Reactivity of the Tungstovanadophosphate Heteropolyanions

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Abstract

The kinetics of redox reactions of tungstovanadophosphate heteropolyanions (HPA) of Keggin structure having different number and arrangement of V atoms, with Fe^{2+}, VO^{2+}, VO_2^+ ions, HPA itself and N_2H_4, H_2S molecules have been studied. The relation between protonoacceptor ability, redox properties and reactivity of individual HPAs and also different position isomers of HPA have been shown. The reactions studied proceed via formation of intermediate complexes of HPA and oxidized substances; the data concerning the nature of such complexes have been obtained.

Introduction

Application of P–M–V (M = Mo, W) heteropolycomplexes (HPC) of the Keggin structure in catalytic oxidation reactions [1] leads naturally to the question about the effect of the number and the arrangement of V atoms in the HPCs on their activity. To study the problem, $Na_xH_{3+n-x}PW_{12-n}V_nO_{40}$ (n = 1–4) can be used as model compounds since the individual heteropolyanions (HPA) with a definite 'n' [2], and also different position isomers [3, 4] have been obtained. P–W–V HPCs were shown to retain their chemical and isomeric composition upon redox cycling due to the low lability of the metal–oxygen sphere [5].

The aim of the present work was to study the reactivity of individual $PW_{12-n}V_nO_{40}^{-(3+n)}$ (n = 1–4) (noted as $PW_{12-n}V_n$) HPAs as well as some of their isomers toward oxidation reactions. Those were $PW_{10}V_2$ isomers (two) with adjacent V atoms and isomers (three) with isolated V atoms [4] and the α-1,2,3-PW_9V_3 isomer where V atoms are located in the three adjacent corner-shared MO_6 octahedra [3].

Reduced P–W–V HPAs [6], Fe(II) [7] and VO^{2+} [8] ions, N_2H_4 and H_2S molecules were chosen as reducing agents (Table 1). Reduced HPA, Fe(II) and VO^{2+} ions appear to be one-electron agents which are common in solutions of HPA catalysts [9]. N_2H_4 and H_2S require the transfer of several electrons for their oxidation to occur, while HPA containing several V atoms are potential multielectron agents. Recently, a four-electron mechanism of reduction of O_2 with heteropolyblues [5] and a two-electron mechanism of hydrogen evolution from water by reduced PW_{12} and SiW_{12} [10] have been shown. The kinetics of oxidation of the substances mentioned above was studied earlier in solutions of P–Mo–V HPAs, containing equilibrium mixtures of HPAs of different compositions and the V(V) and Mo(VI) oxoions [11–14]. The study of reactions (3), (5), (6) allows one to differentiate the reactivity of HPA and free ions of V(V) and Mo(VI). Thus, to solve these problems, the main results on kinetics of reactions (1)–(4) [6–8] and also of reactions (5), (6) are considered.

TABLE 1. HPA reactions: [HPA] = 10^{-3}–10^{-1}, [red] = 10^{-3}–10^{-1} M, pH 1 ÷ 5, 20 ± 1 °C

No.	Reaction	Characteristic reaction time
(1)	$\alpha\text{-1,2,3-}PW_9V^V_2V^{IV} + PW_{11}V^V \longrightarrow \alpha\text{-1,2,3-}PW_9V^V_3 + PW_{11}V^{IV}$	~10 s
(2)	$PW_{10}V^VV^{IV} + \alpha\text{-1,2,3-}PW_9V^V_3 \longrightarrow PW_{10}V^V_2 + \alpha\text{-1,2,3-}PW_9V^V_2V^{IV}$	~10 s
(3)	$Fe^{II} + PW_{12-n}V^V_n \rightleftharpoons Fe^{III} + PW_{12-n}V^V_{n-1}V^{IV}$	0.01–0.1 s
(4)	$VO^{2+} + PW_{12-n}V^V_n + H_2O \rightleftharpoons VO_2^+ + 2H^+ + PW_{12-n}V^V_{n-1}V^{IV}$	1–200 s
(5)	$N_2H_4 + 4PW_{12-n}V^V_n \longrightarrow N_2 + 4H^+ + 4PW_{12-n}V^V_{n-1}V^{IV}$	5–20 h
(6)	$H_2S + 2PW_{12-n}V^V_n \longrightarrow S^0 + 2H^+ + 2PW_{12-n}V^V_{n-1}V^{IV}$	0.1–3 h

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Experimental

Individual $PW_{12-n}V_n$ (n = 1–4) were obtained as described elsewhere [2]. $H_4PW_{11}VO_{40}$ and the isomeric fractions of $H_5PW_{10}V_2O_{40}$ were separated by the etherate method [4]. After extraction the residual concentration of SO_4^{2-} in the HPC solutions was about 15 mol% relative to HPA. The α-1,2,3-PW_9V_3 isomer was obtained as described in ref. 3. The composition of the HPAs was tested by ^{31}P and ^{51}V NMR according to refs. 2–4; the chemical shifts of the HPAs obtained are given in Table 2. The compositions of the HPAs upon redox reactions remained unchanged, which was controlled by NMR spectra of the reoxidized solutions and by EPR spectra of the reduced solutions [5].

The techniques of potentiometric measurements, electrochemical oxidation and reduction of HPAs were described elsewhere [5, 6].

