

# Kinetics of Oxidation of Reduced Phosphorus–Molybdenum–Vanadium Heteropoly Acid Species with Dioxygen in Aqueous Solutions

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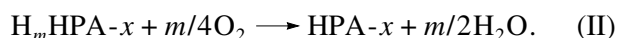
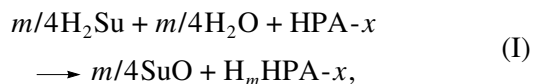
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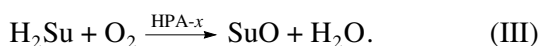
**Abstract**—The kinetics of dioxygen oxidation of the reduced heteropoly acid  $H_{7+m}PV_m^{IV}V_{4-m}^VMo_8O_{40}$  ( $H_m$ HPA-4) in aqueous solutions at atmospheric pressure and 313–363 K was studied, and a rate equation was proposed for this reaction. The reaction was of first order with respect to dioxygen. However, the order of the reaction with respect to  $H_m$ HPA-4 was close to 1 at  $[H_m\text{HPA-4}] > 0.20$  mol/l but increased to  $\approx 2.8$  at  $[H_m\text{HPA-4}] < 0.20$  mol/l. Variable orders of reaction with respect to  $H^+$  ions with high negative values were observed. The introduction of overstoichiometric  $VO^{2+}$  cations into  $H_m$ HPA-4 accelerated the oxidation of the solution. The apparent activation energy of the reaction dramatically increased as the degree of reduction of  $H_m$ HPA-4 decreased. This can be explained by the fact that the heats of endothermic preequilibrium steps of the disproportionation of weakly reduced heteropoly anions are added to the true activation energy of formation of an active intermediate complex of the heteropoly anion with  $O_2$ .

## INTRODUCTION

Aqueous solutions of  $H_{3+x}PV_x^VMo_{12-x}O_{40}$  phosphorus–molybdenum–vanadium heteropoly acids (HPA- $x$ ,  $2 \leq x \leq 6$ ) with the Keggin structure are reversible oxidizing agents commonly used in homogeneous catalysis for the liquid-phase oxidation of various substrates ( $H_2$ Su) with oxygen [1–3]. Usually, this oxidation is performed with the participation of concentrated (0.1–0.4 M) HPA- $x$  solutions in two steps (I) and (II) in different reactors.



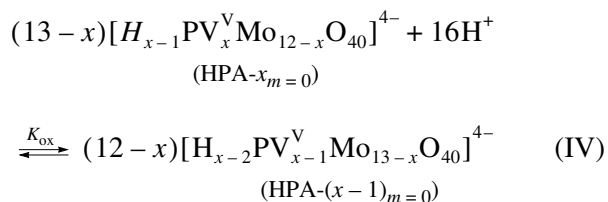
The oxidation of the HPA- $x$  reduced species with oxygen according to reaction (II) in a separate reactor is responsible for the high selectivity of the overall catalytic reaction



Reaction (II) is a common step of all catalytic oxidation processes with the use of HPA- $x$  solutions. In Eqs. (I) and (II),  $H_mHPA-x = H_{3+x+m}PV_m^{IV}V_{4-m}^VMo_{12-x}O_{40}$ ;

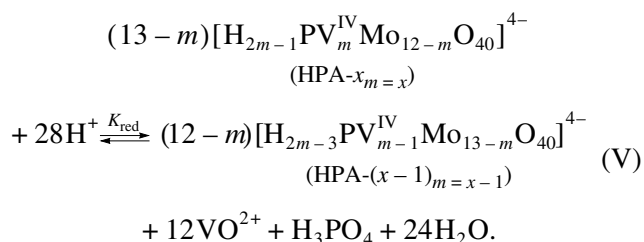
$x$  is the total number of vanadium atoms, and  $m$  is the number of vanadium(IV) atoms in this molecule.

Previously, the kinetics of reaction (II) was studied only in model systems at  $T \leq 313$  K in dilute solutions of  $H_m$ HPA- $x$  in the presence of acetate buffer solutions (pH  $\sim 3$ ) for suppression of reactions (IV) and (V) [4–7]. We [8, 9] initiated a study of this reaction in concentrated ( $\geq 0.1$  mol/l)  $H_m$ HPA- $x$  solutions, which are commonly used in actual practice [3, 10]. However, this study is difficult to perform because various equilibria occur in the solutions of  $H_m$ HPA- $x$  with  $x \geq 2$ . The initial (unreduced) solutions of HPA- $x$  are complex systems, in which  $VO_2^+$  cations are reversibly eliminated from the  $[H_{x-1}PV_x^VMo_{12-x}O_{40}]^{4-}$  heteropoly anions ( $HPA-x_m=0$ )<sup>1</sup> under the action of  $H^+$  ions that occur in solution [13]:



<sup>1</sup> The charge of HPA- $x_m$  anions can vary from  $-3$  to  $-5$  [11]; on the average, it is equal to  $-4$  [12].

In the completely reduced solutions of  $H_m\text{HPA}-x$ ,  $\text{VO}^{2+}$  cations are reversibly eliminated from  $\text{HPA}-x_{m=x}$  [14]:



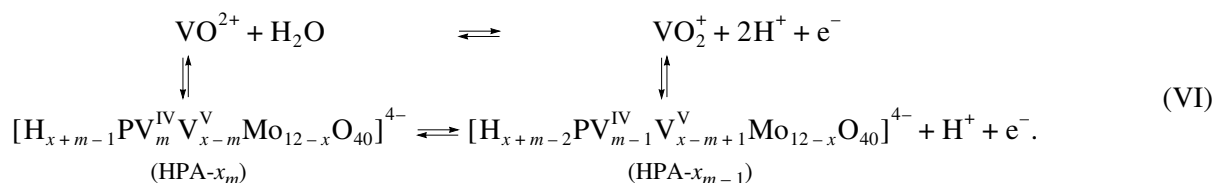
The partially reduced solutions of  $H_m\text{HPA}-x$  are more complex systems. They contain a wide variety of

$\text{HPA}-x_m$  anions with various integer values of  $x$  and  $m$ , as well as both of the  $\text{VO}^{2+}$  and  $\text{VO}_2^+$  cations [12]. The average degree of reduction of these solutions ( $m^*$ ) can be expressed by the equation<sup>2</sup>

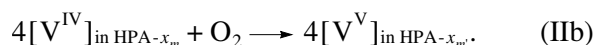
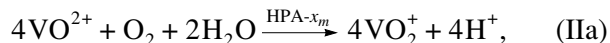
$$m^* = [\text{V}^{\text{IV}}]_{\Sigma} / [\text{H}_m\text{HPA}-x]. \quad (1)$$

In the course of reaction (II), vanadium(IV) as a constituent of heteropoly anions is oxidized to vanadium(V); therefore, the value of  $m^*$  decreases.

