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# The Mechanism of Redox-conversions of Tungstovanadophosphoric Heteropolyanions

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## Abstract

Tungstovanadophosphoric heteropolycomplexes $Na_xH_{3+n-x}PW_{12-n}V_nO_{40}$ can be used as reversible oxidants in homogeneous oxidation of organic compounds. In this work the dependence of their redox-properties on the vanadium content has been studied. Reduced forms of heteropolycomplexes with $n = 1$ and 2 were found to be not themselves reoxidized by dioxygen, while that with $n = 4$ was rapidly and completely oxidized even at 0 °C. The oxidation of the reduced heteropolycomplex with $n = 3$ also occurred but much more slowly. Evidence that four-electron reduction of dioxygen occurs in solutions of reduced heteropolycomplexes is presented.

All stages of the work were carried out using $^{31}P$ and $^{51}V$ NMR control.

## Introduction

Due to their redox-properties molybdovanadophosphoric heteropolycomplexes (P–Mo–V HPC) may be used as catalysts for oxidation of organic compounds [1]. HPC have rather high redox-potentials and their reduced forms can themselves be reoxidized with dioxygen by a multi-electron mechanism [2–4]. However mechanistic studies of such reactions are rather difficult to perform because of the dissociation and disproportionation of P–Mo–V HPC in solution [5, 6]. The exact compositon of the solution is often unknown, and it is difficult to find which of the variety of co-existing species is most active in reaction.

Oxidized P–W–V heteropolyanions (HPAs) are known to be not so labile as their molybdic analogs [6–8]. Therefore they can be used for studying the peculiarities of redox-conversions of HPAs. In the present work individual HPAs in the form of $Na_{3+n-x}H_xPW_{12-n}V_nO_{40}$ ($n$ = 1–4) (noted as $PW_{12-n}V_n$) and $PW_{10}V_2$ isomers as well have been obtained using $^{31}P$ and $^{51}V$ NMR monitoring. Conditions have been found for retaining chemical and isomeric compositions of the P–W–V HPAs during their reduction and reoxidation. This made it possible to study the mechanism of oxidation by dioxygen of the reduced P–W–V HPAs having definite compositions.

## Experimental

### *Preparations*

$PW_{11}V$ HPA was prepared as follows. Sodium metavanadate $NaVO_3 \cdot 2H_2O$ (1.58 g) was dissolved in water (100 ml) and added to a hot (90 °C) solution of sodium tungstate $Na_2WO_4 \cdot 2H_2O$ (36.6 g) in water (100 ml). Then sodium dihydrogen phosphate $NaH_2PO_4 \cdot 2H_2O$ (1.56 g) and aqueous $H_2SO_4$ (1:1, 15 ml) in water (50 ml) were quickly added to the solution so that the pH was 1. The resulting solution was heated at 90 °C for 1 h, the pH being kept at 1 by the addition of several drops of $H_2SO_4$ (1:1).

$PW_{10}V_2$ and $PW_9V_3$ HPAs were prepared in the same way at pH 2 and 5, respectively, by mixing stoichiometric amounts of the reagents.

Pure $PW_8V_4$ HPA was prepared in the form of its sodium salt as described in ref. 9. However it was recrystallized from aqueous solution with pH ~ 5 rather than from a 0.25 M $H_2SO_4$ solution [9], because the high acidity causes a change in the HPA composition.

The solutions obtained were examined by NMR. The contents of the individual anions and those of $PW_{10}V_2$ isomers were measured from integrals. The average error was ±10–15%. NMR peak assignments are given in Table I.

### *NMR and ESR Measurements*

$^{31}P$ (121.47 MHz) and $^{51}V$ (78.88 MHz) NMR spectra were taken on a Bruker CXP-300 spectrometer over the temperature range 293 to 345 K. The chemical shifts ($\delta$) are given relative to $H_3PO_4$ ($^{31}P$), $VOCl_3$ ($^{51}V$) and $H_2O$ ($^{17}O$). The downfield shift is taken as positive. ESR spectra were run on a Bruker ER-210 spectrometer at 9.7 GHs and 77 and 300 K. The concentration of $VO^{2+}$ was determined by comparing the spectrum intensity of the solution examined with that of the $VOSO_4$ solution

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TABLE I. $^{31}P$ and $^{51}V$ Chemical Shifts of P–W–V HPAs

| HPA | pH | $\delta\ ^{31}P \pm 0.1$ ppm | $\delta\ ^{51}V \pm 0.5$ ppm |
|---|---|---|---|
| $PW_{12}$ | | −15 | – |
| $PW_{11}V$ | 3 – −1 | −14.7 | −554 |
| $PW_{10}V_2$ | 6 – 1 | −13.91, −14.11, −14.20 | −555.5, −552, −545, −525 |
| $PW_9V_3$ | 7.5 – 3.5 | several peaks in the range −13 – −13.6 | −554, −551.5, −549.5, −545, −527.5, −525 |
| | 1 | −12.5 – −13.2 | −563, −560, −558, −556, −553 |
| $PW_8V_4$ | 8.5 – 7 | −12.3 – −12.9 | −550, −543, −523, −518 |
| | 1 | −11 – −12 | −573, −563, −559 |

with a known concentration. An average error was about 10%.