$FeSO_4$, $VOSO_4$ and $VOCl_2$ solutions were prepared as described in refs. 7 and 8. A 0.02 M VO_2^+ solution was prepared by dissolving a sample weight of $NaVO_3 \cdot 2H_2O$ in 0.1 M HCl. A 0.01 M solution of H_2S was prepared by dissolving Na_2S in a hermetically sealed flask filled with water nearly completely so that all H_2S produced was in solution, the water being preliminary acidified with H_2SO_4 to pH 2.5 and bubbled with Ar. A 0.1 M solution of hydrazine was prepared by dissolving a sample weight of $N_2H_4 \cdot H_2SO_4$.

In the kinetic runs the degree of reduction which was followed spectrophotometrically did not exceed 1 electron per HPA. The reaction kinetics was studied spectrophotometrically, for $PW_{11}V^{IV}$ at 525 nm ($\epsilon = 675$), $PW_{10}V^VV^{IV}$ at 590 nm ($\epsilon = 320$), for $PW_9V^V{}_2V^{IV}$ and $PW_8V^V{}_3V^{IV}$ at 625 nm (ϵ = 340 and 210, respectively). The wavelengths were chosen so that the absorption of other substances was negligible. The kinetics of the electron transfer between $PW_{11}V$, $PW_{10}V_2$ and α-1,2,3-PW_9V_3 was studied at 770 nm using a KC-19 light filter, the absorption of α-1,2,3-$PW_9V^V{}_2V^{IV}$ ($\epsilon = 550$), $PW_{11}V^{IV}$ ($\epsilon = 150$) and $PW_{10}V^VV^{IV}$ ($\epsilon = 170$) being taken into account. The stopped-flow technique was used for studying the kinetics of fast reactions with participation of Fe(II), VO^{2+}, VO_2^+ ions, reduced HPAs on a SF-3 system combined with a storage oscilloscope and minicomputer. The time of mixing of solutions was about 2 ms. The rate constants were calculated from the linear representations of the kinetic equations with an accuracy of ±5%.

Results and Discussion

Redox Properties of Tungstovanadophosphoric HPA

Redox potentials of P–W–V HPA in solutions change as follows: $PW_{11}V > PW_{10}V_2 > PW_9V_3 \approx PW_8V_4$ [5, 15]. The isomers with adjacent V atoms appear to have, at the same pH values, a higher potential compared with that of the isomers with isolated V atoms (Fig. 1(B), curves 1, 2) [6]. This seems to be due to the different acidic properties of HPAs, since the potentials depend on the acidity of the solution (Fig. 1(A), curves 1, 2). The isomers

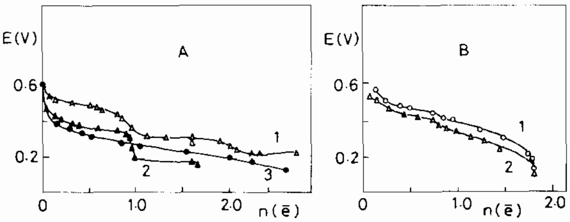


Fig. 1. Variation of redox potentials with respect to silver chloride electrode depending on the HPA reduction degree. (A) 1: α-1,2,3-PW_9V_3, pH 3; 2: α-1,2,3-PW_9V_3, pH 5; 3: PW_9V_3 isomer mixture, pH 3; [HPA] = 0.025 M, 30% CH_3COOH, 0.3 M Na_2SO_4, 25 °C. (B) 1: $PW_{10}V_2$ adj.; 2: $PW_{10}V_2$ isol.; [HPA] = 0.02 M, 1.5 M NaCl, pH 1.5, 25 °C.

TABLE 2. ^{31}P and ^{51}V chemical shifts of P–W–V HPCs in solution

HPC	$\delta^{31}P \pm 0.1$ (ppm)	$\delta^{51}V \pm 0.5$ (ppm)
$H_4PW_{11}VO_{40}$	−14.7	−554
$H_5PW_{10}V_2O_{40}$, isomer mixture	−13.9, −14.1, −14.2	−556, −552, −551, −545, −525
$H_5PW_{10}V_2O_{40}$, two isomers with adjacent V atoms	−13.9, −14.1	−525, −545
$H_5PW_{10}V_2O_{40}$, three isomers with isolated V atoms	−14.1, −14.2	−551, −552, −556
$Na_xH_{6-x}PW_9V_3O_{40}$, isomer mixture, pH 5	several peaks in the range −13 to −13.6	−554, −551.5, −549.5, −545, −528, −525
$Na_xH_{6-x}PW_9V_3O_{40}$, α-1,2,3-isomer, pH 5	−13.3	−529
$Na_xH_{7-x}PW_8V_4O_{40}$, isomer mixture, pH 8	−12.3 to −12.9	−550, −543, −523, −518

with adjacent V atoms show a greater proton-acceptor ability, which can be attributed to the higher negative charge on the O atoms in the $\mathrm{V}\overset{\mathrm{O}}{\diagup\;\diagdown}\mathrm{V}$ bridges, where protonation of HPA occurs. The protonation of the $\mathrm{V^V}\overset{\mathrm{O}}{\diagup\;\diagdown}\mathrm{V^V}$ bridges of the oxidized HPA begins at pH < 1 and <3.5 for $PW_{10}V_2$ and $PW_{10}V_3$, respectively [4, 16]. The reduction of the P–W–V HPAs with $n > 1$ is accompanied by their protonation [15]. The protonation of the reduced HPA also seems to begin with $\mathrm{V}\overset{\mathrm{O}}{\diagup\;\diagdown}\mathrm{V^{IV}}$ bridges, which should result in higher redox potentials for the isomers with the adjacent V atoms.