The eliminated  $\text{VO}^{2+}$  and  $\text{VO}_2^+$  cations occur in equilibria (VI) with heteropoly anions and with one another [12]:



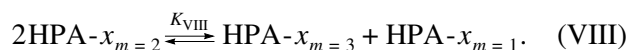
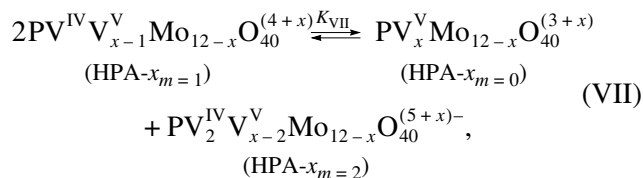
At low pH values in solutions,  $\text{VO}^{2+}$  cations are not oxidized by oxygen [15]. However, these cations readily enter into equilibria (VI) with  $\text{HPA}-x_m$  anions [14]; as the constituents of these anions, they can be oxidized by dioxygen [16]. With consideration for these equilibria, reaction (II) can be written in a simplified form as reaction (IIa) or (IIb):



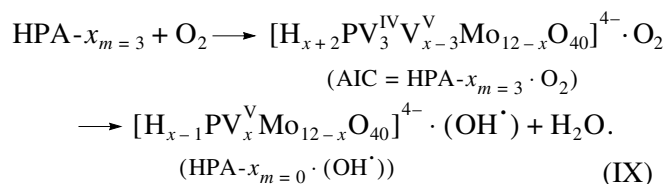
A consequence of equilibria (VI) is that the pH of  $H_m\text{HPA}-x$  solutions decreases as  $m^*$  decreases in the course of reaction (II) [17].

In the oxidation of 0.2 M  $H_m\text{HPA}-x$  solutions, reaction (II) was never complete; that is, vanadium(IV) was incompletely oxidized to vanadium(V) in solution [8, 9]. Thus, in the oxidation of  $H_m\text{HPA}-3$  and  $H_m\text{HPA}-4$  solutions, the final degree of reduction ( $m_f^*$ ) at 343 K and atmospheric pressure was 1.10–1.20 [9]. At low degrees of reduction ( $m^* < \sim 1.5$ ), the rate of reaction (II) in dilute [6] or concentrated [9] solutions is limited by the formation of active intermediate complexes of the  $[\text{HPA}-x_{m \geq 3} \cdot \text{O}_2]$  type. The heteropoly anion as a constituent of these active complexes should contain no less than three  $\text{V}^{\text{IV}}$  atoms.

Kozhevnikov and coauthors [6, 7] demonstrated that  $\text{HPA}-x_{m \geq 3}$  anions active toward  $\text{O}_2$  are formed from weakly reduced  $\text{HPA}-x_{m=1}$  or  $\text{HPA}-x_{m=2}$  anions in the equilibrium reactions (VII) and (VIII)



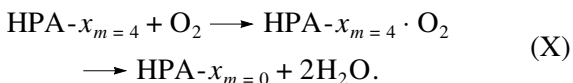
When active  $\text{HPA}-x_{m \geq 3}$  heteropoly anions occur in a sufficient amount in a solution of  $H_m\text{HPA}-x$ , the rate of reaction (II) is limited by the subsequent formation of an active intermediate complex containing  $\text{O}_2$  rather than by the formation of the above anions. The formation and degradation of an active intermediate complex (AIC) with three  $\text{V}^{\text{IV}}$  atoms occurs in accordance with reaction (IX); in this case, the coordinated  $\text{O}_2$  molecule is reduced to the  $\cdot\text{OH}$  radical [6]:



The formation and decomposition of an active intermediate complex with four  $\text{V}^{\text{IV}}$  atoms occurs in accordance with reaction (X) with the reduction of  $\text{O}_2$  to

<sup>2</sup> In Eq. (1), the numerator is the total concentration of vanadium(IV) in a solution of  $H_m\text{HPA}-x$  ( $[\text{V}^{\text{IV}}]_{\Sigma} = [\text{VO}^{2+}] + \sum_{m=1}^x (m[\text{HPA}-x_m])$ ) and the denominator is the total concentration of all heteropoly anions in this solution ( $[\text{H}_m\text{HPA}-x] = \sum_{m=0}^x [\text{HPA}-x_m]$ ).

water [4]:



According to reaction path (X), solutions of  $\text{H}_m\text{HPA-4}$  are oxidized more readily than  $\text{H}_m\text{HPA-3}$  and  $\text{H}_m\text{HPA-2}$  [9]. Therefore, solutions of  $\text{H}_m\text{HPA-4}$  were primarily used in this work in order to study the complex kinetics of reaction (II). Because equilibria like (IV) and (V) for partially reduced solutions of  $\text{H}_m\text{HPA-4}$  are extremely complicated and the total number of these equilibria can be as high as dozens [12], these equilibria cannot be completely taken into consideration. Therefore, in this work, we have restricted ourselves to the empirical functions  $\text{pH} = f(m^*)$ , which were expressed graphically. These generalized functions characterized changes in the composition of  $\text{H}_m\text{HPA-4}$  solutions on oxidation. These functions allowed us to plot required graphs in the  $\log w = f(\text{parameter})$  coordinates without the use of currently unknown constants of many equilibria like (IV) and (V).

## EXPERIMENTAL

Aqueous solutions of HPA-4 and HPA-3 were prepared from  $\text{H}_3\text{PO}_4$ ,  $\text{MoO}_3$ , and  $\text{V}_2\text{O}_5$  in accordance with a published procedure [18]. 0.20 M solutions of the  $(\text{VO}_2)_z\text{H}_{7-2z}\text{PV}_4\text{Mo}_8\text{O}_{40}$  HPA-4 with excessive  $\text{VO}_2^+$  cations ( $(\text{VO}_2)_z\text{HPA-4}_{m=0}$ )<sup>3</sup> were prepared by the addition of a calculated amount of a solution of  $\text{H}_6\text{V}_{10}\text{O}_{28}$ , which was prepared from  $\text{V}_2\text{O}_5$  [19], to a solution of HPA-4; the volume of the solution was subsequently brought to a specified value. 20.0-ml portions of the solutions of HPA-4, HPA-3, and  $(\text{VO}_2)_z\text{HPA-4}_{m=0}$  were reduced with a 10 M  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  solution at boiling temperature for ~5 min [20]. The resulting solutions of  $\text{H}_m\text{HPA-4}$ ,  $\text{H}_m\text{HPA-3}$ , or  $(\text{V}^{\text{IV}}\text{O})_z\text{HPA-4}_m = (\text{V}^{\text{IV}}\text{O})_z\text{H}_{7+m-2z}\text{PV}_m^{\text{IV}}\text{V}_{4-m}^{\text{V}}\text{Mo}_8\text{O}_{40}$  were cooled, and the solution volumes were brought to the initial values ( $[\text{H}_m\text{HPA-}x] = [\text{HPA-}x]_{\text{init}}$ ). The solutions were quantitatively transferred to a thermostated shaking glass reactor. The reactor was flushed with dioxygen and connected to a burette filled with  $\text{O}_2$ .

The oxidation of reduced solutions was performed at various temperatures and atmospheric pressure. The reaction was performed with intense shaking of the reactor (1200 swings per minute). The volume of consumed  $\text{O}_2$  was measured at regular intervals until the rate of consumption decreased to  $\sim 1 \times 10^{-4} \text{ mol O}_2 \text{ l}^{-1} \text{ min}^{-1}$ . We experimentally found that the oxidation occurred in

<sup>3</sup>  $z$  is an integer or half-integer number of excessive  $\text{VO}_2^+$  cations introduced into a solution of HPA-4,  $0 \leq z \leq 2$ . All of the  $\text{VO}_2^+$  cations are converted into  $\text{VO}^{2+}$  by reduction.

the kinetic region. When the partial pressure of oxygen ( $P_{\text{O}_2}$ ) was varied, the reactor was blown with gas mixtures of  $\text{O}_2 + \text{N}_2$  before the experiment. The typical dependence of the volume of absorbed  $\text{O}_2$  on time  $\tau$  was published previously [9].

