniques used—pH, spectrophotometric, and oxygen-evolution measurements—have been described elsewhere.[3]

Solutions were prepared in series with various acidities and constant hydrogen peroxide concentration. Ionic strength was maintained at 0·01 by the addition of sodium perchlorate. Vanadium pentoxide (B.D.H. Laboraory Reagent) was added as the solid to 500-ml. samples of the particular hydrogen peroxide–water mixture, which was then divided into 50 ml. parts for individual acid or alkali additions. The vanadium concentration throughout was 2×10^{-3}M. A comparatively narrow range of hydrogen peroxide concentrations was studied (0·55—0·75 mole fraction). At concentrations below 0·55, catalysis was too slow to be measured, and above 0·75 decomposition was very fast, causing very erratic results owing to self-heating. As in previous investigations, pH measurements were carried out at 25°, oxygen-evolution measurements at 22°, and spectrophotometric measurements at room temperature, which was kept at 22° ± 1°.

In conformity with the other papers of this series results are expressed, whenever possible, as mole fractions. Molarities have been retained in certain descriptive passages, and also in certain graphs showing results at more than one hydrogen peroxide concentration, where, since there is not strict linearity between molarity and mole fraction, conversion from the working unit, molarity, into mole fractions would result in differing catalyst concentrations being presented on the same graph.

RESULTS

pH *Measurements*.—Addition of vanadium pentoxide to a hydrogen peroxide–water mixture lowers the pH, showing that the pervanadic acid which is formed is at least partially ionized. At hydrogen peroxide concentrations below about 0·55 the lowering of pH by vanadium pentoxide corresponds to the quantitative formation of the $H_2VO_5^-$ ion according to the equation

$$H_3VO_5 \overset{K}{\rightleftharpoons} H^+ + H_2VO_5^- \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

Even addition of perchloric acid does not measurably decrease the concentration of the $H_2VO_5^-$ ion. The value of K in this range is too large to be measured by this technique.

At hydrogen peroxide concentrations above ~0·55 the lowering of the pH by addition of vanadium pentoxide is less than would be expected on the basis of complete ionization according to equation (1), and with the addition of increments of perchloric acid values for K may be calculated. These are shown in Table 1 for a typical run at 0·72 mole fraction of hydrogen peroxide. It can be seen that the values of K calculated according to equation (1) vary with hydrogen-ion concentration even at constant hydrogen peroxide concentration. Other equilibria were tested, and it was found that the dissociation constant for reaction (2) was independent

$$H_4VO_5^+ \overset{K'}{\rightleftharpoons} 2H^+ + H_2VO_5^- \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

of hydrogen-ion concentration. Table 1 shows calculated values for K' at $[H_2O_2] = 0{\cdot}72$. The positively charged pervanadyl ion has been written without elimination of water because no discernible difference exists between the visible spectrum of the pervanadyl ion and that of the singly charged pervanadate anion.

It may be stated with confidence that equation (2) adequately describes the equilibrium which is set up when vanadium pentoxide is dissolved in hydrogen peroxide–water mixtures.

[3] Lewis, Richards, and Salter, *J.*, 1963, 2434.

Because of the large errors resulting from the use of the square of the hydrogen-ion concentration, the direct determination of K' at each experimental hydrogen peroxide concentration gave results which, although showing a large increase with decreasing peroxide concentration, were rather scattered. To minimize the scatter the following procedure was adopted.

TABLE 1.

$10^5[H^+_0]$	$10^5[H^+]$	10^5K	$10^9K'$
0	2·94	6·5	4·7
1·7	4·26	6·4	7·2
3·4	5·28	4·1	7·2
5·1	6·28	2·4	6·8
6·8	7·38	1·1	7·0

In Fig. 1, the observed pH is plotted against the mole fraction of hydrogen peroxide, each curve representing one concentration of added perchloric acid or sodium hydroxide. In this way errors due to inaccuracies in the value taken for E_0 for a particular solvent mixture are minimized. Smoothed values of the pH at the various plotted values of $[H^+_0]$ may now be read off at any hydrogen peroxide concentration, and the values of K' calculated. Values of K' so obtained are listed in Table 2. At every solvent concentration, K' was reasonably independent of the hydrogen-ion concentration. It will be seen that K' changes rapidly with hydrogen peroxide concentration. So, at concentrations below ~0·55, almost all the vanadate is present as the singly negative charged pervanadate ion, $H_2VO_5^-$. It will be shown later that the variation in K' with peroxide concentration is responsible for the dependence of rate of decomposition on peroxide concentration, and the implications of this will be discussed.