The potential drops for both individual isomers and isomeric mixtures are observed for reduced $PW_{10}V_2$ (Fig. 1(B); (A), curve 2). The stepwise reduction is also observed for the α-1,2,3-PW_9V_3 isomer (Fig. 1(A), curves 1, 2). A smooth change of the potential of $PW_{12-n}V_n$ at $n > 2$ (Fig. 1(A), curve 3) which was reported earlier [5], seems to be due to the overlapping of several stepwise curves from different isomers and HPAs with different degrees of protonation.

Intermolecular Electron Transfer in P–W–V HPA Solutions

The task of determining the rates of electron transfer between HPAs results from studying the mechanism of the multi-electron HPA redox reactions [5]. Since the reduced α-1,2,3-PW_9V_3 isomer has an intense absorption band at $\nu \lesssim 11\,000$ cm^{-1}, it is possible to study the electron transfer between this isomer and the P–W–V HPAs (Table 1, reactions (1) and (2)) [6] by measuring absorption at this ν. The reactions were carried out in acetate buffer, pH 3, 30% CH_3COOH, immediately after electrochemical reduction of HPA by 1 electron. The destruction of HPA was not observed during the experiments. Both reactions were completed judging from the observed D_∞ value. Reaction (1) was studied at $[PW_{11}V^V] \gg [\alpha\text{-}1,2,3\text{-}PW_9V^V{}_2V^{IV}]$. The pseudo-first order rate constant depends linearly on the $PW_{11}V$ concentration, and the rate constant was determined from this dependence (Table 3). Reaction (2) was studied at a comparable concentration of the reagents. The bimolecular rate constant was determined according to the equation

$$\ln \frac{[\alpha\text{-}1,2,3\text{-}PW_9V_3]_0 - [\alpha\text{-}1,2,3\text{-}PW_9V^V{}_2V^{IV}]}{[PW_{10}V^VV^{IV}]_0 - [\alpha\text{-}1,2,3\text{-}PW_9V^V{}_2V^{IV}]} = k\tau$$

It should be noted that the rate constants of reactions (1) and (2) are roughly similar, which corresponds to the equality of the potential difference, ΔE, of the oxidizing and reducing agents measured under reaction conditions at HPA degree of reduction of 0.5 electron (Table 3).

TABLE 3. Rate constants of electron transfer between reduced and oxidized P–W–V HPAs (30% CH_3COOH, pH 3, 20 °C)

Reaction	$[HPA_{ox}]_0$ (M)	$[HPA_{red}]_0$ (M)	$k \times 10^{-2}$ (dm^3/mol s)	ΔE (V)
(1)	0.010–0.025	0.0015	1.1 ± 0.2	0.1
(2)	0.018–0.003	0.002–0.003	1.4 ± 0.2	0.1

Oxidation of Fe(II) Ions with HPA $PW_{12-n}V_nO_{40}{}^{-(3+n)}$

$VO_2{}^+$ ions resulting from a fast HPA dissociation in solution are the oxidizing particles in reduction of P–Mo–V HPAs with Fe(II) ions. The rate constant of PMo_8V_4 reduction with Fe(II) ions, estimated theoretically for the outer sphere electron transfer reaction, is equal to ~10^4 dm^3 mol^{-1} s^{-1}, 40% CH_3COOH. This value is in agreement with the reaction rates observed and shows the possibility of participation of HPA itself in reaction with Fe(II) ions [11]. P–W–V HPAs were used for mechanistic studies of the electron transfer reaction between HPA and Fe(II) ions [7].

At comparable reagent concentrations reaction (3) is irreversible for $PW_{11}V$ and $PW_{10}V_2$ and reversible for PW_9V_3 and PW_8V_4. The reaction rate constants correspond to the redox potentials of various HPAs, measured under the reaction conditions (Table 4). However, the rate constants obtained do not correspond to the correlation obtained in ref. 17 for some redox reactions of HPA ZW_{12}, assuming the outer sphere electron transfer mechanism.

An analysis of the dependence of observed k and k_{rev} on the HPA, Fe(II) and Na_2SO_4 concentrations showed [7] that the interaction of HPA with Fe(II) ions consists of two stages

$$HPA^{-(3+n)} + Fe(II) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [HPA\cdot Fe(II)]^{-(1+n)} \qquad (7)$$

$$[HPA\cdot Fe(II)]^{-(1+n)} \xrightarrow{k_2} HPA_{red}{}^{-(4+n)} + Fe(III) \quad (8)$$

The reduction of $PW_{11}V$ and different isomers of $PW_{10}V_2$ was studied at $[Fe(II)]_0 \gg [HPA]_0$, when equilibrium (7) is markedly shifted towards the formation of the intermediate complex. In this case the reaction rate is given by the equation

$$W = \frac{k_1k_2[Fe(II)]_0[HPA]_\Sigma}{k_1[Fe(II)]_0 + k_{-1} + k_2} = k_{obs}[HPA]_\Sigma \qquad (9)$$

where $[HPA]_\Sigma$ is the total concentration of oxidized

TABLE 4. Kinetics of the reduction of Fe(II) ions with HPA: pH 1.1 ($PW_{11}V$), pH 1.5 ($PW_{10}V_2$), pH 2.5 (PW_9V_3 and PW_8V_4), 0.5 M Na_2SO_4

