500. *The Reduction of Quinquevalent Vanadium by Hydrogen Peroxide in Solutions of Strong Acids.*

By G. Kakabadse and H. J. Wilson.

The reduction of quinquevalent vanadium by hydrogen peroxide in acid solution depends upon the VO^{++}–$VO_2{}^+$ and the H_2O_2–O_2 redox system, which, in turn, are affected by the nature and concentration of acid, the time, and the temperature. Simultaneous peroxidation of quinquevalent vanadium renders the mechanism of reduction rather complex. A scheme is suggested in which pale yellow vanadyl(V), red-brown monoperoxyvanadyl(V), yellow diperoxyorthovanadate, and blue vanadyl(IV) ions are related to hydrogen-ion and hydrogen peroxide concentrations.

The VO^{++}–$VO_2{}^+$ *and* H_2O_2–O_2 *Redox Systems.*—Earlier interpretations [1] of the reduction of quinquevalent vanadium with hydrogen peroxide in acid solution fail to assign a function to the redox behaviour of the ions involved and suffer from a rather incomplete knowledge of the chemistry of quinquevalent vanadium, partly owing to the complexity [2] of the vanadium–hydrogen peroxide system comprising simultaneous peroxidation and reduction.

It has been established that the redox potentials of the VO^{++}–$VO_2{}^+$ (refs. 3, 4) and the H_2O_2–O_2 (ref. 5) system are pH-dependent. These findings were extended to more concentrated solutions of sulphuric acid; the results (Fig. 1) show that the difference in the redox potentials of these systems increases with increasing hydrogen-ion activity up to 16N-sulphuric acid.

Effect of Acid Concentration.—Potentiometric titrations of vanadyl(V) solutions with hydrogen peroxide in sulphuric acid (4—20N) convey (Fig. 2) that appreciable reduction occurred in 4N-acid, and that the degree of reduction increased (increase in potential change) as acidity increased, although even in 20N-sulphuric acid reduction was still incomplete as judged by the green colour of the solution in the presence of excess of hydrogen peroxide. In the case of 24N-sulphuric acid (Fig. 3, curve *a*) the solution attained the characteristic blue colour of the reduced form within a few minutes and the

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[1] Cain and Hostetter, *J. Amer. Chem. Soc.*, 1912, **34**, 274; Hothersall, *J. Soc. Chem. Ind.*, 1924, **43**, 270T; Auger, *Compt. rend.*, 1921, **172**, 1355.

[2] Kakabadse and Wilson, *Nature*, 1957, **180**, 861.

[3] Carpenter, *J. Amer. Chem. Soc.*, 1934, **56**, 1857; Hart and Partington, *J.*, 1940, 1532.

[4] Ducret, *Ann. Chim.* (*France*), 1951, **6**, 705.

[5] Delahay, Pourbaix, and Van Rysselberghe, *Ind. chim. belge*, 1951, **16**, 396; Berl, *Trans. Electrochem. Soc.*, 1943, **83**, 253.

completeness of reduction was checked (Fig. 3, curve *b*) by oxidation with N/10-potassium permanganate.

Effect of Time and Nature of the Acid.—It has been seen that solutions of quinquevalent vanadium in concentrated acids are reduced rapidly. In order to make a comparative study of the reaction of vanadyl(V) ions with hydrogen peroxide in solutions of different acids, more dilute solutions (0·5—6N) of sulphuric, perchloric, and nitric acids have been used to determine absorptiometrically the effect of time and of the nature of the acid. Under these conditions, the intensely coloured, red-brown monoperoxyvanadyl(V) ions which are instantly formed are reduced relatively slowly to the paler blue vanadyl(IV) ions. Absorptiometric measurements were taken of freshly prepared solutions and repeated after 2 and 4 days (Fig. 4). It is seen in Fig. 4 that a general decrease in optical density occurs with time and that the maximum optical density for all three acids is at about 2N-hydrogen-ion concentration.

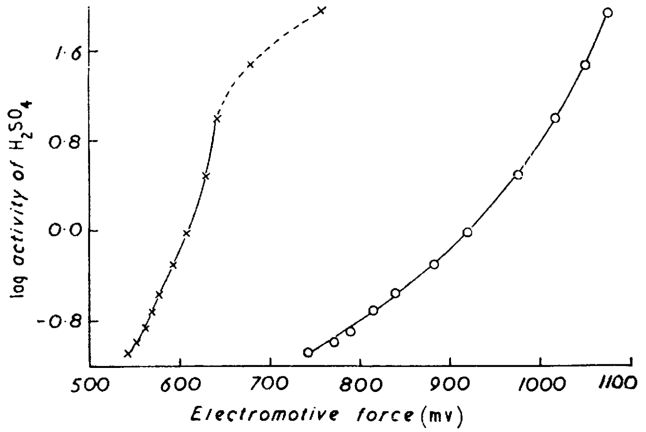


FIG. 1. *Variation of redox potential with activity of sulphuric acid for the systems* VO^{++}–VO_2^+, ○, *and* H_2O_2–O_2, ×.