A careful voltammetric study of P–W–V HPAs was made earlier in ref. 9. In our case, an electrochemical procedure was used mainly for preparing reduced forms in a rather high concentration. This required a lot of electrolyses. Reduction and reoxidation of HPAs were carried out on a PI-50 potentiostat with Pt electrodes at room temperature. The solutions (40 $cm^3$) contained HPA (0.01–0.05 mol $dm^{-3}$), $Na_2SO_4$ (0.3 mol $dm^{-3}$) and $CH_3COOH$ (30 vol.%) at pH 1 to 4. HPAs were reduced under Ar at +0.1 V ($PW_{11}V$ and $PW_{10}V_2$) and 0.0 V ($PW_9V_3$ and $PW_8V_4$) and reoxidized at +0.8 V (with respect to the silver chloride electrode) in accordance with the results obtained in ref. 9. The working electrode in the form of a Pt wire spiral had an area of about 10 $cm^2$. The electrode compartments were separated by a ground glass stopper. Solutions were stirred with a magnetic stirrer. The time of the reduction and oxidation cycle was about 6 h. On reducing HPAs up to the necessary reduction degree electrolysis was terminated, and the potential of the resulting solution (*E*) was measured with the Pt and silver chloride electrodes. The degree of reduction was calculated as the mean number of electrons per molecule

$$m = \frac{\sum_{i=0}^{n} i\,[PW_{12-n}V_i{}^{IV}V_{n-i}{}^{V}]}{[PW_{12-n}V_n]_0}$$

and was checked by titration with $KMnO_4$.

HPAs were also reduced with carbon monoxide in the presence of $PdSO_4$ ($10^{-4}$ mol $dm^{-3}$) in a static volumetric system with a shaked reactor. The gas phase was circulated through 10% NaOH to absorb the $CO_2$. The reaction time was 30–60 min.

*Kinetic Studies*

Kinetics of HPA oxidation was studied by measuring $O_2$ absorption as described in ref. 2. Reactions rates were found from the parts of the kinetic curves corresponding to definite reduction degrees of HPAs. The $VOSO_4$ oxidation kinetics in the presence of HPAs were studied in the same way. Reactions were carried out at the concentrations of HPA and $VOSO_4$ 0.006–0.05 and 0.05–0.2 mol $dm^{-3}$ respectively in acetate buffer (40% $CH_3COOH$). The calculated amount of HPA was added to an acetic solution of $VOSO_4$ and the pH was adjusted to 2.5–4.5 by adding NaOH solution.

## Results and Discussion

### *I. Identification and Redox-Properties of HPAs*

As revealed by NMR [10], P–Mo–V and P–W–V HPAs as normally prepared [11–13] are complex mixtures of HPAs with various contents of vanadium. The composition of P–W–V HPAs has been shown recently [14] to be largely dependent on the solution acidity during their synthesis. However, once produced, they retain their composition over a rather wide pH range. We have found the conditions for preparing individual $PW_{12-n}V_n$ ($n$ = 1–4) with a yield of about 90% (Fig. 1).

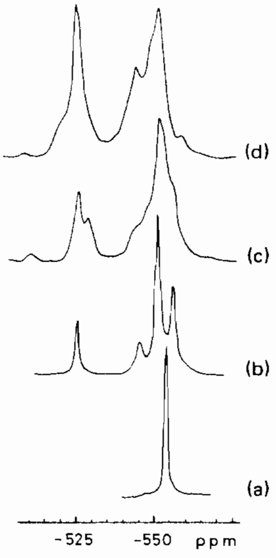

Fig. 1. $^{51}V$ spectra of non-protonated HPAs: (a) $PW_{11}V$ (pH 1); (b) $PW_{10}V_2$ (pH 2); (c) $PW_9V_3$ (pH 5); (d) $PW_8V_4$ (pH 7.6); [HPC] ≈ 0.1 mol $dm^{-3}$.

The solutions of $PW_{11}V_1$, $PW_{10}V_2$ and $PW_9V_3$ obtained as described above can be used without further purification since they do not contain any initial reagents. They can also be crystallized in the form of their acid sodium salts or extracted with ether in the form of acids. However, the latter procedure is not suitable for preparing $PW_9V_3$ and $PW_8V_4$ since they are contaminated with $PW_{10}V_2$ and $PW_{11}V$ admixtures during extraction because of their partial degradation in strong acid solutions.

Assignment of $^{31}P$ and $^{51}V$ NMR spectra of $PW_{12-n}V_n$ (Table I) was discussed elsewhere [15].

The substituting of W atoms in $PW_{12}$ by V atoms influences the δ-value of the P atom. The δ-value depends on both the number of V atoms and their arrangement in the anion. Mixed HPAs with the same number but a different arrangement of V atoms were called positional stereoisomers [16]. At present such isomers can only be observed by NMR when in solution.

While the increase in the number of V atoms gives a monotonous downfield shift of $^{31}P$ NMR of about 0.5–1 ppm per V atom, the different arrangement has a considerably less effect within these intervals. As a result, the groups of peaks arising from anions with different *n* do not practically overlap with each other which makes it possible to evaluate the relative content of an individual HPA from the integral intensity of its group of peaks.