HPA	E (V) (relative to hydrogen electrode)	$[HPA]_0 \times 10^3$ (M)	$[FeSO_4]_0 \times 10^3$ (M)	$k \times 10^{-2}$ ($dm^3\ mol^{-1}\ s^{-1}$)	k_{rev} ($dm^3\ mol^{-1}\ s^{-1}$)	t (°C)
$PW_{11}V$	0.86	1.5–7.5	1.4–10	360 ± 60		24
$PW_{10}V_2$	0.64	3.0–20	5.0–30	30 ± 6		24
PW_9V_3	0.55	5.0	10	2.3	5.2	19
PW_8V_4	0.55	5.0	10	3.4	4.7	19

TABLE 5. Reactions constants of reduction of HPA with Fe(II) ions: pH 1.1 ($PW_{11}V$), pH 1.5 ($PW_{10}V_2$)

HPA	k_2 (s^{-1})	$k_1/(k_{-1} + k_2)$ ($dm^3\ mol^{-1}$)	E_{HPA} (V) (relative to hydr. electrode)
$PW_{11}V$	1.25 10^3	20	0.86
$PW_{10}V_2$ adj.	2.5 10^2	10	0.67
$PW_{10}V_2$ isol.	1.25 10^2	10	0.62

HPA, free and bonded with Fe(II) ions, k_{obs} values were obtained from linear plots $\ln D_\infty/(D_\infty - D)$ versus τ. The rate constants of the limiting step (k_2) and $k_1/(k_{-1} + k_2)$ (Table 5) were obtained from the linear plots of eqn. (9) versus $[Fe(II)]_0$ variation. The isomers of $PW_{10}V_2$ with adjacent V atoms possess a higher oxidizing potential compared to those with isolated V atoms, the rate constant of the limiting step changing accordingly (Table 5).

Reduction of $PW_{12-n}V_nO_{40}^{-(3+n)}$ HPA with VO^{2+} Ions

Reduction of HPA with VO^{2+} ions is an important stage in the processes of liquid-phase oxidation with oxygen in the presence of P–Mo–V HPC [1]. The interaction of individual $PW_{12-n}V_nO_{40}^{-(3+n)}$ (n = 1–4) with VO^{2+} ions was studied at $[HPA]_0$ = 0.0025–0.01, $[VOSO_4]_0$ = 0.05–0.1 or $[VOCl_2]_0$ = 0.02–0.35 M, pH 1–2.7 [8]. Reaction (4) is completed for $PW_{11}V$ but is reversible for the other HPAs. The rate constants were determined from the linear plots of the pseudo-first order reaction for $PW_{11}V$ and of reversible bimolecular reaction for other HPAs. As for PW_9V_3 and PW_8V_4 linear plots were invalid, the rate constants were estimated from the initial parts of the curves [8]. Different $PW_{10}V_2$ isomers revealed different activity in accordance with their potentials, PW_9V_3 and PW_8V_4 are more active in spite of their lesser potentials (Table 6). The rate constants obtained earlier [18] fail to characterize the activity of the individual $PW_{12-n}V_n$ HPA since the kinetics was studied at $[VO^{2+}] \ll [HPA]$ and the solutions contained mixtures of HPAs of different composition.

TABLE 6. Rate constants of P–W–V HPA reduction with $VOSO_4$: $[HPA]_0$ = 0.015, $[VOSO_4]_0$ = 0.05, $[Na_2SO_4]$ = 0.5 M, pH 2.7, 20 °C

HPA	k ($dm^3\ mol^{-1}\ s^{-1}$)	k_{rev} ($dm^3\ mol^{-1}\ s^{-1}$)
$PW_{11}V$	0.16	
$PW_{10}V_2$ adj.	0.12	1.6
$PW_{10}V_2$ isol.	0.042	2.7
$PW_{10}V_2$ mixt.	0.062	2.6
PW_9V_3	0.6	300
PW_8V_4	0.3	200

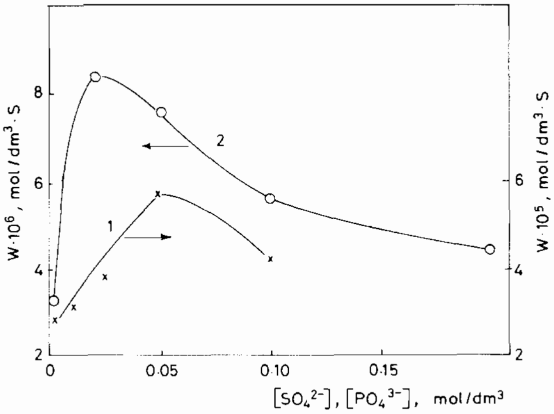


Fig. 2. Rate of $PW_{11}V$ interaction with $VOCl_2$ vs. SO_4^{2-} (1) and PO_4^{3-} (2) concentration. 1: $[HPA]_0$ = 0.01, $[VOCl_2]_0$ = 0.2 M; 2: $[HPA]_0$ = 0.0025, $[VOCl_2]_0$ = 0.1; $[SO_4^{2-}]$ = 0.0004 M; pH 0.95, 24 °C.

