

Recovery of Catalysts Around $H_5PV_2Mo_{10}O_{40}$ Heteropoly Acid Solutions under a Pressure of Oxygen

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Abstract

The possibility in principle for applying the concentrated aqueous solutions of heteropoly acid of composition $H_5PV_2Mo_{10}O_{40}$ (HPA-2) as the stable reversibly reacting oxidizers was shown. The reduced form of HPA-2 can be oxidized by oxygen at 353–433 K under a pressure of as much as 8 kg/cm² thereby reclaiming HPA-2. An effect of temperature and pressure on the depth and reaction rate of oxidation has been investigated. Reduced and oxidized HPA-2 solutions are stable up to 463 K.

INTRODUCTION

The specialty chemical processes very often involve such irreversible oxidizer as CrO_3 for oxidation of organic compounds [1, 2]. It is used to oxidize anthracene to anthraquinone, 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone (vitamin K_3), linalyl ester to citral, and the like. In this case, CrO_3 is reduced to the compounds of chrome (III), which are classed as the harmful production wastes. Alternative irreversible oxidizers, such as $KMnO_4$, compounds of Co(III) and Ce(IV), and the like have been reported too [1]. The reduced species of these compounds containing Mn(IV), Co(II), Ce(III) need to be dispatched to waste or to be submitted for an advanced processing.

We offer Mo–V-phosphoric heteropoly acids of Keggin type structure [3, 4] as the *reversibly reacting* oxidizers (RRO) for organic compounds instead of irreversible ones. They are $H_{3+x}PV_x^V Mo_{12-x}O_{40}$ = HPA- x in composition, where x is the number of vanadium atoms in HPA- x ($2 \leq x \leq 6$) molecule. The reduced HPA- x species, which are $H_{3+x+m}PV_m^{IV}V_{x-m}^V Mo_{12-x}O_{40}$ = H_m HPA- x in composition, can be oxidized by molecular oxygen [5, 6].

A two-stage process of substrate (H_2Su) oxidation in the presence of HPA- x typically takes place. First, H_2Su is oxidized using HPA- x as an oxidizer, which is reduced by m electrons:

$$\begin{aligned} \frac{m}{4}H_2Su + \frac{m}{4}H_2O + HPA-x \\ \rightleftharpoons \frac{m}{4}SuO + H_mHPA-x \end{aligned} \quad (1)$$

Then HPA- x is recovered by oxygen:

$$H_mHPA-x + \frac{m}{4}O_2 \rightleftharpoons HPA-x + \frac{m}{2}H_2O \quad (2)$$

One of the most typical HPA- x is HPA-2 ($H_5PV_2Mo_{10}O_{40}$), the producing method of which has been known since 70s of 20th century [7]. HPA-2 is employed as a catalyst, for example, in the high-temperature heterogeneous oxidation of metacrolein to methacrylic acid [8]. Water solutions of HPA-2 thus far have not been applied in homogeneous catalysis, as their recovery by oxygen goes extremely slowly [9]. A gain of the recovery rate by several orders of magnitude for HPA-2 solutions would allow their adoption as RRO.

Previously, we have suggested water solutions of vanadium-rich HPA- x as RRO [10–12], which can be recovered much easier than HPA-2 [6]. However, above 433 K such solutions start precipitating the deposits of mixed-valence hydroxides V^V and V^{IV} [13], since vanadium-bearing HP-anions in these solutions

readily interact with H^+ ions to eliminate VO_2^+ cation [14]. Resulting from this is that the HPA- x solutions with $x \geq 3$ are thermally unstable. Solutions of HPA-2 are more stable with respect to H^+ ions action as compared to HPA-4 solutions [14].

In the present work, we succeeded in drastic acceleration of the recovery of HPA-2 solutions by oxygen as we performed it at elevated temperatures (up to 433 K) under a pressure of O_2 up to 8 kg/cm². It has opened up the prospects for putting HPA-2 solutions to work as effective and stable RRO for various organic compounds. This work describes the regularities in the recovery of HPA-2 solutions for the first time.

COMPOSITION OF HPA-2 WATER SOLUTIONS

Reduced HPA-2 solutions (*i.e.* H_m HPA-2) represent the complex equilibrium system, which includes HP-anions $H_3PV_2^{IV}Mo_{10}O_{40}^{4-}$ (HPAN-2 _{$m=2$}), $H_2PV^{IV}V^VMo_{10}O_{40}^{4-}$ (HPAN-2 _{$m=1$}), and $HPV_2^VMo_{10}O_{40}^{4-}$ (HPAN-2 _{$m=0$})^a, together with VO^{2+} and VO_2^+ cations [15, 16]. Anions HPAN-2 _{$m=0$} and HPAN-2 _{$m=2$} disproportionate in such solutions to form a series of HP-anions HPAN- x_m with the other x values, for example [17]: $HPAN-2_{m=0} (x=2) \ll HPAN-3_{m=0} + HPAN-1_{m=0}$. In addition, semi-reduced HPAN-2 _{$m=1$} anions disproportionate to form HPAN-2 _{$m=0$} and HPAN-2 _{$m=2$} [15]. The Keggin type structure is preserved upon the reduction and disproportionation of HP-anions [18].