In the case of $PW_{10}V_2$ it is also possible to evaluate the contents of its individual isomers using $^{51}V$ NMR provided the solution studied does not contain large amounts of $PW_{11}V$ and $PW_9V_3$ admixtures. The theoretical number of the $PW_{10}V_2$ isomers is 5 [16]. There are five signals in its $^{51}V$ NMR spectrum (two of them overlapping) and three peaks in the $^{31}P$ spectrum (Table I, Fig. 2a). Their intensity ratios were not constant for various specimens but were dependent on the conditions of $PW_{10}V_2$ preparation.

Earlier the −525 peak was supposed [15, 17] to arise from isopolycomplex $VW_5O_{19}^{3-}$ present as an admixture which has nearly the same δ-value (−522). However on intentionally adding this complex to the solution of $PW_{10}V_2$ (at pH 2) we observed both peaks separately. Moreover we have found that the intensity of the $^{31}P$ peak at −13.91 correlates with that of the $^{51}V$ peak at −525 only, thus showing that they both arise from the same complex. This complex was then concluded to be one of the $PW_{10}V_2$ isomers (noted as **1**). The four other isomers (noted as **2**, **3** etc. according to the order of increasing their $^{51}V$ δ-values) are observed by two $^{31}P$ signals at $\delta = -14.11$ and $-14.20$.

On comparing $^{51}V$ NMR spectra of $PW_{12-n}V_n$ with different *n* (Fig. 1) it is natural to suppose that the $PW_{10}V_2$ peaks at the δ values −552 to −556, very similar to that of the $PW_{11}V$ peak (−554), arise from the three isomers each containing non-adjacent V atoms, while the −545 and −525 peaks arise from the isomers with adjacent V atoms. On the other hand, the $^{31}P$ peak of the **1** is shifted markedly relative to the others. It allows us to conclude that **1** contains two edge-shared $VO_6$ octahedra because it is the only case when both V atoms are arranged in the same $M_3O_{13}$ subunit of the Keggin structure and are linked to the $PO_4$ tetrahedron by the same O atom. This may result in the strongest deformation of the tetrahedron and the most downfield $^{31}P$ NMR shift compared to the four other cases including the second isomer with adjacent V atoms, where two V atoms are arranged in different $M_3O_{13}$ groups and linked to $PO_4$ by two different O atoms. We, therefore, assign the −525 and −545 $^{51}V$ resonances to the isomers containing edge- and corner-shared $VO_6$ octahedra respectively.

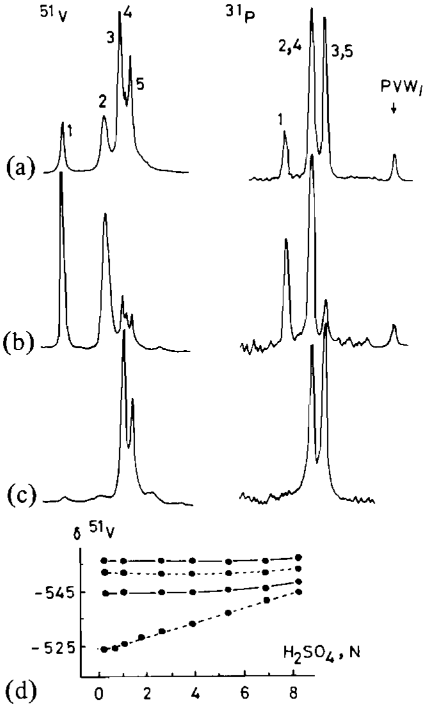

Fig. 2. NMR spectra of $PW_{10}V_2$ (a) and its fractions extracted from 5 N (b) and 8 N (c) solutions of $H_2SO_4$; (d) the pH dependence of the $^{51}V$ δ-values for different isomers.

Due to the increasing of the number of isomers for $PW_9V_3$ and $PW_8V_4$, their $^{51}V$ NMR spectra are more complex and contain more numerous overlapping peaks, the δ-values depending upon solution acidity [15]. The unprotonated $PW_9V_3$ and $PW_8V_4$ anions have resonances at closely similar $^{51}V$ δ-values as $PW_{10}V_2$, *i.e.* in the region of non-adjacent (−550), corner- (−543) and edge-shared (−525) $VO_6$ octahedra (Table I, Fig. 1).

$^{51}V$ NMR resonances of polyanions containing vanadium are known to shift highfield on protonation [15, 17]. Therefore, the pH range of protonation of various species can be found by studying their $^{51}$V NMR on acidification of a solution. The $PW_{10}V_2$ isomer **1** differs from the other four in its ability to accept a proton (Fig. 2d). As revealed by $^{51}$V and $^{17}$O NMR, it begins to accept a proton first (at $pH \leqslant 1$). the proton being bound to the O atom in the bridge V–O–V. The isomer **2** accepts a proton in more acidic media (~4 N $H_2SO_4$), the three isomers with non-adjacent V atoms resist protonation until 5–6 N $H_2SO_4$.

Of special interest is the fact that when solution acidity is gradually increasing from 4 to 8 N $H_2SO_4$, the isomers form etherates successively in accordance with their ability to accept a proton (and with the sequence of their $^{51}$V resonances as well). The first fraction extracted at 4–5.5 N $H_2SO_4$ contains mainly both isomers (**1** and **2**) with adjacent V atoms, while the fifth fraction (at 8 N $H_2SO_4$) contains only isomers **4** and **5**. This shows that with more highly charged HPAs ($n \geqslant 2$) protonation aids in forming their etherate complexes which may be considered as ionic associates between HPAs and protonated ether molecules (like HPA complexes with high molecular amines [18]).