The dependence of the reaction rate on the SO_4^{2-} and PO_4^{2-} concentrations has a maximum (Fig. 2). At the concentrations comparable to that of HPA these anions accelerate the reaction. At higher concentrations the rate decreases since it is proportional to the concentration of VO^{2+} not bound with SO_4^{2-} (β = 55 [19]).

The reduction kinetics of $PW_{11}V$ was studied at a low concentration of SO_4^{2-} ions ($[HPA]/[SO_4^{2-}]$ = 6) [8]. The rate of $VOCl_2$ oxidation has a minus one order with respect to the H^+ concentration at pH 1–2 and does not depend on the ionic strength of the solution. The reaction order less than unity with respect to $PW_{11}V$ was determined from the kinetic curves as well as from the dependence of the initial rate on $[PW_{11}V]_0$. It depends on the pH [8]. The reaction order with respect to VO^{2+} ions varies from 1 to 4 as the initial $VOCl_2$ concentration increases from 0.02 to 0.35 M ($[PW_{11}V]_0 = 0.005$, $[NaCl] = 1.5$ M, pH 1); similar dependences were observed for $PW_{10}V_2$. The complicated kinetics dependences obtained for the reaction of HPA with $VOCl_2$ indicate a more complex interaction in this case compared to that of Fe(II) ions.

The states of HPA and V(IV) ions under the reaction conditions were studied by ^{51}V NMR and ESR. The NMR spectra of $PW_{11}V$ and $PW_{10}V_2$ were found not to change with HPA concentration. Upon reoxidation of HPA reduced with $VOCl_2$ their chemical and isomeric composition remains unchanged. In the absence of HPA vanadyl ions in HCl solutions exist only as the monomer species, as was ascertained by a linear dependence of the VO^{2+} signal intensity on the total $VOCl_2$ concentration.

The reaction order with respect to vanadyl ions, varying from 1 to 4, indicates the formation of intermediate complexes of the oxidized HPA with one or more V(IV) ions. The rate of electron transfer in these complexes increases with the number of attached V(IV) ions as well as with the number of V(V) atoms in HPA (Table 6). The mechanism of formation of such complexes has not been studied yet. However, it is unlikely that complexes of this type between $PW_{12-n}V_nO_{40}^{-(4+n)}$ and 1–4 VO^{2+} ions form only due to electrostatic interaction.

The low reaction order with respect to HPA at a low SO_4^{2-} concentration proves that only a part of HPAs is in the active form. As shown in ref. 20, the following reactions take place in HPA solutions

$$PW_{11}O_{39}^{7-} + VO_2^+ + 2H^+ \rightleftharpoons [PW_{11}O_{39}{\cdot}VO]^{4-} + H_2O \qquad (10)$$

$$[PW_{11}O_{39}{\cdot}VO]^{4-} \rightleftharpoons PW_{11}VO_{40}^{4-} \qquad (11)$$

$[PW_{11}O_{39}{\cdot}VO]^{4-}$ was assumed to be an active particle at HPA reduction, with VO^{3+} being partially involved in the coordination vacancy of HPA. VO^{2+} ions bind with them without reconstruction of the HPA skeleton. The reaction acceleration by SO_4^{2-} and PO_4^{3-} ions can be attributed to increasing concentration of active particles as these ions interact with the cationic forms of V(V) [19, 21].

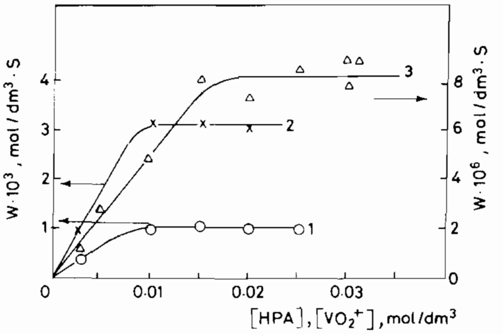


Fig. 3. Rate of $PW_{10}V^VV^{IV}$ isol. (1, 2) and $PW_{11}V^{IV}$ (3) oxidation by VO_2^+ ions vs. initial HPA (2) and VO_2^+ (1, 3) concentrations. 1: $[PW_{10}V^VV^{IV}]_0 = 0.005$, 2: $[VO_2^+]_0 = 0.01$ M, pH 1.5; 3: $[PW_{11}V^{IV}]_0 = 0.015$ M, pH 1; 1 M NaCl, 20 °C.

Oxidation of the Reduced HPA with VO_2^+ Ions

The kinetics of the reverse reaction (4) between $PW_{11}V^{IV}$ or $PW_{10}V^VV^{IV}$ and VO_2^+ was studied at $[HPA]_0 = 0.0025$–0.02, $[NaCl] = 1$ M, pH 1.0–1.5. $NaVO_3$ concentration and pH ranges were chosen so that there were no decavanadate ions ($-\lg K = 6.75$ [22]) and only VO_2^+ formed in the solution. The reaction of VO_2^+ with $PW_{11}V^{IV}$ is reversible and is completed with $PW_{10}V^VV^{IV}$. For both HPAs the reaction rate determined from the initial parts of the kinetic curves is proportional to the concentration of the reagent when its amount is less than a stoichiometric one, and becomes independent of it even at small excess (Fig. 3). This proves the formation of an intermediate complex with the HPA reduced/V(V) ratio of 1:1 in which the electron transfer from HPA to V(V) occurs, V(V) being included as a VO^{3+} particle [20]

$$PW_{10}V^VV^{IV}O_{40}^{6-} + VO_2^+ + 2H^+ \overset{\text{fast}}{\rightleftharpoons} [PW_{10}V^VV^{IV}O_{40}{\cdot}VO]^{3-} \xrightarrow{k} PW_{10}V^V_2O_{40}^{5-} + VO^{2+} \qquad (12)$$