After cooling of the oxidized test solution, the concentration of residual vanadium(IV) ( $[\text{V}^{\text{IV}}]_{\text{f}}$ ) in this solution was determined by potentiometric titration with a 0.10 N  $\text{KMnO}_4$  solution in the presence of  $\text{H}_3\text{PO}_4$  [21]. From the final degree of reduction  $m_{\text{f}}^* = [\text{V}^{\text{IV}}]_{\text{f}}/[\text{HPA-}x]_{\text{init}}$ , all of the intermediate degrees of reduction  $m_i^* = [\text{V}^{\text{IV}}]_i/[\text{HPA-}x]_{\text{init}}$  were calculated by the equation

$$m_i^* = m_{\text{f}}^* + \frac{(P_{\text{atm}} - P_{\text{H}_2\text{O}})4V_i273}{101.3 \times 22.41 [\text{H}_m\text{HPA-}x] V_{\text{solution}} T}, \quad (2)$$

where  $P_{\text{atm}}$  is the atmospheric pressure (kPa),  $P_{\text{H}_2\text{O}}$  is the pressure of water vapor (kPa) at the absolute temperature  $T$ , 101.3 kPa is the normal atmospheric pressure,  $V_i$  is the total volume of absorbed oxygen (l) at the point  $\tau_i$  in time, 22.41 is the molar volume of an ideal gas (l/mol),  $[\text{H}_m\text{HPA-}x]$  is the concentration of  $\text{H}_m\text{HPA-}x$  (mol/l), and  $V_{\text{solution}}$  is the volume of the  $\text{H}_m\text{HPA-}x$  solution (l). Next, the numerical differentiation of the function  $V_i = f(\tau_i)$  was performed and the functions  $w = f(m^*)$  were obtained, where  $w$  is the rate of reaction (II) calculated in  $\text{mol O}_2 \text{ l}^{-1} \text{ min}^{-1}$ . Calculations by Eq. (2) followed by numerical differentiation were performed using a special computer program.

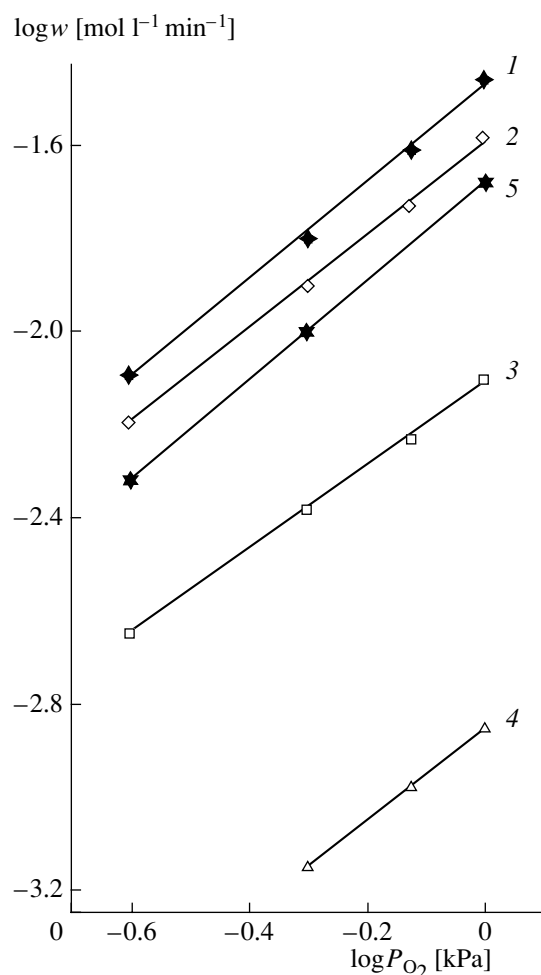
For the most part, the experiments were performed with  $\text{H}_m\text{HPA-4}$  solutions; however, 0.20 mol/l  $\text{H}_m\text{HPA-3}$  solutions were used in particular experiments. The experiments were replicated three or four times under the same conditions, and the average values of  $w$  were calculated.

The pH values of the test solutions of  $\text{H}_m\text{HPA-}x$  were measured at room temperature using an ESL-43-07 glass electrode, an ESL-1M3 saturated silver–silver chloride electrode, and an I-130 digital ion meter [12]. The accuracy of measurements was  $\pm 0.01$  pH units.

## RESULTS AND DISCUSSION

Figure 1 shows the dependence of  $\log w$  on  $\log P_{\text{O}_2}$  ( $w$  is the rate of reaction (II)) for the solutions of  $\text{H}_m\text{HPA-4}$  and  $\text{H}_m\text{HPA-3}$  at  $1.8 \leq m^* \leq 2.8$ . These data indicate that the order of reaction with respect to  $\text{O}_2$  is 1 over the specified range of  $m^*$ .

Figure 2a shows the dependence of  $\log w$  on  $m^*$  for various concentrations of  $\text{H}_m\text{HPA-4}$ . At fixed values of  $m^*$ ,  $w$  decreased rather than increased, as would be expected, as the concentration of  $\text{H}_m\text{HPA-4}$  was increased from 0.05 to 0.30 mol/l. In this case,  $m_{\text{f}}^*$  (final degree of reduction) also increased; that is, the

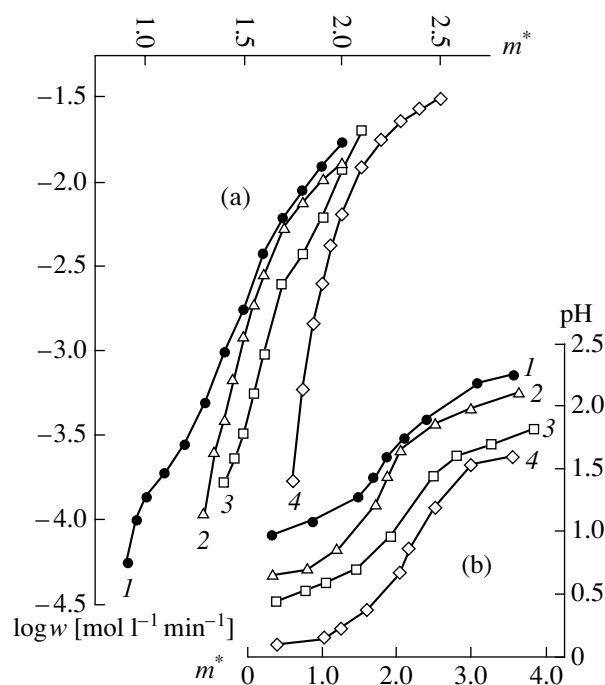


**Fig. 1.** Dependence of  $\log w$  on  $\log P_{O_2}$  for reaction (II) in 0.2 M solutions of (1–4)  $H_m\text{HPA-4}$  and (5)  $H_m\text{HPA-3}$ .  $m^* =$  (1) 2.8, (2) 2.5, (3) 2.0, (4) 1.8, and (5) 2.8.

higher the concentration of  $H_m\text{HPA-4}$  solutions, the lower the degree of oxidation. For example, at  $[H_m\text{HPA-4}] = 0.05 \text{ mol/l}$ ,  $m_f^* = 0.75$ , whereas this value increased to 1.72 at  $[H_m\text{HPA-4}] = 0.30 \text{ mol/l}$  (Fig. 2, Table 1).