Complex composition of the reduced H_m HPA-2 solutions can be characterized by an average degree of their reduction $m^* = [V^{IV}]/[H_mHPAN-2]$, where $[V^{IV}]$ is the total concentration of vanadium (IV), $[H_mHPAN-2]$ is the total concentration of HP-anions in H_m HPAN-2 solution. For all H_m HPA-2 solutions $0 \leq m^* \leq 2$ holds true. The magnitude m^* decreases during the reaction (2) due to partial oxidation of vanadium (IV) to vanadium (V):

$$4[V^{IV}]_{HPA-2} + O_2 \rightleftharpoons 4[V^V]_{HPA-2} \quad (3)$$

Such oxidation of vanadium (IV) takes place only within the structure of HP-anions, since

^aFirst of these HP-anions is reduced completely, the second is half-reduced, the third is not reduced.

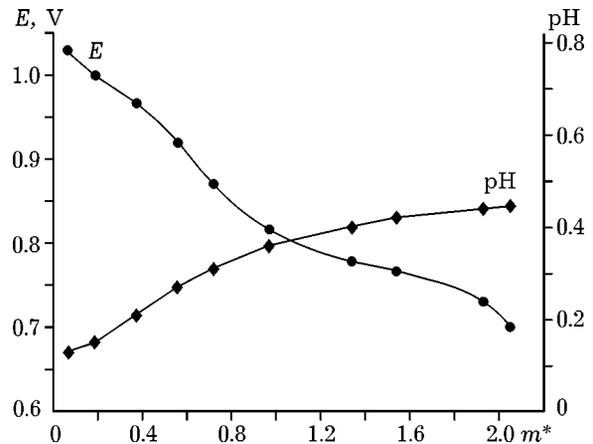


Fig. 1. Redox potential E and pH of the 0.2 M H_m HPA-2 solution versus its reduction degree m^* .

VO^{2+} cation cannot be oxidized by oxygen in acidic medium [19].

EXPERIMENTAL

Water solutions of HPA-2 of 0.1–0.4 M concentration were obtained from V_2O_5 , MoO, and H_3PO_4 following the procedure [20]. Before the experiments, they were reduced by 10 M $N_2H_4 \cdot H_2O$ water solution to produce H_m HPA-2 [21]. The value m^* of H_m HPA-2 solution before and after its oxidation by oxygen was found from the calibration curve $E = f(m^*)$ [22], where E was the redox potential of H_m HPA-2 solution (Fig. 1). The initial value m_r^* in the bulk of experiments was 1.84 ($E_r = 0.740$ V), whereas the final value m_t^* varied from 1.8 up to 0.3.

Reaction (2) was studied in a temperature-controlled stainless steel autoclave of 150 ml capacity from [14]. The autoclave was loaded with a glass cup with 20 ml of H_m HPA-2 solution being investigated and with a magnetic rod for stirring the solution on a magnetic stirrer. Upon stabilizing the temperature, O_2 was delivered to the autoclave. The pressure ($p_{O_2} + p_{H_2O}$)^b was measured by an exemplary manometer with an accuracy of ± 0.05 kg/cm². Reaction (2) was let to proceed for a fixed time (2–30 min), then stirring and heating was discontinued, the O_2 pressure was promptly dissipated through a reflux condenser and the

^b p_{H_2O} is the temperature-dependent pressure of water vapour above the H_m HPA-2 water solution.