For comparing oxidizing abilities of the different $PW_{10}V_2$ isomers the potential values of their electrochemical reduction, obtained at the same conditions, were used. At pH 3 in 30% $CH_3COOH$ the reduction of the first $PW_{10}V_2$ fraction begins to occur at the more positive potential (+0.6 V) than that of the fifth fraction (+0.5 V). Therefore, on reducing the $PW_{10}V_2$ solution the −525 and −545 resonances disappear first. The higher redox-potential of the isomers **1** and **2** appears to be due to the stabilizing effect of protonation of reduced forms of HPA. It is also possible that V atoms are more highly charged in these isomers than in the others. At pH 1 to 3 a stepwise reduction of the V atoms in $PW_{10}V_2$ occurs (Fig. 3). At $m = 1$ no $^{51}$V NMR signals of $PW_{10}V_2$ were observed indicating that only the one-electron reduced form was present in solution.

At the same reduction degree the potentials of solutions of $PW_{12-n}V_n$ decrease according to the sequence $PW_{11}V > PW_{10}V_2 > PW_9V_3 \approx PW_8V_4$ (Fig. 3). The one- and two-electron potentials of $PW_9V_3$ and $PW_8V_4$ differ insignificantly (Fig. 3, curves 3 and 4), which allows the coexistence of anions with different reduction degrees. At $m \leqslant 1$ the concentrations of nonreduced $PW_9V_3$ and $PW_8V_4$ as measured by $^{51}$V NMR were about 10% higher than those calculated using equation

$$[HPA - V_n{}^V] = [HPA]_0 - [HPA - V^{IV} - V_{n-1}{}^V]$$

Hence, anions containing several $V^{IV}$ atoms are present even at low reduction degrees of HPCs.

Reduced $PW_{12-n}V_n$ have the same absorption bands (12 000–12 500, weak; 15 000–15 500; 19 000–20 000; 24 000–25 000 cm$^{-1}$) that are typical for reduced P–W–V anions [19, 20]. There is also an additional band at about 11 000 cm$^{-1}$ in the spectra of partially reduced $PW_9V_3$ and $PW_8V_4$ which may be due to the V(IV) → V(V) charge-transfer transition.

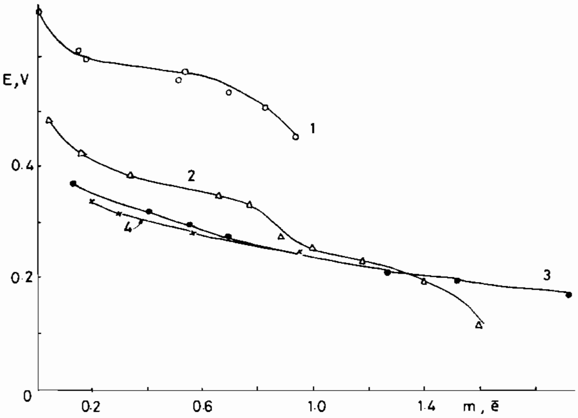

Fig. 3. Potentials of HPCs solutions (*vs.* silver chloride electrode) as a function of their reduction degree ($m$): (1) $PW_{11}V$; (2) $PW_{10}V_2$; (3), $PW_9V_3$; (4) $PW_8V_4$; [HPC] = 0.025 mol dm$^{-3}$, pH 3, 30% $CH_3COOH$, [$Na_2SO_4$] = 0.3 mol dm$^{-3}$, 20 °C.

The optical density at 20 000 cm$^{-1}$ of the $PW_9V_3$ and $PW_8V_4$ reduced solutions decreases to some extent on storing under argon. This is accompanied by the appearance of free vanadyl ions, $VO^{2+}$ (*i.e.* not included in HPA), which may be quantitatively examined by ESR at $pH \leqslant 4$ in 40% $CH_3COOH$ ($g_0 = 1.965$, $a = 105 \times 10^{-4}$ cm$^{-1}$). After storing reduced solutions under argon for 24 h the amount of free $VO^{2+}$ ions was about 3 and 30% of the overall V(IV) content for $PW_9V_3$ and $PW_8V_4$ respectively but tended to decrease as the solution acidity decreased (Table II). However, immediately after the rapid (20–30 min) reduction of these HPAs with carbon monoxide there was no free V(IV) in the solution.

The absorption spectra of the reduced $PW_{11}V$ and $PW_{10}V_2$ solutions did not change on storing over the pH range 1 to 4, and no free $VO^{2+}$ ions were observed. After reduction and electrochemical reoxidation $PW_{11}V$ and $PW_{10}V_2$ retain their chemical and isomeric (for $PW_{10}V_2$) composition. After the rapid reduction with CO and reoxidation with $O_2$ at pH 3 to 4 the composition of $PW_9V_3$ and $PW_8V_4$ also remained unchanged. When reoxidized after storing under argon for 24 h $PW_8V_4$ solutions contained $PW_9V_3$ and hydrophosphate anions as admixtures. In $PW_9V_3$ solutions under the same conditions the admixutre of $PW_{10}V_2$ was formed. The amount of HPA with a lower content of V in the reoxidized $PW_8V_4$ and $PW_9V_3$ solutions is correlated with the amount of free V(IV) in their reduced solutions (Table II).