FIG. 2. *Potentiometric titration curves of vanadyl*(V) *solution with hydrogen peroxide in the presence of varying amounts of sulphuric acid.* (The normalities of the sulphuric acid are indicated on the curves.)

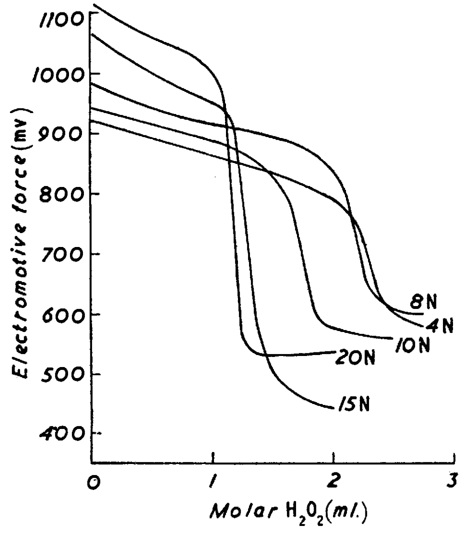
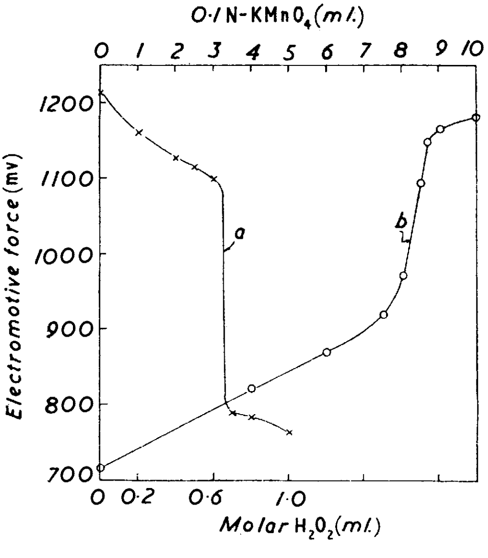


FIG. 3. *Potentiometric titration curves:* (*a*) *reduction of vanadyl*(V) *solution with hydrogen peroxide in* 24N-*sulphuric acid;* (*b*) *oxidation of the resulting vanadyl*(IV) *solution with standard potassium permanganate.*



Reduction experiments in concentrated selenic acid, which is reputed[6] to be stronger than sulphuric acid, yielded the characteristic deep blue colour when excess of hydrogen peroxide had been added.

Effect of Temperature.—The effect of temperature on the completeness of reduction was checked for 10N- and 24N-sulphuric acid. In the former case, 4 reductions, under conditions identical except for temperature and time, were followed potentiometrically (Fig. 5); in the first two experiments the reduction was followed immediately by titration with permanganate. Here, the amounts of reduced vanadium were 25% at 24° (curve *a*) and 91% at 75° (curve *b*). Next, the experiments were repeated but the solutions were stored for 4 days before back-titration of the reduced form. In this case, reduction at 24° (curve *c*) was 95% complete, and that at 75°, 89% complete. On the other hand, the detrimental effect of high temperature on reduction was not noticed in the case of 24N-sulphuric acid, reduction at 81° being quantitative.[2]

FIG. 4. *Absorptiometric measurements taken* (*a*) *immediately,* (*b*) *after* 2 *days, and* (*c*) *after* 4 *days of solutions containing vanadyl*(V) *ions, hydrogen peroxide, and varying amounts of sulphuric* (——), *nitric* (– – – –), *and perchloric* (— — —) *acid.*

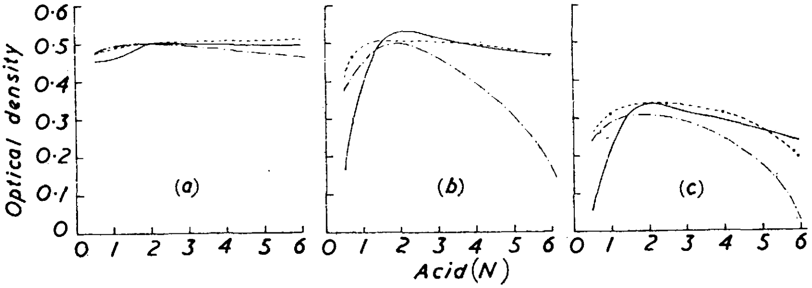
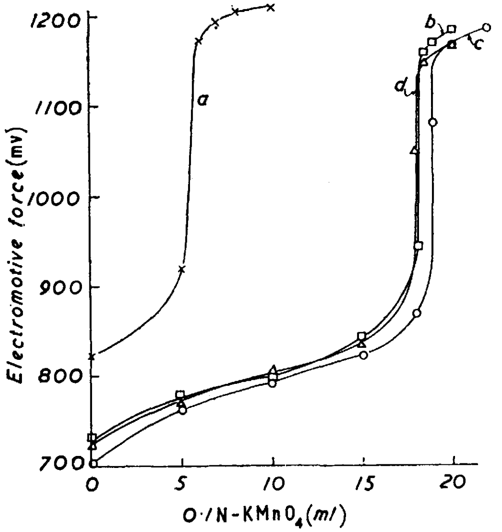