TABLE 2.

$[H_2O_2]$	0·74	0·72	0·70	0·68	0·66	0·64	0·60	0·56
$10^8K'$	0·46	0·70	0·90	1·35	1·73	2·20	3·51	5·32
pK'	8·34	8·15	8·05	7·87	7·76	7·66	7·45	7·27

Oxygen-evolution Measurements.—The rate of decomposition of hydrogen peroxide in the presence of vanadate ions is increased by (*a*) increasing the hydrogen-ion concentration and (*b*) increasing the hydrogen peroxide concentration. In the light of the previous discussion it appears likely that catalysis is due wholly or partly to the pervanadyl ion, $H_4VO_5^+$.

The concentration of the pervanadyl ion at a particular added perchloric acid concentration $[H^+_0]$ may be calculated. Then, if for a particular hydrogen peroxide concentration the pervanadyl ion concentration is calculated at each value of $[H^+_0]$ and then plotted against the decomposition rate for these same values of $[H_2O_2]$ and $[H^+_0]$, the kinetic relation between pervanadyl-ion concentration and rate of decomposition is obtained. A smoothing process, similar to that previously described for pH measurements, was adopted. Fig. 2 shows the variation in decomposition rate with hydrogen peroxide concentration, each curve representing a particular value of $[H^+_0]$. The smoothed values at regular $[H_2O_2]$ intervals were then read off and plotted against smoothed values of the pervanadyl-ion concentration obtained from Fig. 1. Straight lines are obtained, showing a first-order relationship between the $H_4VO_5^+$ ion and decomposition rate. The variation in the slope of these lines with hydrogen peroxide concentration will indicate whether or not hydrogen peroxide appears in the irreversible decomposition equation. Table 3 gives these slopes at various hydrogen peroxide concentrations.

TABLE 3.

$[H_2O_2]$	0·74	0·72	0·70	0·68	0·66	0·64	0·60	0·56
Slope of curve, decompn. rate *v.* $[H_2VO_5^-]$ ...	24·2	14·2	12·1	11·7	9·8	8·9	10·4	10·4

Although clearly there is an overall drop in the value of the slope from $[H_2O_2] = 0·74$ to $[H_2O_2] = 0·56$, this drop is by no means regular. There is not sufficient evidence to say whether decomposition takes place through a first-order reaction of the pervanadyl ion

$$H_4VO_5^+ \xrightarrow{k_1} \text{Products} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

or through a second-order reaction between a pervanadyl ion and a hydrogen peroxide molecule

$$H_4VO_5^+ + H_2O_2 \xrightarrow{k_2} \text{Products} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

But it is certain that the really large changes in rate with hydrogen peroxide concentration are due to the large changes in the value of K' and the large associated changes in the concentration of the pervanadyl ion. Any variation in rate due to the introduction of a hydrogen peroxide concentration into the rate equation is of secondary importance.

The value of k_1 calculated for reaction (*a*) has an average of ~10·4. This is the same order of magnitude as the first-order decomposition of the perchromic acid molecule ($k = 7$)[4] and much larger than the second-order constants found in the investigations of other Group VI metals.[5,6]

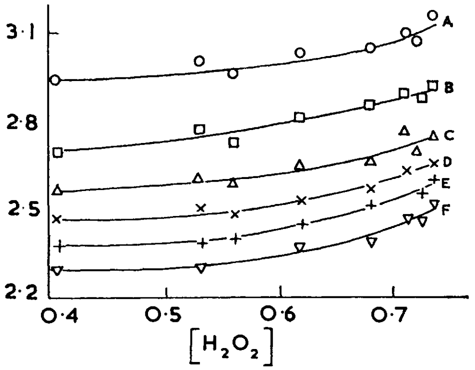

FIG. 1. Variation of pH with hydrogen peroxide concentration at various values of $[H^+_0]$.

(A) $[OH^-_0] = 0·8 \times 10^{-3}$M. (B) No added acid or alkali. $[H^+_0]$: (C) 0·8, (D) 1·6, (E) 2·4, (F) $3·2 \times 10^{-3}$M.