TABLE II. The pH Dependence of the Free V(IV) Proportion in the Reduced Solutions ($[HPC]_0 = 0.025$ mol dm$^{-3}$) and the contents of different $PW_{12-n}V_n$ (in %) in them when reoxidized after storing under argon for 24 h ($[HPC]_0 = 0.05$ mol dm$^{-3}$): $m = 2$ ($PW_9V_3$) and 2.5 ($PW_8V_4$) in 40% $CH_3COOH$ at 20 °C

| Initial composition | pH | Reduced solutions, proportion of free $VO^{2+}$ (%) | Reoxidized solutions, content of HPA (%) | | |
|---|---|---|---|---|---|
| | | | $PW_8V_4$ | $PW_9V_3$ | $PW_{10}V_2$ |
| $PW_9V_3$ | 2.5 | 3.0 | | 85 | 15 |
| | 3.05 | 2.5 | | 90 (85)[a] | 10 |
| | 3.7 | 1.0 | | 100 | 0 |
| | 4.2 | 1 | | 100 | 0 |
| $PW_8V_4$ | 1.1 | 65 | – | – | |
| | 2.3 | 30 | 55 | 45 | |
| | 3.15 | 15 | 65 (75)[b] | 35 | |
| | 3.85 | 10 | 70 | 30 | |
| | 4.1 | 5 | 75 | 25 | |

[a] The reduced solution was stored under argon for 30 days and then reoxidized. [b] The solution was reoxidized after being reduced electrochemically for 5 h.

Thus, at pH 1 to 4 the reduced $PW_8V_4$ and, to a lesser extent, $PW_9V_3$ anions dissociate slowly with the removing of $VO^{2+}$ ions and formation of 1:12 HPAs with the lower content of V, according to eqns. (1) and (2)

$$PW_8V_2{}^{V}V_2{}^{IV} \rightleftharpoons [PW_8V_2{}^{V}V^{IV}] + V(IV) \quad (1)$$

$$9[PW_8V_2{}^{V}V^{IV}] \rightleftharpoons 8PW_9V_2{}^{V}V^{IV} + P(V) + 2V(V) + V(IV) \quad (2)$$

The low rate of such conversions shows that the chemical exchange with metal ions between reduced $PW_{12-n}V_n$ and the solution is rather slow which makes it possible to study the mechanisms of the electron transfer reactions with the participation of these anions.

## *II. Oxidation of P–W–V Heteropolyanions with Dioxygen*

Reduced $PMo_{12-n}V_n$ ($n = 2$–6) HPCs were shown to be all oxidized by dioxygen with comparable rates [21]. It was concluded from comparing kinetic dependences for HPCs with different $n$ that the 4-electron reduction of the $O_2$ molecule, coordinated by HPC, is most rapid [2–4]. The following rapid reactions may provide the formation of reduced species with the necessary number of V(IV) atoms: (1) electron transfer between reduced HPAs; (2) disproportionation of HPAs producing species with higher than the initial number of V atoms; (3) association of HPAs and free $VO^{2+}$ ions. To distinguish the above possibilities, it is very important to study species with a definite composition which remains unchanged during redox-conversions, as is the case with $PW_{12-n}V_n$.

$PW_{11}V^{IV}$ and $PW_{10}V_2{}^{IV}$ anions themselves were found not to be oxidized with dioxygen. Immediately after reduction with CO, $PW_8V_4$ was very rapidly and completely oxidized with $O_2$. Oxidation of reduced $PW_9V_3$ was much slower at the same $m$ (Fig. 4). The rate of oxidation of reduced $PW_8V_4$ was so high that it could be measured accurately only at 0 °C and low degrees of reduction. The rate is proportional to the $O_2$ concentration (Fig. 5, curve 1). This shows that the reduction of $O_2$ with the reduced HPA is the rate-determining step of the reaction, while the equilibrium of the electron exchange between HPAs producing species with the necessary number of V(IV) atoms is reached rapidly.

The dependence of the $PW_9V_m{}^{IV}V_{3-m}{}^{V}$ oxidation rate upon the $O_2$ concentration is quite different (Fig. 5, curve 2). In the range where the rate is

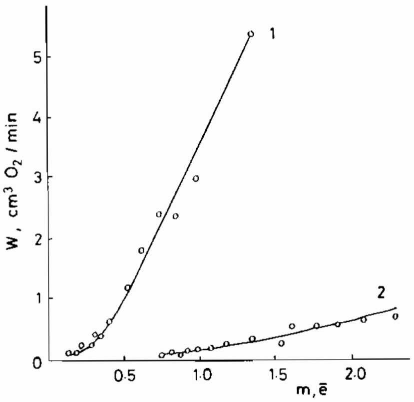

Fig. 4. Rates of oxidation of HPAs by dioxygen as functions of their reduction degrees: (1) $[PW_9V_3] = 0.05$ mol dm$^{-3}$, pH 3.45, 45 °C; (2) $[PW_8V_4] = 0.05$ mol dm$^{-3}$, pH 3.0, 0 °C; 40% $CH_3COOH$, V = 10 cm$^3$.