FIG. 5. *Oxidation curves of vanadyl*(IV) *solutions with standard potassium permanaganate. The solutions were obtained from vanadyl*(V) *solutions by reduction with hydrogen peroxide in* 10N-*sulphuric acid at* 24° [(*a*) *and* (*c*)] *and at* 75° [(*b*) *and* (*d*)]. [*In cases* (*a*) *and* (*b*), *oxidations were carried out immediately after reduction; in cases* (*c*) *and* (*d*), *the solutions were stored for* 4 *days after reduction.*]



"*Reverse*" *Procedure.*[2]—The solvent action of hydrogen peroxide on vanadium and its compounds renders the volumetric determination of vanadium selective in the presence of some impurities naturally occurring in its ores. Vanadium pentoxide or ammonium metavanadate was dissolved in hydrogen peroxide, and the resulting yellow solution was

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[6] Sidgwick, "The Chemical Elements and Their Compounds," Oxford, 1951, Vol. II, p. 975.

acidified with concentrated sulphuric acid. Reduction to the blue vanadyl(IV) ion was quantitative within a few minutes. Detailed analytical results of the " reverse " procedure will be published elsewhere.

A similar approach to the reduction of quinquevalent vanadium with hydrogen peroxide was to prepare the solid ammonium diperoxyorthovanadate [7] and treat this with acid. In this case, hydrogen peroxide was not added externally but came from the peroxy-compound itself. Reduction to the blue vanadyl(IV) cation then occurred by way of the red monoperoxyvanadyl(V) cation.

EXPERIMENTAL

Solutions.—Vanadium(V) solution: prepared from " AnalaR " ammonium metavanadate. Vanadium(IV) solution: prepared by reducing the vanadium(V) solution with sulphur dioxide. Hydrogen peroxide: 100-vol. analytical reagent. Acids: 97% w/w sulphuric acid; 60% w/w " AnalaR " perchloric acid; 95% w/w " AnalaR " nitric acid, freed from nitrous oxides by boiling with urea. (We thank Mr. B. Manohin for suggesting this method.)

VO^{++}–VO_2^+ *and* H_2O_2–O_2 *Redox Systems*.—The vanadium solutions were M/50 in total vanadium, having an identical vanadium concentration throughout, and a 1 : 1 ratio $VO^{++} : VO_2^+$ The redox potentials were measured at 21° with platinum–calomel electrodes, a Cambridge pH meter being used (constant e.m.f. values were obtained more quickly in 12—24N-sulphuric acid solutions than in the more weakly acidic solutions).

The hydrogen peroxide solutions were M/10 and the electrodes used were oxygen–calomel. The oxygen pressure was adjusted with a Towers flowmeter to approx. 1 atm. The temperature was kept at 25°. A series carried out at 0° (to reduce possible decomposition of hydrogen peroxide), under otherwise identical conditions, gave a similar redox curve (see Table).

Variation in acid normality was achieved by adding calculated amounts of acid to each of the VO^{++}–VO_2^+ and H_2O_2 solutions. The corresponding molal activities were obtained [8] and are given in the Table.

Redox potentials of the H_2O_2–O_2 *system at* 0° *and* 25°.

H_2SO_4 (N)	Molal activity of H_2SO_4 [8]	Log_{10} activity of H_2SO_4	E.m.f. at 0° (mv)	E.m.f. at 25° (mv)
1·0	0·0807	−1·0931	523	542
1·5	0·104	−0·9832	534	552
2·0	0·126	−0·8988	537	561
3·0	0·192	−0·7167	546	568
4·0	0·271	−0·566	558	576
6·0	0·496	−0·3041	567	592
8·0	0·960	−0·0177	583	607
12·0	3·14	0·4964	589	628
16·0	9·80	0·9912	617	641
20·0	29·6	1·4711	—	679
24·0	86·8	1·9385	747	758

Effect of Acid Concentration.—The course of the titration was followed potentiometrically by means of a Mullard potentiometer unit, platinum and calomel electrodes being used. The solutions, which were M/20 in vanadium, were titrated with 3% hydrogen peroxide solution at 20°.