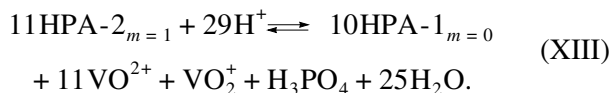
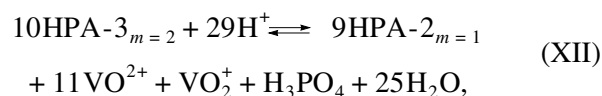
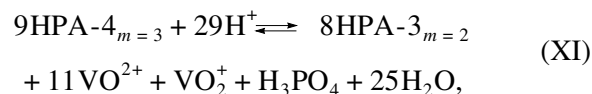
Figure 2b demonstrates the  $m^*$  dependence of the pH of  $H_m\text{HPA-4}$  solutions with different concentrations. It follows from Fig. 2b that the curves of  $\text{pH} = f(m^*)$  shifted to a more acidic region as  $[H_m\text{HPA-4}]$  was increased. The same behavior was observed previously [17]. The fact that the rate of reaction (II) decreased with  $[H_m\text{HPA-4}]$  at the same value of  $m^*$  suggests that it depends much more strongly on the pH of  $H_m\text{HPA-4}$  solutions than on the concentration of  $H_m\text{HPA-4}$ .

A decrease in the reaction rate with increasing concentration of  $H_m\text{HPA-4}$  solutions can be explained by an increase in the concentration of intrinsic  $H^+$  ions in these solutions. In this case, the  $\text{HPA-4}_{m=3}$  anions active toward  $O_2$  reversibly dissociate to form inactive



**Fig. 2.** Dependence of (a)  $\log w$  of reaction (II) and (b) the pH of  $H_m\text{HPA-4}$  solutions on the degree of reduction ( $m^*$ ).  $[H_m\text{HPA-4}]$ , mol/l: (1) 0.05, (2) 0.10, (3) 0.20, and (4) 0.30.

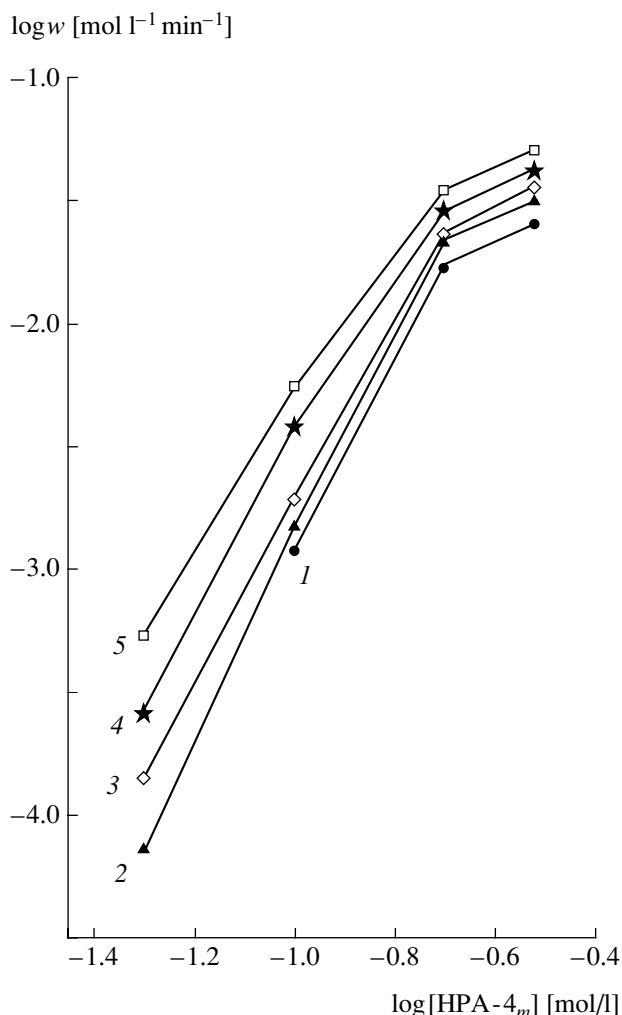
$\text{HPA-3}_{m=2}$  and  $\text{HPA-2}_{m=1}$  anions, as well as  $\text{VO}^{2+}$  and  $\text{VO}_2^+$  cations, by the following equilibrium reactions [12]:



In Eqs. (XI)–(XIII), the stoichiometric coefficient of  $\text{H}^+$  (equal to 29) is higher than the stoichiometric coeffi-

**Table 1.** Dependence of the values of  $m^*$  on the concentration of  $H_m\text{HPA-4}$  at fixed pH values (Fig. 2)

$[H_m\text{HPA-4}]$ , mol/l	0.05	0.10	0.20	0.30
$m_{\{\text{pH} = 1.20\}}^*$	1.30	1.70	2.24	2.53
$m_{\{\text{pH} = 1.05\}}^*$	0.73	1.52	2.05	2.32



**Fig. 3.**  $\log w$  versus  $\log [\text{H}_m\text{HPA-4}]$  for reaction (II) at pH (1) 1.05, (2) 1.08, (3) 1.10, (4) 1.15, and (5) 1.20.

cients of  $\text{HPA-}x_m$  (equal to 9, 10, and 11, respectively). This fact provides support for the conclusion that  $w$  depends on  $[\text{H}^+]$  more strongly than on  $[\text{H}_m\text{HPA-4}]$ .

The active  $\text{HPA-4}_{m=4}$  anion also underwent analogous equilibrium dissociation (V) with the elimination of the inactive  $\text{VO}^{2+}$  cation [12].

Equilibria like (XI)–(XIII) occur in aqueous solutions of all  $\text{H}_m\text{HPA-}x$  with  $x > 1$  [12]. The relative concentration of active  $\text{HPA-}x_{m \geq 3}$  anions decreases because of a shift of these equilibria to the right as the acidity of  $\text{H}_m\text{HPA-}x$  increases. Therefore, to evaluate the true effect of the concentration of  $\text{H}_m\text{HPA-}x$  on the rate of reaction (II), we compared the values of  $\log w$  for various concentrations of  $\text{H}_m\text{HPA-4}$  at fixed pH values of these solutions.

We chose values of pH equal to 1.05, 1.08, 1.10, 1.15, and 1.20.<sup>4</sup> It follows from Fig. 2b that, in solutions with different concentrations of  $\text{H}_m\text{HPA-4}$ , fixed values of pH were reached at different degrees of reduction of these solutions ( $m_{\{\text{pH}\}}^*$ ); in this case, the higher  $[\text{H}_m\text{HPA-4}]$ , the higher the value of  $m_{\{\text{pH}\}}^*$  at which a given pH value is reached (see Table 1). The corresponding values of  $m_{\{\text{pH}\}}^*$  at five fixed pH values were calculated from Fig. 2b for four concentrations of  $\text{H}_m\text{HPA-4}$ . Next, the values of  $\log w$  corresponding to  $m_{\{\text{pH}\}}^*$  were found from Fig. 2a and graphs were plotted in the  $\log w = f(\log [\text{H}_m\text{HPA-4}])$  coordinates for fixed pH values (Fig. 3). The resulting functions were almost linear over the range  $0.05 \text{ mol/l} \leq [\text{H}_m\text{HPA-4}] \leq 0.20 \text{ mol/l}$ , and the slope of the straight lines was 2.65–2.95 (the average value was  $\approx 2.8$ ). At  $[\text{H}_m\text{HPA-4}] > 0.20 \text{ mol/l}$ , the slope decreased to unity. These results suggest that, at  $\text{H}_m\text{HPA-4}$  concentrations higher than  $0.20 \text{ mol/l}$ , the order of reaction (II) with respect to  $\text{H}_m\text{HPA-4}$  changed from 3 to 1.