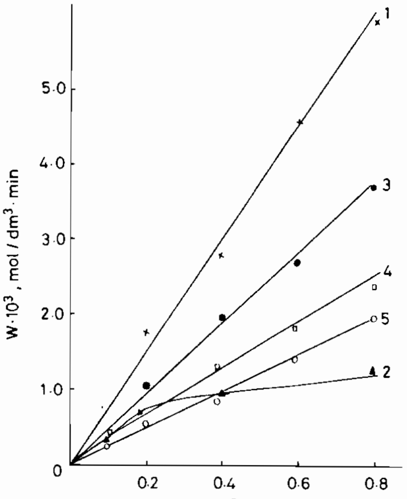

Fig. 5. Dependence of the rate of oxidation of reduced HPAs (1, 2) and of $VOSO_4$ in the presence of HPAs (3–5) on the $O_2$ concentration: (1) $[PW_8V_4] = 0.05$ mol dm$^{-3}$, $m = 0.7$, pH 3.0, 0 °C; (2) $[PW_9V_3] = 0.05$ mol dm$^{-3}$, $m = 2.4$, pH 3.6, 35 °C; (3) $[PW_9V_3] = 0.035$ mol dm$^{-3}$, $[VOSO_4] = 0.2$ mol dm$^{-3}$, pH 3.0, 25 °C; (4) and (5) $[PW_{10}V_2] = 0.025$ mol dm$^{-3}$, pH 3.65, $[VOSO_4] = 0.2$ mol dm$^{-3}$, 25 °C, the rate was measured in the initial parts of kinetic curves (4) and at 20% oxidation of $VOSO_4$ (5).

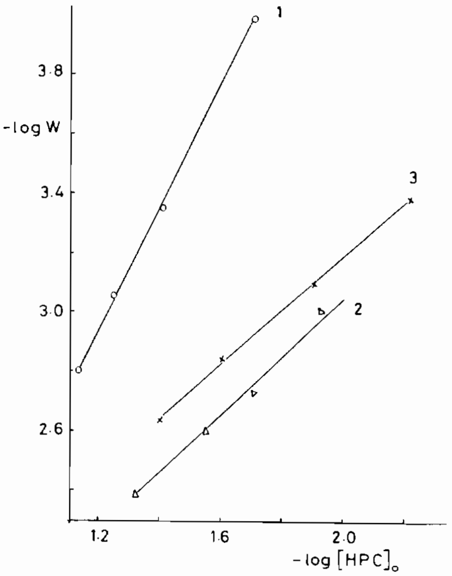

Fig. 6. A plot of logarithm of the rate of oxidation reduced $PW_9V_3$ (1) and $VOSO_4$ in the presence of HPAs (2, 3) *vs.* logarithm of the total HPA concentration: (1) $PW_9V_3$, pH 3.8, $m = 2.4$, 35 °C; (2) $PW_9V_3$, $[VOSO_4] = 0.2$ mol dm$^{-3}$, pH 3.0, 25 °C; (3) $PW_{11}V$, pH 3.0, 25 °C; $[O_2] = 0.8 \times 10^{-3}$ mol dm$^{-3}$; 40% $CH_3COOH$.

independent of the $O_2$ concentration the reaction order is 2 with respect to the overall $PW_9V_3$ concentration (Fig. 6, curve 1). At $m = 1$ and 2.4 the activation energy is $E_a = 74$ kJ mol$^{-1}$ in the interval 293 to 318 K. This appears to show that the formation of species from two $PW_9V_3$ anions is the rate-determining step in this case.

When the oxidation of $PW_8V_4$ and $PW_9V_3$ was carried out in the presence of isopropanol (2 mol dm$^{-3}$) to discover OH radicals in solution [2] the yield of acetone was less than 10% of the amount of the oxidized V(IV). This shows that the 3-electron reduction of the $O_2$ molecule which should produce OH radicals practically does not occur.

Taking into account similar structures and close potentials of both anions the difference in their reactivity with respect to $O_2$ should be ascribed to the different number of V atoms in them. To be rapidly reoxidized, the HPA must contain more than three V(IV) ions. This conclusion was supported by the fact that the addition of $VO^{2+}$ to the $PW_9V_3$ solution gave a substantial improvement in the rate of oxidation, the activation energy lowering down to 46 kJ mol$^{-1}$ and the reaction order with respect to oxygen (Fig. 5, curve 3) and HPC (Fig. 6, curve 2) becoming equal to 1. The reaction rate is now limited by the interaction between HPAs and $O_2$ molecules as in the case of $PW_8V_4$ oxidation.

Such a change in the oxidation kinetics may be due to the formation of the complexes between HPAs and $VO^{2+}$ leading to the increase in the concentration of the species containing four V atoms. The persistence of the $PW_9V_3$ composition after the complete oxidation of V(IV) shows that such complexes are of the outer sphere type.

Since reduced $PW_{11}V$ and $PW_{10}V_2$ are not labile and are not themselves oxidized with $O_2$ they can be used for studying the role of the HPA–$VO^{2+}$ complexes in the reduction of dioxygen. The rapid oxidation of $VOSO_4$ was observed in the presence of unreduced $PW_{11}V$ and $PW_{10}V_2$ as well as $PW_9V_3$. The reaction was carried out at the HPA concentrations 0.006 to 0.05 mol dm$^{-3}$ in 40% $CH_3COOH$ at pH 2 to 4. As revealed by NMR all V(IV) was oxidized to V(V) in the form of decavanadate, $H_xV_{10}O_{28}{}^{-6+x}$ ($\delta\,{}^{51}V$ −423, −503, −521), the composition of the HPAs being unchanged in spite of the large excess of free vanadium in the solutions.