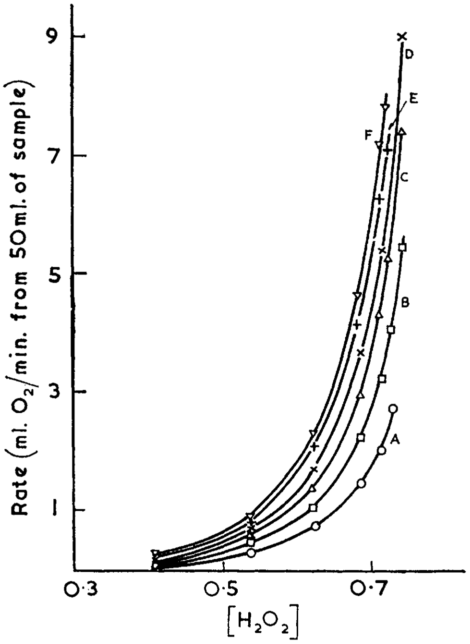

FIG. 2. Variation of rate of oxygen evolution with hydrogen peroxide concentration.

(A)—(F) as in Fig. 1.

Spectrophotometric Measurements.—Addition of perchloric acid does not appreciably alter the visible spectrum of vanadium pentoxide in hydrogen peroxide, and it is concluded that $H_4VO_5^+$ and $H_2VO_5^-$ have similar absorption. Additions of sodium hydroxide, on the other hand, progressively lighten the colour until in slightly alkaline solutions a light yellow colour is obtained. Further addition of sodium hydroxide produces no further colour change. The singly charged pervanadate ion is undergoing further ionization.

Suppose that this further ionization may be represented by the equation:

$$H_2VO_5^- \overset{K_2}{\rightleftharpoons} H^+ + HVO_5^{2-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

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[4] Flood, Lewis, and Richards, *J.*, 1963, 2446.
[5] Dedman, Lewis, and Richards, *J.*, 1963, 2456.
[6] Dedman, Lewis, and Richards, *J.*, 1963, 5020.

Since both the $H_2VO_5^-$ and the HVO_5^{2-} ions absorb in the useful wavelength range, to calculate K_2 use must be made of the method previously employed in the investigation of the ferric ion in hydrogen peroxide–water mixtures.[3] When smoothed optical density values from Fig. 3 were used, a plot of $\Delta[H^+]/\Delta D$ against $[H^+]$ gave a straight line at each peroxide concentration, showing that in this case, unlike that in more acid solution, a simple acid–base equilibrium is being observed (Equation 5). Table 4 gives the collected values of K_2 calculated by this method. As in the case of K' there is an overall increase in the value of K_2 with decreasing hydrogen peroxide concentration.

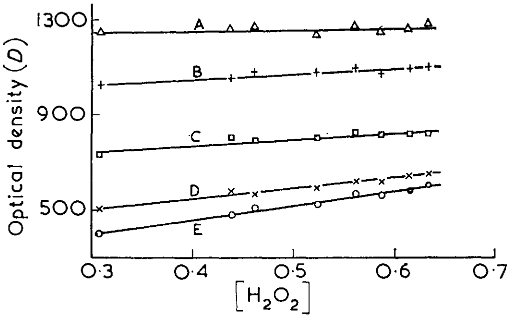

FIG. 3. Variation of optical density at 410 mμ with hydrogen peroxide concentration for various additions of sodium hydroxide. (A) No NaOH added. NaOH: (B) 2·4, (C) 3·2, (D) 4·0, (E) 6·0 × 10^{-3}M.

TABLE 4.

$[H_2O_2]$	0·74	0·72	0·70	0·68	0·66	0·64	0·60	0·56
10^7K_2	1·69	2·03	2·24	2·67	3·12	3·53	4·54	5·74
pK_2	6·77	6·69	6·65	6·57	6·51	6·45	6·34	6·24

DISCUSSION

The rapid decrease in K' and K_2 with increase in hydrogen peroxide concentration could possibly be explained by postulating the formation of a series of vanadium peroxy-complexes, the ionization constants of which decrease rapidly with increase in the degree of peroxidation. We do not hold this view for the following reasons.