Previously, it was found that, in model systems at  $m^* \leq 0.84$ , reaction (II) was of third order with respect to  $\text{H}_m\text{HPA-}x$  [6]. This was explained by the occurrence of equilibrium steps (VII) and (VIII), which are required for the formation of a heteropoly anion with three  $\text{V}^{\text{IV}}$  atoms. However, as follows from Table 1, the values of  $m_{\{\text{pH}\}}^*$  for solutions with  $[\text{H}_m\text{HPA-4}] \geq 0.20 \text{ mol/l}$  are always higher than 2 over the range  $1.05 \leq \text{pH} \leq 1.20$ . Therefore, at these  $\text{H}_m\text{HPA-4}$  concentrations, equilibria (VII) and (VIII) are significantly shifted to the right and the fraction of active  $\text{HPA-4}_{m \geq 3}$  anions is close to the total concentration of  $\text{H}_m\text{HPA-4}$ . The first orders of reaction (II) with respect to  $\text{O}_2$  and  $\text{H}_m\text{HPA-}x$  at  $m^* \geq 2.0$  found from graphs in Figs. 1 and 3 suggest that the rate of reaction (II) in this region of  $m^*$  is limited by the formation of the active intermediate complex  $[\text{HPA-}x_{m \geq 3} \cdot \text{O}_2]$  [6]. It is expressed by the simple rate equation

$$w = k_{\text{IX}}[\text{HPA-}x_{m \geq 3}][\text{O}_2]. \quad (3)$$

In previous publications devoted to the oxidation of  $\text{VO}^{2+}$  to  $\text{VO}_2^+$  with dioxygen in the presence of  $\text{H}_m\text{HPA-6}$  [4] and  $\text{H}_m\text{HPA-3}$  [5], the first order of reaction with respect to  $\text{H}_m\text{HPA-}x$  was also found. In this case (at  $[\text{VO}^{2+}] \gg [\text{H}_m\text{HPA-}x]$ ), all equilibria (VI) were shifted to the formation of heteropoly anions with maximum values of  $m$ , that is,  $\text{HPA-}x_{m=x}$  ions. Moreover, in

<sup>4</sup> We failed to use values outside the range of pH 1.05–1.20 because the values of  $w$  very strongly changed even over narrow ranges of pH and  $m^*$  values. Table 1 demonstrates the functions  $m_{\{\text{pH}\}}^* = f([\text{H}_m\text{HPA-4}])$  at the fixed limiting values of pH 1.20 and 1.05.

the studies of the oxidation of  $\text{VO}^{2+}$  to  $\text{VO}_2^+$ ,  $\text{H}_m\text{HPA}-x$  molecules contained no less than three  $\text{V}^{\text{IV}}$  atoms [5]. Therefore, the concentration of active  $\text{HPA}-x_{m \geq 3}$  ions was always close to the total concentration of  $\text{H}_m\text{HPA}-x$ .

In this work, we found for the first time that the limiting value of  $m^*$  that corresponds to a change from the third order of the reaction with respect to  $\text{H}_m\text{HPA}-4$  to the first order is  $\sim 1.9$ – $2.0$ . The third order of the reaction with respect to  $\text{H}_m\text{HPA}-x$  at low values of  $m^*$ , which was found previously [6, 7], as well as observed in this work, provides support for the occurrence of pre-equilibria (VII) and (VIII), which are responsible for the formation of the active  $\text{HPA}-x_{m \geq 3}$  anion. Thus, our results are consistent with data published in [4, 5] (where the first order with respect to  $\text{H}_m\text{HPA}-x$  was found at  $m^* \approx x$ ) and [6, 7] (the third order with respect to  $\text{H}_m\text{HPA}-x$  at  $m^* \leq 0.84$ ).

Using data given in Fig. 3, we plotted  $\log w$  as a function of  $\log [\text{H}^+]$  for four fixed values of  $[\text{H}_m\text{HPA}-4]$  (Fig. 4). The value of  $w$  decreased with  $[\text{H}^+]$ ; however, the order of the reaction with respect to  $\text{H}^+$  ( $n_{\text{H}^+}$ ) was variable. At  $[\text{H}_m\text{HPA}-4] = 0.05, 0.10, 0.20$ , or  $0.30$  mol/l, it was equal to  $-7.1, -4.9, -2.5$ , or  $-0.4$ , respectively. Thus, the inhibition of reaction (II) by  $\text{H}^+$  ions rapidly weakened as the concentration of  $\text{H}_m\text{HPA}-4$  was increased.

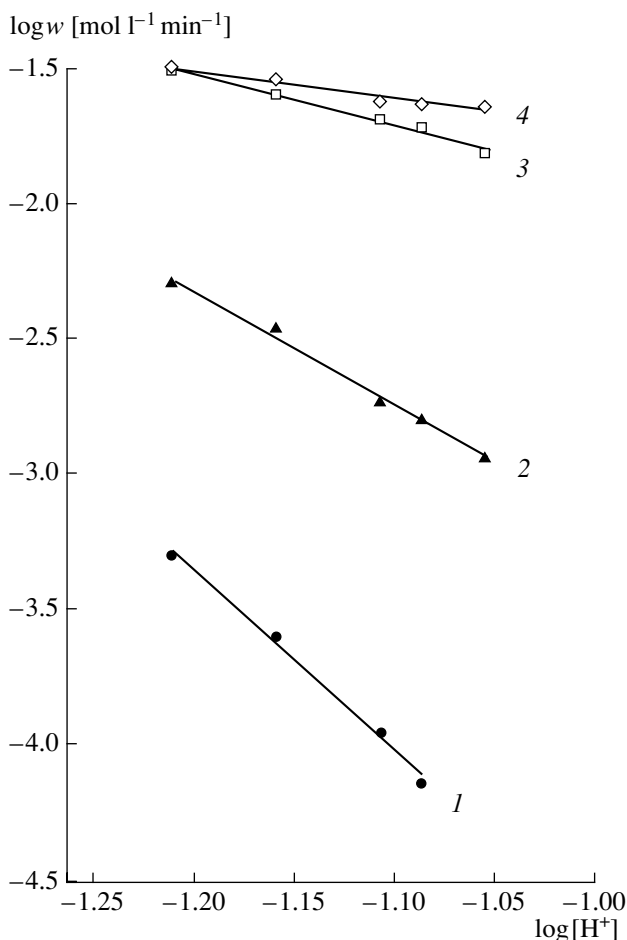
The theoretical value of  $n_{\text{H}^+}$  can be calculated for the set of equilibria (XI)–(XIII). It can vary from zero to  $-9.75$  depending on  $\text{H}^+$  concentration.<sup>5</sup> At  $n_{\text{H}^+} = 0$ , all of these three equilibria are shifted to the left, whereas they are shifted to the right at  $n_{\text{H}^+} = -9.75$ . The experimental values of  $n_{\text{H}^+}$  found from Fig. 4 did not go beyond the theoretical limits  $0 \geq n_{\text{H}^+} \geq -9.75$ .