The rate constant k was determined from the linear plots of the equations for the monomolecular reaction

$$k\tau = \ln \frac{[PW_{10}V^VV^{IV}]_0}{[PW_{10}V^VV^{IV}]} \quad \text{at } [PW_{10}V^VV^{IV}] < [VO_2^+] \qquad (13)$$

$$k\tau = \ln \frac{[VO_2^+]_0}{[VO_2^+]_0 - ([PW_{10}V^VV^{IV}]_0 - [PW_{10}V^VV^{IV}])}$$
$$\text{at } [PW_{10}V^VV^{IV}] > [VO_2^+] \qquad (14)$$

k values obtained from eqns. (13) and (14) are similar being 0.16 ± 0.2 s^{-1} (1 M NaCl, pH 1.5, 20 °C).

The interaction of $PM_{12-n}V_n$ with VO^{2+} (reaction (4)) or with VO_2^+ (reaction (12)) might occur by means of the exchange of VO^{2+} and VO^{3+} ions in the

HPA coordination sphere. However even in the case of the labile P–Mo–V HPA the electron transfer from VO^{2+} ion into HPA proved to be a faster process than the dissociative substitution of vanadium in HPA [11]. P–W–V HPAs do not exchange V ions with solutions [23, 5]. This is good evidence for the occurrence of reactions (4) and (12) according to the electron transfer mechanism. Nevertheless the kinetic data obtained for the reaction of HPA with VO_2^+ or VO^{2+} do not exclude the possibility of the associative mechanism of VO^{2+} and VO^{3+} exchange in the intermediate HPA complex.

Reduction of $PW_{12-n}V_nO_{40}^{-(3+n)}$ *with Hydrazine*

In P–Mo–V HPA solutions hydrazine is readily oxidized by VO_2^+ ions resulting from HPA dissociation [12, 24]. Hydrazine oxidation was found to be much slower in P–W–V HPA solutions. The kinetics of reaction (5) was studied at $[N_2H_4]_0 = 0.0025$–0.016, $[HPA]_0 = 0.017$–0.15 M, pH 2–3. The reaction rate was determined from the initial parts of the kinetic curves. $PW_{11}V$ does not oxidize N_2H_4. N_2H_4 oxidation by $PW_{10}V_2$ and PW_8V_4 HPAs occurs with comparable rates. The effective reaction order with respect to HPA is higher than 1 ($n = 1.5$ for $PW_{10}V_2$, $n = 1.7$ for PW_8V_4) while that with respect to N_2H_4 is less than 1 ($n = 0.3$ for $PW_{10}V_2$) (Fig. 4). The kinetic data obtained allow one to suppose that N_2H_4 is oxidized in the complex of two HPAs, apparently, according to the two- or four-electron mechanism.

Reduction of $PW_{12-n}V_nO_{40}^{-(3+n)}$ *with* H_2S

$PMo_{12}O_{40}^{3-}$ and P–Mo–V HPAs were assumed to be reduced with H_2S due to the fast interaction of H_2S with Mo(VI) isopolyanions existing in the HPA solutions ($k \sim 10$ s^{-1}, pH 3, 25 °C) [14].

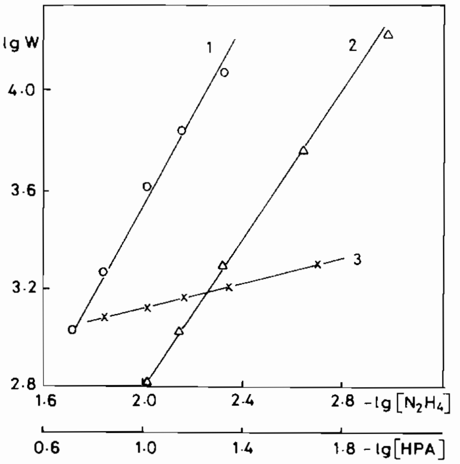


Fig. 4. Logarithm of the rate of HPA reduction with hydrazine vs. logarithm of PW_8V_4 (1), $PW_{10}V_2$ (2) and N_2H_4 (3) concentrations. 1, 2: $[N_2H_4] = 0.0025$ M, pH 2.55; 3: $[PW_{10}V_2] = 0.05$ M, pH 2.0; 0.5 M Na_2SO_4, 21 °C.

TABLE 7. Kinetics of H_2S oxidation by $PW_{12-n}V_n$-$O_{40}^{-(3+n)}$ ions

	$[HPA]_0$ (M)	$[H_2S]_0 \times 10^3$ (M)	$[Na_2SO_4]$ (M)	pH	$k_{obs} \times 10^2$ (min^{-1})
$PW_{11}V$	0.045	0.5–3.0	0.25	2.6	4.6 ± 0.8
	0.045	2.5	0	2.6	3.3
	0.045	2.5	0.25	2.6	4.3
	0.045	2.5	0.5	2.6	4.1
	0.045	2.5	1.0	2.6	6.6
	0.045	2.5	2.0	2.6	8.6
PW_9V_3	0.05	1.0–2.5	0.5	2.6	12.7 ± 1.0
	0.05	2.5	0	2.6	13.6
	0.05	2.5	0.25	2.6	13.7
	0.05	2.5	0.375	2.6	14.6
	0.05	2.5	0.5	2.6	13.9
	0.05	2.5	0.75	2.6	16.8
	0.05	2.5	1.0	2.6	15.3

P–W–V HPA reduction proceeds more slowly. The kinetics of the oxidation of H_2S to S^0 by the $PW_{12-n}V_n$ isomeric mixtures as well as by the $PW_{10}V_2$ isomers with the adjacent V atoms and the α-1,2,3-PW_9V_3 isomer were studied.