In the first stage of the reaction the rapid reduction of HPA with vanadyl ions occurs, the electrons being transferred to the V(V) atoms of HPA. The degree of reduction of HPA at different $[VOSO_4]/[HPA]$ ratios was estimated from the following equation

$$E_{HPA} + 0.059 \log \frac{[HPA]_0 - x}{x} = E_{V(V)/V(IV)} + 0.059 \log \frac{x}{[VOSO_4]_0 - x}$$

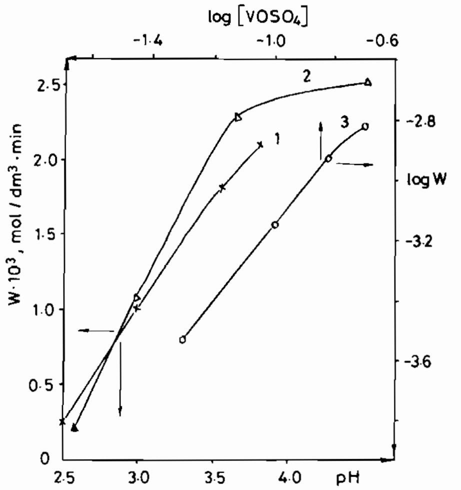

Fig. 7. The pH dependence of the rate of oxidation of $VOSO_4$ in the presence of HPAs (1, 2) and a plot of log W *vs.* $\log[VOSO_4]$ (3): (1) $[PW_{11}V] = 0.025$ mol $dm^{-3}$, $[VOSO_4] = 0.2$ mol $dm^{-3}$; (2) $[PW_{10}V_2] = 0.025$ mol $dm^{-3}$, $[VOSO_4] = 0.15$ mol $dm^{-3}$; $[O_2] = 0.6 \times 10^{-3}$ mol $dm^{-3}$; (3) $[PW_{11}V] = 0.025$ mol $dm^{-3}$, $[O_2] = 0.8 \times 10^{-3}$ mol $dm^{-3}$, pH 3.0; 40% $CH_3COOH$, 25 °C.

where $x$ is the equilibrium concentration of the reduced HPA, $E_{HPA}$ is the potential of the one-electron reduction ($m = 0.5$) (Fig. 3), $E_{V(V)/V(IV)}$ is the potential of vanadium under the same conditions and is equal to 0.435 V relative to a silver chloride electrode. $PW_{11}V^V$ was found to be completely reduced to $PW_{11}V^{IV}$ under the conditions studied while $PW_{10}V_2$ and $PW_9V_3$ were only partly reduced ($m < 0.5$). Their degree of reduction increases with an increase in the $VOSO_4$ concentration. The persistence of the composition of HPAs after complete oxidation of $VO^{2+}$ shows that the reaction occurs without substituting W(VI) atoms by V(IV) atoms. The catalytic oxidation of $VO^{2+}$ in the presence of P–W–V HPAs is therefore caused only by the formation of the HPA–$VO^{2+}$ complexes. Previously [10] such complexes were observed by ESR in $PV^{IV}Mo_{11} + VO^{2+}$ solutions at pH 2 to 4, their concentration increasing with pH. In the complex the $VO^{2+}$ ions may be attached to HPA in the same manner as the $VO^{3+}$ subunits in $PV_{14}O_{42}{}^{9-}$ [22]. The number of bound $VO^{2+}$ ions may increase with increasing HPA charge.

The rate of oxidation of $VOSO_4$, measured from initial parts of the kinetic curves and at the 20% conversion, is proportional to the concentration of $O_2$ (Fig. 5, curves 4, 5). The increase in the rate with pH can be explained by the increase in the concentration of the active complexes (Fig. 7, curves 1, 2). In the presence of $PW_{11}V$ the rate is proportional to the HPA concentration (Fig. 6, curve 3) and reaction order is 1.2 with respect to the $VOSO_4$ concentration (Fig. 7, curve 3). The kinetic dependences of $VOSO_4$ oxidation in the presence of $PW_{12-n}V_n$ are closely similar for $n = 1$–3 (Table III). The temperature coefficients of the reaction, as calculated from the plot of log W against $1/T$ in the range 273 to 298 K, are very similar as well (Table III). The kinetic dependences show the reduction of the $O_2$ molecules with the HPA–$VO^{2+}$ complexes to be the rate-determining step of the reaction.

The activation of the $O_2$ molecule is possible, provided HPA contains at least one V(IV) atom. HPAs without vanadium, for example $SiW_{12}O_{40}{}^{4-}$, do not catalyze the oxidation of $VOSO_4$ although they form complexes with $VO^{2+}$ ions [23]. The reaction order with respect to $VO^{2+}$ ions (>1) and the fact that $PW_{10}V_2{}^{IV}$ cannot be reoxidized with $O_2$ indicate that the active complexes contain more than two V(IV) atoms. However, from the kinetic data only it is impossible to find the exact number of bound $VO^{2+}$ ions. In the presence of isopropanol merely a small amount of acetone was produced (Table III).

This shows that the V(IV) ions of the complex rapidly reduce the coordinated $O_2$ to $H_2O$, only a small part of the products (*i.e.* radicals) of its three-electron reduction going out of the complex.