To support the possibility of formation of active  $\text{HPA}-4_{m \geq 3}$  anions in a strongly acidic medium through equilibria (XIII)–(XII)–(XI), we studied the effect of an excess of  $\text{VO}^{2+}$  cations in solutions of  $(\text{VO})_z\text{HPA}-4_m$  ( $0 \leq z \leq 2$ ) on the rate of reaction (II). The resulting functions  $\log w = f(m^*)$  for solutions with various values of  $z$  are plotted in Fig. 5a, whereas Fig. 5b shows the dependence of pH on  $m^*$  in the above solutions of  $(\text{VO})_z\text{HPA}-4_m$ .

To determine the dependence of  $\log w$  on  $z$ , we chose, in Fig. 5b, the fixed values of pH 0.7, 0.8, 0.9, and 1.0 for the solutions of  $(\text{VO})_z\text{HPA}-4_m$  and found the corresponding values of  $m_{\{\text{pH}\}}^*$  for each of the above pH values (for example, see Table 2).<sup>6</sup> Next, for each particular value of  $m_{\{\text{pH}\}}^*$  in each of the curves in Fig. 5a, we found the corresponding values of  $\log w$ . Based on

<sup>5</sup> The value of  $9.75 = 29/8 + 29/9 + 29/10$ , where 29 is the stoichiometric coefficient of  $\text{H}^+$  ions and 8, 9, and 10 are the stoichiometric coefficients of heteropoly anions in equilibria (XI)–(XIII).

<sup>6</sup> Table 2 gives only the limiting fixed values of pH 0.7 and 1.0. We failed to use values of pH beyond this range.



**Fig. 4.**  $\log w$  for reaction (II) versus  $\log [\text{H}^+]$  at various fixed values of  $[\text{H}_m\text{HPA}-4]$ , mol/l: (1) 0.05, (2) 0.10, (3) 0.20, and (4) 0.30.

these data, we plotted  $\log w$  as a function of  $z$  (Fig. 6). According to the calculations, the shapes of the curves depend on the pH of the  $(\text{VO})_z\text{HPA}-4_m$  solutions. At pH  $\sim 0.7$ – $0.8$ , the rate of reaction increased with  $z$ , whereas it became independent of  $z$  at pH  $\sim 0.9$ – $1.0$ .

The experimental results demonstrate that, at pH  $\leq 0.8$ , the destructive dissociation of active  $\text{HPA}-4_{m \geq 3}$  anions in accordance with reaction scheme (XI)–(XIII) is significant and the rate-limiting step of reaction (II)

**Table 2.** Dependence of  $m^*$  in 0.20 M  $(\text{V}^{\text{IV}}\text{O})_z\text{HPA}-4_m$  solutions on  $z$  at fixed pH values (Fig. 5)

$z = [\text{VO}^{2+}]_{\text{excess}}/[\text{H}_m\text{HPA}-4]$	0	1.0	1.5	2.0
$m_{\{\text{pH} = 0.7\}}^*$	1.43	1.68	1.84	1.95
$m_{\{\text{pH} = 1.0\}}^*$	1.95	2.03	2.27	2.39

is the formation of HPA-4<sub>m≥3</sub> anions by the interaction of HPA-4<sub>m≤2</sub> with the VO<sup>2+</sup> cation in the reverse reactions of (XIII)–(XII)–(XI). At pH ≥ ~0.9, the concentration of active HPA-4<sub>m≥3</sub> anions is sufficiently high and the rate of reaction (II) is limited by the formation of an active intermediate complex by reaction (IX) [9] rather than the formation of these active ions. At the same time, at  $z > 0$ , another active intermediate complex can be formed, which has the composition [HPA-4<sub>m</sub> · (VO<sup>2+</sup>)<sub>y</sub> · O<sub>2</sub>], where  $m + y ≥ 3$  [9].

The temperature dependence of the rate of reaction (II) in H<sub>m</sub>HPA-4 solutions was studied over the range  $313 ≤ T ≤ 363$  K. A decrease in the temperature resulted in the termination of the reaction at higher values of  $m_f^*$ . For example, at 363, 343, 323, or 313 K, the reaction was practically terminated at  $m_f^* = 1.06, 1.20, 1.71$ , or  $1.79$ , respectively.

The partial pressure of dioxygen ( $P_{O_2}$ ) in the reactor over a solution of H<sub>m</sub>HPA-4 depends on temperature because the pressure of water vapor ( $P_{H_2O}$ ) is temperature-dependent [22]. With consideration for the first order of reaction (II) with respect to O<sub>2</sub> (Fig. 1) and the values of  $P_{H_2O}$  at the corresponding temperature, the values of  $w$  were converted to  $P_{O_2} = 101.3$  kPa (1 atm) and used for plotting  $\log w = f(T^{-1})$  (Fig. 7).

The found activation energy ( $E_a$ ) of reaction (II) was a variable. At  $m^* ≥ 1.9$ ,  $E_a$  was low and equal to  $(10 ± 4)$  kJ/mol over the entire range of temperatures (313–363 K). As  $m^*$  decreased below 1.9, the value of  $E_a$  rapidly increased. Moreover, at low values of  $m^*$  ( $≤ 1.8$ ), it depended on the range of temperatures (Fig. 8). Thus, at  $m^* = 1.8$ ,  $E_a = 44, 53$ , or even 190 kJ/mol over

the range 358–363, 338–348, or 313–318 K, respectively. A decrease in the value of  $m^*$  to  $< 1.8$  (for example, over the range 338–348 K) was accompanied by an increase in  $E_a$  to values higher than 200 kJ/mol (Fig. 8, curve 2).

As mentioned above, at low values of  $m^*$ , the rate of reaction (II) strongly depended on preequilibria (VII) and (VIII). If these preequilibria are considered endothermic, the variable value of  $E_a$  can be explained by different contributions of these preequilibria to the overall reaction (II) at various values of  $m^*$ .

If  $m^* > 1.9–2.0$ , preequilibria (VII) and (VIII) did not limit the rate of reaction (II). As  $m^*$  decreased, equilibrium (VIII) began to limit the rate of reaction (II). In this case, the rate of reaction is expressed by Eq. (4), which is similar to the Michaelis–Menten equation [23]:

$$w = k_{IX}[\text{HPA-}x_{m=3}][\text{O}_2] = k_{IX} \times \left[ \frac{K_{VIII}[\text{HPA-}x_{m=2}]^2[\text{HPA-}x_{m=1}]^{-1}}{1 + K_{VIII}[\text{HPA-}x_{m=2}]^2[\text{HPA-}x_{m=1}]^{-1}} \right] [\text{O}_2]. \quad (4)$$

The values of  $k_{IX}$  and  $K_{VIII}$  depend on temperature:

$$k_{IX} = k_{IX}^0 \exp\left(-\frac{E_{a,IX}}{RT}\right), \quad (5)$$

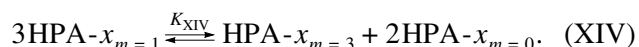
$$K_{VIII} = K_{VIII}^0 \exp\left(\frac{\Delta_r H_{VIII}}{RT}\right), \quad (6)$$

where  $E_{a,IX}$  is the activation energy of formation of the active intermediate complex [HPA- $x_{m≥3}$  · O<sub>2</sub>] and  $-\Delta_r H_{VIII}$  characterizes the heat of equilibrium step (VIII). With consideration for Eqs. (5) and (6), Eq. (4) may be rearranged to give

$$w = k_{IX}^0 \exp\left(-\frac{E_{a,IX}}{RT}\right) \left[ \frac{K_{VIII}^0 \exp\left(\frac{\Delta_r H_{VIII}}{RT}\right) [\text{HPA-}x_{m=2}]^2 [\text{HPA-}x_{m=1}]^{-1}}{1 + K_{VIII}^0 \exp\left(\frac{\Delta_r H_{VIII}}{RT}\right) [\text{HPA-}x_{m=2}]^2 [\text{HPA-}x_{m=1}]^{-1}} \right] [\text{O}_2]. \quad (7)$$

If  $m^* ≈ 1.9–2.0$ , unity in the denominator of Eq. (6) can be ignored. In this limiting case,  $E_a ≈ E_{a,IX}$ . As  $m^*$  decreases, the fraction of more strongly oxidized HPA- $x_{m=1}$  anions increases; therefore, the second term in the denominator of Eq. (7) can be ignored. Then,  $E_a ≈ E_{a,IX} - \Delta_r H_{VIII}$ . Between these two limiting cases,  $E_{a,IX} < E_a < E_{a,IX} - \Delta_r H_{VIII}$ .