At bubbling HPC solutions (0.01–0.15 M) with H_2S all V(V) in HPA is reduced to V(IV). After the electrochemical oxidation of the reduced solutions the chemical and isomeric HPA compositions are completely retained.

The reaction kinetics was studied at HPA excess (Table 7) when HPA was reduced by not more than one electron. No changes in pH of the solution were detected after the reaction. The reaction proceeded until H_2S was completely oxidized, as shown by a comparison of D_∞ with the calculated value. k_{obs} values determined from the linear plots of $\lg D_\infty/(D_\infty - D)$ versus τ are given in Table 7. k_{obs} weakly depends on the ionic strength varied with Na_2SO_4 addition. At concentrations studied k_{obs} does not depend on HPA for $PW_{11}V$ and $PW_{10}V_2$. The reaction has the first order for PW_9V_3 and PW_8V_4 at low concentrations, while the dependence becomes weaker at higher HPA concentrations (Fig. 5). For all HPAs k_{obs} increases with pH, the effective order with respect to H^+ changing from −1 to 0 (Fig. 6).

Based on the data presented here the kinetic scheme for H_2S oxidation can be described as follows

$$HPA + H_2S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [HPA{\cdot}H_2S] \qquad (15)$$

$$[HPA{\cdot}H_2S] \overset{K_p}{\rightleftharpoons} [HPA{\cdot}HS^-] + H^+ \qquad (16)$$

$$[HPA{\cdot}HS^-] \xrightarrow{k_2} \text{products} \qquad (17)$$

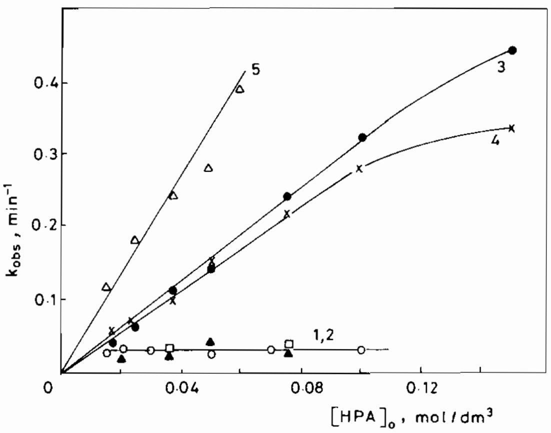


Fig. 5. Rate constant of H_2S oxidation vs. HPA concentration. 1: (○) $PW_{11}V$; 2: (▲) $PW_{10}V_2$ isol., (□) $PW_{10}V_2$ adj.; 3: PW_9V_3; 4: PW_8V_4; 5: α-1,2,3-PW_9V_3; $[H_2S]_0 = 0.0025$ M, pH 2.6, 0.5 M Na_2SO_4, 21 °C.

At $[HPA]_0 \gg [H_2S]_0$ the reaction rate is expressed as

$$W = \frac{k_1 k_2 K_p [HPA]_0 [H_2S]_\Sigma}{k_1([H^+] + K_p)[HPA]_0 + k_{-1}[H^+] + k_2 K_p} = k_{obs}[H_2S]_\Sigma \qquad (18)$$

where $[H_2S]_\Sigma$ is the total H_2S concentration at the moment τ, equal to $([H_2S]_0 - 1/2[HPA]_{red})$.

For $PW_{11}V$ and $PW_{10}V_2$ k_{obs} does not depend on $[HPA]_0$ within the pH interval 1.4–3.0. This means that in the denominator of eqn. (18) the last two members are small compared to the others

$$W = \frac{k_2 K_p [H_2S]_\Sigma}{[H^+] + K_p} \qquad (19)$$

k_2 and K_p were determined from the linear plots of eqn. (19) $1/k_{obs} - [H^+]$. The obtained values of $K_p = 5 \times 10^{-3}$ mol/l are much higher than the dissociation constant of free H_2S ($pK_1 = 7$) [25] which implies an easier acidic dissociation of HPA-coordinated H_2S.

To determine k_2 for PW_9V_3 and PW_8V_4, a dependence of k_{obs} on $[HPA]_0$ at pH 4.5–5 was obtained, when k_{obs} is independent of pH (Fig. 6). Under such conditions at sufficiently high HPA concentrations (0.05–0.15 M) k_{obs} appears to be independent of $[HPA]_0$ too. Then, $k_{obs} = k_2$. k_2 values obtained are given in Table 8.

Thus, the rate constants of the limiting step are different for various HPA compositions. k_2 variations in HPA fail to correspond to changes in oxidation potentials of these HPAs (Fig. 1). PW_9V_3 and PW_8V_4 have the lowest potentials, but k_2 is 5–6 times higher compared to $PW_{11}V$ and $PW_{10}V_2$. The highest activity is observed for the α-1,2,3-PW_9V_3 isomer.