Let us consider the extreme case where two acids are formed differing by n peroxide groups, and that only the ionization of the less peroxidated is significant. Then

$$H_4VO_x^+ + nH_2O_2 \xrightleftharpoons{K} (H_4VO_{x+n})^+ + H_2O$$

and

$$H_4VO_x^+ \xrightleftharpoons{K''} 2H^+ + H_2VO_x^-$$

It may be shown that the apparent ionization constant K' is given by

$$\frac{1}{K'} = \frac{1}{K''} + \frac{K}{K''} \cdot \frac{[H_2O_2]^n}{[H_2O]^n}$$

Calculations show that the variation in K' with $[H_2O_2]$ predicted by this equation approximates to that observed experimentally only when $n \approx 4$. The two peroxy-complexes would have to differ from each other by four oxygen atoms. But the oxygen-evolution measurements show that the decomposition rate is proportional to the sum of the concentrations of all the positive vanadium species present. The ions $H_4VO_x^+$ and $(H_4VO_{x+n})^+$ would have to have the same rate constant for decomposition. This is clearly unlikely, especially in view of the fact that the only pair of acids which can be easily envisaged are $H_4VO_4^+$ and $H_4VO_8^+$. The former is derived from non-peroxidated vanadic acid and would be catalytically inactive.

A similar argument, when applied to the trends in K_2, shows that in this case the decrease can be explained only when $n \approx 2$. Therefore a peroxy-complex would have to be postulated in alkaline solution which was different from any found in acid solution at the same peroxide concentrations.

In view of these difficulties, we believe that the results are best explained by postulating only one peroxy-complex. The dissociation constants of this complex must change with solvent composition, but it is noteworthy that the changes in the value of pK_2 (where only one hydrogen is involved in the dissociation) are roughly the same as the changes found by Beck and Wynne-Jones [7] and by ourselves for the dissociation constants of certain indicator acids in the same solvent range. Indeed, the present investigation throws considerable light on to the nature of these variations.

Consider the thermodynamic equilibrium constants for the reactions (2) and (5).

These may be written:

$$(K')_a = \{H^+\}^2\{H_2VO_5^-\}/\{H_4VO_5^+\} = K'\gamma^2_{H^+}\ \gamma_{H_2VO_5^+}/\gamma_{H_4VO_5^+} \qquad (6)$$

and

$$(K_2)_a = \{H^+\}\{HVO_5^{2-}\}/\{H_2VO_5^-\} = K_2\gamma_{H^+}\ \gamma_{HVO_5^{2-}}/\gamma_{H_2VO_5^-}. \qquad (7)$$

The activity coefficients γ refer to a hypothetical molar solution in water as the standard state and are therefore the so-called " degenerate activity coefficients." Since $(K')_a$ and $(K_2)_a$ are universal constants the variation in the observed values of K' and K_2 with hydrogen peroxide concentration must be due either to changes in the activity coefficient of the hydrogen ion or to changes in the activity coefficients of the various vanadate peroxy-complexes, or to changes in both. Several authors [8] have recently suggested that the changes observed in the dissociation constant of an uncharged acid in passing through various concentration ranges of a mixed solvent are due to changes in the activity coefficient of the uncharged acid, the activity coefficient of the hydrogen ion and that of the conjugate base remaining relatively constant. We have accumulated considerable evidence, which will be discussed in a separate paper, to challenge this view. For hydrogen peroxide–water mixtures at least, we consider it more likely that changes in acid-dissociation constant are largely due to changes in the activity coefficient of the hydrogen ion. If this hypothesis is true, then a plot of $\Delta pK'$ against $2\Delta pK_2$ should be a straight line passing through the origin and having a slope of 45°, since K' depends upon the square of the hydrogen-ion concentration and K_2 is linearly related to it. Such a plot is shown in Fig. 4. A reasonable approximation to such a slope is obtained, strongly suggesting that it is alteration of the activity coefficient of the hydrogen ion, and not that of the peroxy-complexes, which leads to the variation of dissociation constants with solvent composition.

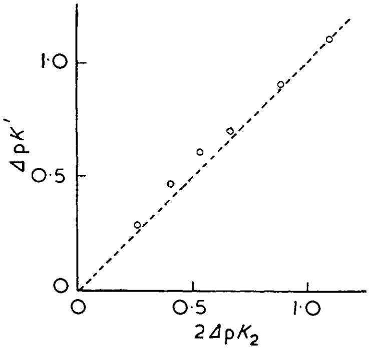

FIG. 4. Plot of $\Delta pK'$ against $2\Delta pK_2$. The broken line is the theoretical slope.

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[7] Beck and Wynne-Jones, *J. Chim. phys.*, 1952, **49**, C.97.

[8] Dunsmore and Speakman, *Trans. Faraday Soc.*, 1954, **50**, 236; Bell and Robinson, *ibid.*, 1961, **57**, 965.