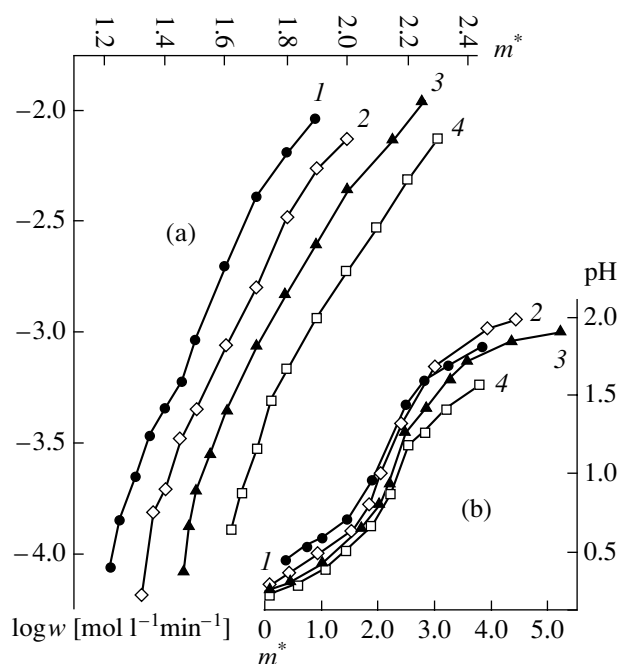
At very low values of  $m^*$  ( $→ m_f^*$ ), both equilibria (VII) and (VIII) are shifted to the left. They are equivalent to the overall equilibrium



Therefore, at  $m^* → m_f^*$ , the following equation is true:

$$w = k_{IX}^0 K_{XIV}^0 \exp\left(-\frac{E_{a,IX} - \Delta_r H_{XIV}}{RT}\right) \times \frac{[\text{HPA-}x_{m=1}]^3}{[\text{HPA-}x_{m=0}]^2} [\text{O}_2]. \quad (8)$$

Equation (8), which gives the third order of reaction with respect to the weakly reduced HPA- $x_{m=1}$  species (i.e., with respect to V<sup>IV</sup>), is consistent with published

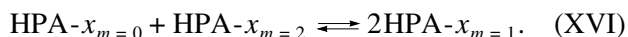
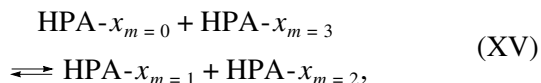


**Fig. 5.** (a)  $\log w$  for reaction (II) and (b) the pH of 0.20 M solutions of  $(V^{IV}O)_z\text{HPA-}4_m$  versus the degree of reduction ( $m^*$ ).  $z = (1) 0, (2) 1.0, (3) 1.5$ , and  $(4) 2.0$ .

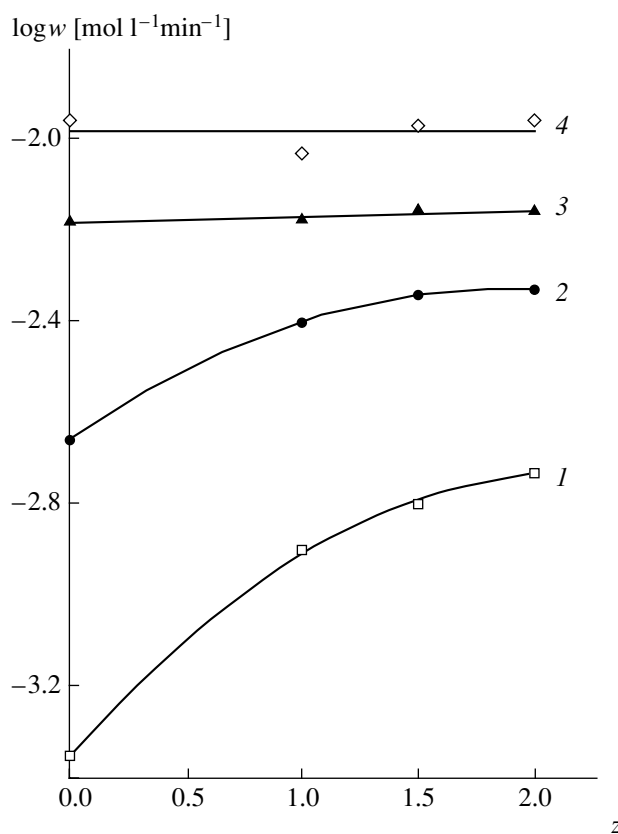
data [6, 7]. At  $m^* \rightarrow m_f^*$ , the value of  $E_a$  falls within the range  $E_{a,IX} - \Delta_r H_{VIII} < E_a < E_{a,IX} - \Delta_r H_{XIV}$ .

The value of  $-\Delta_r H_{XIV}$  characterizes the enthalpy of overall equilibrium (XIV). The contributions of  $-\Delta_r H_{VIII}$  or  $-\Delta_r H_{XIV}$  to the value of  $E_a$  can vary from 0 to 190 kJ/mol or higher depending on the shifts of pre-equilibria (VIII) or (XIV). The actual position of these pre-equilibria depends on the value of  $m^*$ .

In the course of reaction (II), the solutions of  $H_m\text{HPA-}x$  were enriched in oxidized  $\text{HPA-}x_{m=0}$  anions after the decomposition of an active intermediate complex in accordance with reaction (IX) or (X). These oxidized anions rapidly reacted with more strongly reduced  $\text{HPA-}x_{m=3}$  or  $\text{HPA-}x_{m=2}$  anions via equilibrium reactions (XV) and (XVI), which are the reverse of reactions (VII) and (VIII), respectively. In this case, anions with intermediate values of  $m$  were formed.



Equilibria (XV) and (XVI) are the reactions of averaging all of the heteropoly anions over the value of  $m^*$ . Because forward reactions (VII) and (VIII) are endothermic, reverse reactions (XV) and (XVI), respectively, are exothermic.