Effect of Nature of Acid.—The absorptiometric investigation was accomplished with a Hilger " Spekker " absorptiometer. As maximum absorption for the red-brown complex occurs at 450 mμ,[9] a No. 2 Kodak filter, having maximum transmittancy at 430 mμ, was employed. A 1 cm. cell was used throughout. The solutions were M/50 in vanadium and had a 25-fold excess of hydrogen peroxide.

" *Reverse* " *Procedure*.—Ammonium metavanadate (" AnalaR "), containing *ca.* 0·1 g. of

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[7] Kakabadse, Dr.-Ing. Thesis, Berlin, 1943.

[8] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 1958, p. 735.

[9] Davis and Bacon, *J. Soc. Chem. Ind.*, 1948, **316**; Wright and Mellon, *Ind. Eng. Chem., Analyt.*, 1937, **9**, 375.

vanadium, was dissolved in 5 ml. of hydrogen peroxide (100-vol.). Concentrated sulphuric acid was added slowly with constant shaking and cooling until the solution became bright blue. The solution was stored for 15 min., diluted with 200 ml. of distilled water, and titrated at *ca.* 80° with standard potassium permanganate. An analogous procedure was adopted in the presence of various added substances.

DISCUSSION

The reduction of quinquevalent vanadium with hydrogen peroxide in acid solution involves two stages: the instantly occurring peroxidation[10] of the pale yellow vanadyl(v) cation[3,11]

$$VO_2^+ + H_2O_2 = [OV(O{\cdot}O)]^+ + H_2O \quad \ldots\ldots\ldots\ldots (1)$$

followed by the relatively slow reduction[2] to the blue vanadyl(IV) cation:

$$2VO_2^+ + 2H^+ + H_2O_2 = 2VO^{2+} + 2H_2O + O_2 \quad \ldots\ldots\ldots (2)$$

Under weakly acid conditions, peroxidation predominates, *i.e.*, the equilibrium of reaction (1) lies far to the right. But as the difference in the redox potentials of the two systems involved increases with increasing hydrogen-ion concentration (Fig. 1), thus promoting the ease of reduction, a gradual withdrawal of VO_2^+ ions to satisfy reaction (2) occurs. In consequence, equilibrium (1) is now displaced to the left.

A similar explanation would hold for the " reverse " procedure: vanadium pentoxide dissolves in hydrogen peroxide as the bright yellow diperoxyorthovanadic acid:[10]

$$V_2O_5,3H_2O + 4H_2O_2 = 2[VO_2(O{\cdot}O)_2]^{3-} + 6H^+ + 4H_2O \quad \ldots\ldots (3)$$

On addition of hydrogen ions an equilibrium with the red-brown monoperoxyvanadyl(v) cation is established:[10]

$$[VO_2(O{\cdot}O)_2]^{3-} + 4H^+ = [OV(O{\cdot}O)]^+ + H_2O_2 + H_2O \quad \ldots\ldots\ldots (4)$$

the subsequent stages being identical with those shown in reactions (1) and (2).

The complexity of the vanadium-hydrogen peroxide system is well illustrated by optical density curves in Fig. 4. The maximum, occurring at about 2N-hydrogen-ion concentration, corresponds to optimum formation of the red monoperoxidised form; the decrease in optical density to the right of the maximum ($H^+ > 2N$) is due to the presence of the blue reduced form. As to be expected, this effect is displayed most markedly by the strongest acid used, *i.e.*, perchloric acid. On the other hand, the observed decrease in optical density to the left of the maximum ($H^+ < 2N$) is mainly due to an equilibrium between the red and the yellow peroxy-form of quinquevalent vanadium, and, according to equation (4), the yellow form will predominate in the presence of a weaker acid, *i.e.*, more readily with sulphuric acid than with perchloric acid. The position of the nitric acid curve in Fig. 4 may have been affected by the presence of excess of urea.

The apparent anomaly of the redox curve of the H_2O_2–O_2 system as regards the abrupt rise of the e.m.f. above 16N-sulphuric acid (Fig. 1) may be attributed to decomposition[12] or dehydration of hydrogen peroxide with formation of ozone.[13] Analytical results prove that reduction occurs more readily in 24N- than in 16N-sulphuric acid.

The dependence of the overall reduction reaction upon hydrogen peroxide and hydrogen-ion concentration (eqn. 2) is clearly shown by the horizontal displacement of the potentiometric curves in Fig. 2.

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[10] Jahr, " F.I.A.T. Review of German Science, 1939—1946," Part 3, p. 176; *Z. Elektrochem.*, 1941, **47**, 810.

[11] La Salle and Cobble, *J. Phys. Chem.*, 1955, **59**, 519.

[12] Roth and Shanley, *Ind. Eng. Chem.*, 1953, **45**, 2343.

[13] Arnold and Mentzel, *Ber.*, 1902, **35**, 2902.