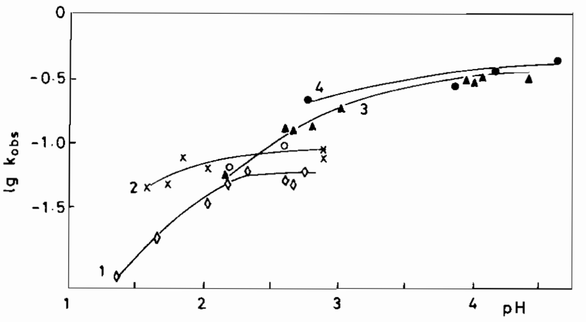
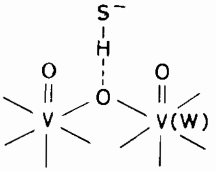


Fig. 6. Logarithm of the observed rate constant of H_2S oxidation vs. pH. 1: $PW_{11}V$; 2: (○) $PW_{10}V_2$ mixt., (X) $PW_{10}V_2$ adj.; 3: PW_9V_3; 4: PW_8V_4; $[HPA]_0 = 0.05$, $[H_2S]_0 = 0.0025$ M, 0.5 M Na_2SO_4, 20 °C.

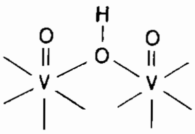
TABLE 8. Rate constants of H_2S oxidation by HPA of different composition, $[Na_2SO_4] = 0.5$ M, 20 ± 1 °C

HPA	k_2 (min^{-1})	pH range determined k_2
$PW_{11}V$	0.1	1.4–2.8
$PW_{10}V_2$ isomer mixt.	0.1	1.3–2.9
$PW_{10}V_2$ isomers with adj. V atoms	0.1	1.3–2.9
PW_9V_3 isomer mixt.	0.6	5.3
α-1,2,3-PW_9V_3	1.3	4.5
PW_8V_4 isomer mixt.	0.5	5.1

The data obtained allow one to assume that H_2S oxidation occurs in the outer sphere of the HPA complex with HS^-, which seems to be formed by hydrogen bonds with bridging oxygen atoms:



Two-electron oxidation of H_2S in such a complex does not take place, since k_2 values for $PW_{11}V$ and different $PW_{10}V_2$ isomers are equal. High activity of PW_9V_3, PW_8V_4 and particularly of α-1,2,3-PW_9V_3 might be explained by the fact that the reaction with these HPAs occurs according to the mechanism of H atom transfer because these HPAs accept protons during reduction with formation of the fragments [16]:



Conclusions

Data on redox reactions of heteropolycomplexes accumulated at the moment make it possible to distinguish the following types of mechanisms.

1. The reaction with oxidizing particles – oxo ions, which are thought to result from a fast dissociation of HPA and incorporate again into HPA after the reduction with forming heteropolyblue.

For example, in P–Mo–V HPC solutions Fe(II) ions, Pd(O) complexes, N_2H_4 are oxidized by VO_2^+ ions [12].

2. HPA interaction with one-electron reductants or oxidatants according to the mechanism of outer sphere electron transfer. This mechanism seems to take place for reactions of ZW_{12} (Z = P, Si, Co) HPA with a number of inorganic ions and organic substances [17]. The electron transfer between P–W–V HPAs studied in the present work seems to occur as the outer sphere reaction as well.

3. HPA oxidation or reduction occurring with formation of the intermediate complex of reacting particles. The reduction of molecular oxygen with P–Mo–V and P–W–V heteropolyblues occurs via inner sphere electron transfer in HPA complex containing oxygen [26, 5]. Redox reactions of P–W–V HPAs studied in this work can be attributed to such a type of reaction.

Kinetic and mechanistic studies of the oxidation of a number of substances having different natures by individual P–W–V HPAs have revealed quite a rich chemistry. HPA reduction and oxidation by transition metal ions proceed at a high rate. HPA reduction by Fe(II) ions proceeds via formation of an intermediate complex like the ion pair. HPA reduction with VO^{2+} takes place in an active complex where V(IV) ions are polymerized in the HPA coordination sphere.

P–W–V HPAs are less active in N_2H_4 and H_2S oxidation than simple V(V) or Mo(VI) ions, since the formation of metal-substrate bonds is complicated in HPAs of this type. These reactions seem to proceed via formation of outer sphere HPA complexes with reductants.

The dependence of the rate constant on the number and mutual arrangement of V atoms in HPA has been found for the reactions studied. In some cases qualitative correspondence of the rate constants to the HPA redox potentials was observed. For example, $PW_{10}V_2$ isomers with the adjacent V atoms in the $V\overset{O}{\diagup\;\diagdown}V$ bridges, due to the higher proton-acceptor ability at equal pH, have a higher oxidation potential compared to that of the isomers with isolated V atoms and are more active in the reaction with Fe(II) and VO^{2+}. Variation of the proton-acceptor properties in the HPA row might change the reaction mechanism. For example, H_2S oxidation by PW_9V_3 and PW_8V_4 anions seems to proceed according to the mechanism of H atom transfer in the outer sphere HPA complex with HS^-, which explains the higher activity of these HPAs compared to $PW_{11}V$ and $PW_{10}V_2$. This example shows an interrelation between acidic and oxidation properties of P–W–V HPA having different compositions.

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