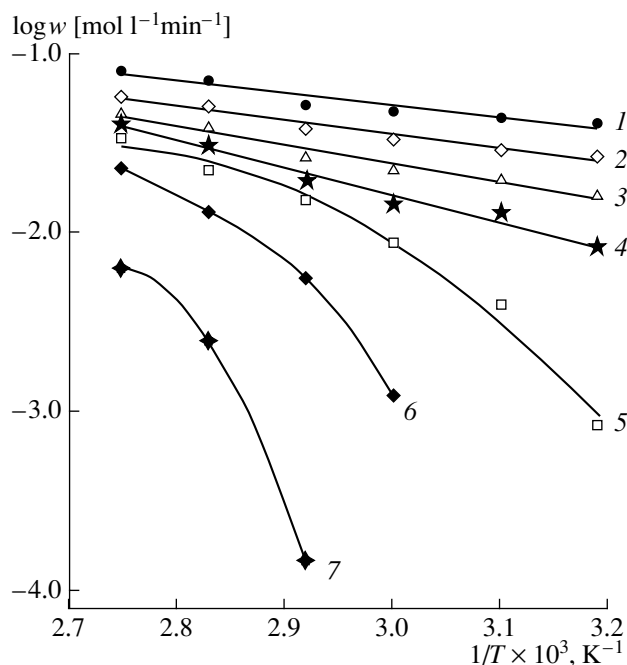


**Fig. 6.**  $\log w$  for reaction (II) versus the value of  $z$  for 0.20 M solutions of  $(V^{IV}O)_z\text{HPA-}4_m$  at various fixed pH values: (1) 0.7, (2) 0.8, (3) 0.9, and (4) 1.0.

At high values of  $m^*$  ( $>1.9$ ), the concentration of active  $\text{HPA-}x_{m \geq 3}$  ions is high and the contribution of endothermic steps (VII) and (VIII) to overall reaction (II) is small. Therefore, these steps have a minimum effect on the apparent activation energy of reaction (II). In a previous thermochemical study [20], we found that, at high values of  $m^*$  ( $\geq 1.9$ ), the heat of reaction (II),  $-\Delta_r H_{II}$ , is high. Thus, at  $m^* = 2.5$ , it is equal to 290 kJ/mol  $\text{O}_2$ , whereas it is 210 kJ/mol  $\text{O}_2$  at  $m^* = 1.9$ . At these high values of  $m^*$ , the value of  $-\Delta_r H_{II}$  is primarily affected by exothermic steps (XV) and (XVI).

On the contrary, at low values of  $m^* \rightarrow m_f^*$ , exothermic steps (XV) and (XVI) make a minimum contribution to the overall heat of reaction (II); however, the contribution of endothermic steps (VII) and (VIII) is high. Thus, at  $m^* = 1.3$ , the value of  $-\Delta_r H_{II}$  was as low as 150 kJ/mol  $\text{O}_2$  [20]. At these low values of  $m^*$ , the  $E_a$  of reaction (II) increases because of the contribution of endothermic components  $-\Delta_r H_{XV}$  and  $-\Delta_r H_{XVI}$  (Fig. 8). Therefore, the degree of oxidation of both  $H_m\text{HPA-}4$  and other  $H_m\text{HPA-}x$  can be increased by a considerable increase in the rate of reaction (II) with increasing reaction temperature. In order not to





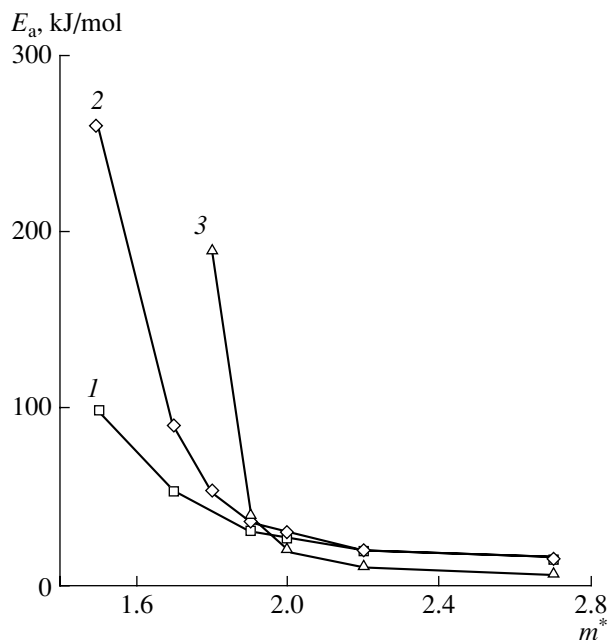
**Fig. 7.**  $\log w$  for reaction (II) versus the reciprocal of absolute temperature for 0.20 M solutions of  $H_m\text{HPA-4}$  (at  $P_{\text{O}_2} = 1$  atm).  $m^* = (1)$  2.7, (2) 2.2, (3) 2.0, (4) 1.9, (5) 1.8, (6) 1.7, and (7) 1.5.

decrease  $P_{\text{O}_2}$  at higher temperatures, the reaction should be performed under a pressure of  $\text{O}_2$ .

Thus, the mechanism of  $H_m\text{HPA-}x$  oxidation with oxygen consists of the following four steps: (1) the formation of strongly reduced  $\text{HPA-}x_{m \geq 3}$  anions due to the disproportionation of weakly reduced  $\text{HPA-}x_{m \leq 2}$  anions in preequilibrium reactions (VII) and (VIII); (2) the formation of the active intermediate complexes  $[\text{HPA-}x_{m \geq 3} \cdot \text{O}_2]$  in reactions (IX) and (X); (3) the transfer of three or four electrons from  $\text{HPA-}x_{m \geq 3}$  anions to the coordinated  $\text{O}_2$  molecule within the active intermediate complex in reactions (IX) and (X) followed by the degradation of the active intermediate complex to form either an unreduced  $\text{HPA-}x_{m=0}$  anion or a weakly reduced  $\text{HPA-}x_{m=1}$ ; and (4) the averaging of the degrees of reduction of all heteropoly anions in the solution of  $H_m\text{HPA-}x$  in reactions (XV) and (XVI).

In the region of high degrees of reduction ( $m^* > 1.9$ ), preequilibria (VII) and (VIII) are shifted to the right and the concentration of active  $\text{HPA-}x_{m \geq 3}$  anions is high. Because the contribution of step (1) to the apparent rate of reaction is insignificant in this region of  $m^*$ , it was not mentioned previously by Berdnikov and coauthors [4, 5]. On the contrary, in the region of low values of  $m^*$ , exothermic equilibrium steps (XV) and (XVI) of step (4) of reaction (II) “faded.”

Based on the experimental data, the rate of oxidation of 0.2 M  $H_m\text{HPA-4}$  solutions in accordance with reaction (II) at  $m^* \geq 1.9$  and  $\text{pH} \geq 0.9$  over the temperature



**Fig. 8.** Dependence of the activation energy of reaction (II) on the degree of reduction ( $m^*$ ) for 0.20 mol/l solutions of  $H_m\text{HPA-4}$  over various temperature ranges, K: (1) 358–363, (2) 338–348, and (3) 313–318.

range  $303 \leq T \leq 363$  K can be approximately described by the equation

$$w = k_{\text{apparent}} [\text{H}_m\text{HPA-4}]^{2.8} [\text{H}^+]^{-2.5} P_{\text{O}_2} \exp\left(-\frac{10 \pm 4}{RT}\right). \quad (9)$$

However, at low values of  $m^*$  and  $\text{pH}$  ( $m^* < 1.9$ ;  $\text{pH} \leq 0.8$ ), the reaction kinetics becomes dramatically more complicated because inactive  $\text{HPA-4}_{m \leq 2}$  anions, which occur in equilibria (VIII) and (VII) with active  $\text{HPA-4}_{m \geq 3}$  anions, begin to predominate among the heteropoly anions. The consideration of these equilibria dramatically complicates the kinetics of reaction (II). For this reason, the entire range of  $m^*$  cannot be described by a single rate equation.

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