TABLE III. Kinetic Dependences of Oxidation of Reduced $PW_{12-n}V_nO_{40}{}^{(3+n)-}$

| Reaction | Effective orders with respect to | | | $m, \bar{e}$ | $E_a$ (kJ $mol^{-1}$) | Yield of acetone in % of amount of oxidized V(IV) |
|---|---|---|---|---|---|---|
| | HPA | $O_2$ | $VOSO_4$ | | | |
| $PW_{11}V + VOSO_4 + O_2$ | 1 | 1 | 1.2 | 1 | 39 | 10 |
| $PW_{10}V_2 + VOSO_4 + O_2$ | 0.8[a] | 1 | 1.3[b] | 0.4–0.7 | 41 | 9 |
| $PW_9V_3 + VOSO_4 + O_2$ | 1[a] | 1 | 1[b] | 0.2–0.4 | 46 | 4 |
| $PW_9V_3 + O_2$ | 2[a] | 1 | – | 2.4–0.7 | 74 | 7 |

[a] An order with respect to the overall concentration of HPA. [b] An order determined with respect to the initial concentration of $VOSO_4$.

Thus, species containing HPA and two $VO^{2+}$ ions are to some extent oxidized with $O_2$. However, the complex $PW_{11}V{-}3VO^{2+}$ seems to be the most active.

The data obtained makes it possible to describe the reaction in the presence of $PW_{11}V$ as follows

$$PW_{11}V^{V}O_{40}{}^{4-} + VO^{2+} + H_2O \longrightarrow PW_{11}V^{IV}O_{40}{}^{5-} + VO_2{}^{+} + 2H^{+}\ \text{(rapidly)} \qquad (3a)$$

$$PW_{11}V^{IV}O_{40}{}^{5-} + VO^{2+} \overset{K_1}{\rightleftharpoons} [PW_{11}V^{IV}O_{40}\cdot VO]^{3-} \quad (I) \qquad (4)$$

$$I + VO^{2+} \overset{K_2}{\rightleftharpoons} [PW_{11}V^{IV}O_{40}\cdot 2VO]^{-} \quad (II) \qquad (5)$$

$$II + VO^{2+} \overset{K_3}{\rightleftharpoons} [PW_{11}V^{IV}O_{40}\cdot 3VO]^{+} \quad (III) \qquad (6)$$

$$III + O_2 \overset{K_0}{\rightleftharpoons} [PW_{11}V^{V}O_{40}\cdot(O_2{}^{-})\cdot 3VO]^{+} \quad (IV) \qquad (7)$$

$$IV + H_2O \xrightarrow{k} PW_{11}V^{V}O_{40}{}^{4-} + 3VO_2{}^{+} + 2H^{+} \qquad (8)$$

Equations (7′) and (8′) can be written for the reaction of the complex **II** with $O_2$. Without isopropanol OH radicals will oxidize $VO^{2+}$ ions [24]:

$$II + O_2 \overset{K_0'}{\rightleftharpoons} [PW_{11}V^{V}O_{40}\cdot(O_2{}^{-})\cdot 2VO]^{-} \quad (V) \qquad (7')$$

$$V + H_2O \xrightarrow{k'} PW_{11}V^{V}O_{40}{}^{4-} + 2VO_2{}^{+} + OH + H^{+} \qquad (8')$$

$$VO^{2+} + OH \longrightarrow VO_2{}^{+} + H^{+} \qquad (9)$$

As a result, the following rate equation can be derived

$$W = \frac{kK_1K_2K_3K_0[O_2][HPA]_0[VO^{2+}]^3}{1 + K_1[VO^{2+}] + K_1K_2[VO^{2+}]^2 + K_1K_2K_3[VO^{2+}]^3 + K_1K_2K_3K_0[O_2][VO^{2+}]^3} + \frac{k'K_1K_2K_0'[O_2][HPA]_0[VO^{2+}]^2}{1 + K_1[VO^{2+}] + K_1K_2[VO^{2+}]^2 + K_1K_2K_0'[O_2][VO^{2+}]^2} \qquad (10)$$

The last terms of both denominators are small compared with the others because of the low stability of the $HPA\cdot O_2$ complexes, and the equilibrium constants ($K_i$) of the $HPA\cdot iVO^{2+}$ complexes are in the range 10 to 20 $mol^{-1}\ dm^3$ [23]. Taking this into account we consider the formula (10) to be consistent with the experimental data.

Oxidation of $VOSO_4$ in the presence of $PW_{10}V_2$ and $PW_9V_3$ occurs in the same manner, but there is an equilibrium (3b) instead of the rapid stage (3a):

$$PW_{10}V_2{}^{V}O_{40}{}^{5-} + VO^{2+} + H_2O \rightleftharpoons PW_{10}V^{V}V^{IV}O_{40}{}^{6-} + VO_2{}^{+} + 2H^{+} \qquad (3b)$$

It is shifted to the right with an increase in the pH and the concentration of HPA and $VO^{2+}$.

The data obtained have completely confirmed our earlier conclusion [21] that the oxidation of reduced $PM_{12-n}V_n$ (M = Mo, W) occurs mainly through species containing four V(IV) ions. The rapid reactions of electron exchange and formation of the $HPA{-}VO^{2+}$ complexes (when $VO^{2+}$ ions are present) precede the oxidation of HPAs with dioxygen.

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