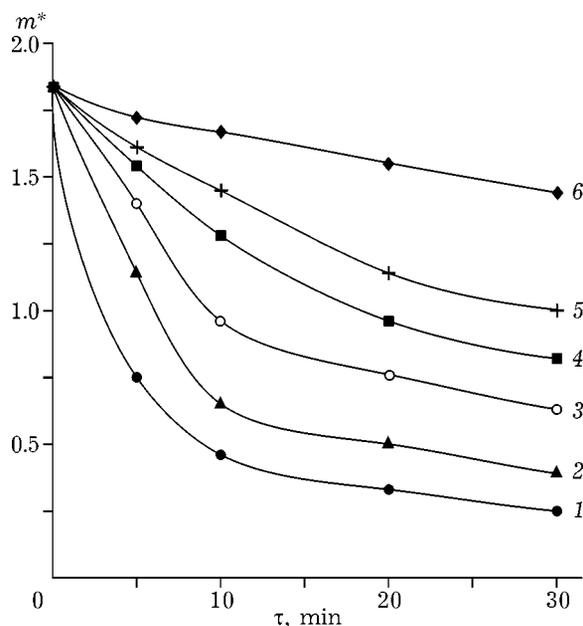


Fig. 2. Dependences of m^* on the time τ of oxidation of 0.2 M H_m HPA-2 solution by oxygen at different temperatures, K: 433 (1), 413 (2), 393 (3), 384 (4), 373 (5), 353 (6). At all temperatures $p_{O_2} = 4.0$ atm ($p_{O_2} = p_{tot} - p_{H_2O}$), $m_r^* = 1.84$.

autoclave was opened. The solution under investigation was cooled down to ambient temperature and its volume (20 ml) was checked.

The values E_r and E_f (initial and final) of H_m HPA-2 solutions were measured at ambient temperature using ionomer I-130 with EPV platinum electrode and saturated silver-chloride reference electrode ESL-1M3. The stationary value E with an accuracy of ± 0.001 V was established for 2–3 min.

Each experiment with H_m HPA-2 solution was performed 3–4 times so that the average values E_f and m_f^* be found. From the set of experiments, which have been performed with various time τ (from 2 to 30 min), the curves $m^* = f(\tau)$ were plotted for each value of temperature and O_2 pressure (Fig. 2). The rate of the reaction (3) was estimated as the rate of O_2 absorption by H_m HPA-2 solution for the region from m_τ^* to $m_{\tau+\Delta\tau}^*$ of $m^* = f(\tau)$ curve:

$$W_2 = (Dm/4) \frac{[H_m\text{HPA-2}]}{\Delta\tau} \quad (4)$$

Here $D\tau$ is a change of oxidation time, min; $Dm^* = m_\tau^* - m_{\tau+\Delta\tau}^*$ is a variation of m^* with time $D\tau$; W_2 is the reaction rate, mol $O_2/(l \text{ min})$;

$[H_m\text{HPA-2}]$ is given in mol/l; 4 is the stoichiometrical coefficient of the reaction (3).

The reaction rates for the chosen m^* values were determined from the slope ($Dm^*/D\tau$) of the curves $m^* = f(\tau)$; the values obtained were multiplied by $[H_m\text{HPA-2}]/4$ according to the formula (4).

RESULTS AND DISCUSSION

The reduction degree m^* of H_m HPA-2 solutions *versus* their time τ of oxidation by oxygen at various temperatures T are presented in Fig. 2. The magnitude of m^* strongly drops with the temperature rise at the same value of τ , which bears witness to a more complete HPA-2 recovery. Given below are the data about the temperature effect of oxidation of 0.2 M H_m HPA-2 solution by oxygen on the final reduction degree m_f^* at $p_{O_2} = 4$ atm (405 kPa), $m_r^* = 1.84$, and $\tau = 30$ min:

T, K	m_f^*
353	1.44
373	1.00
383	0.82
393	0.63
413	0.39
433	0.25

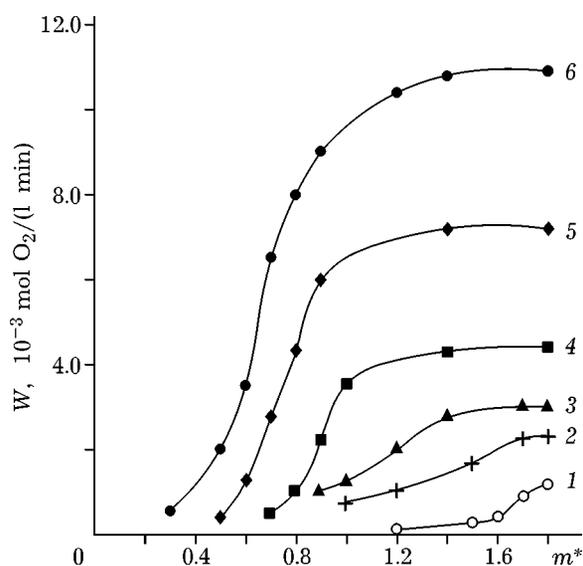


Fig. 3. Dependences of the rate of oxidation of 0.2 M H_m HPA-2 solution by oxygen on the magnitude of m^* for different temperatures, K: 353 (1), 373 (2), 383 (3), 393 (4), 413 (5), 433 (6). $m_r^* = 1.84$, $p_{O_2} = 4.0$ atm.

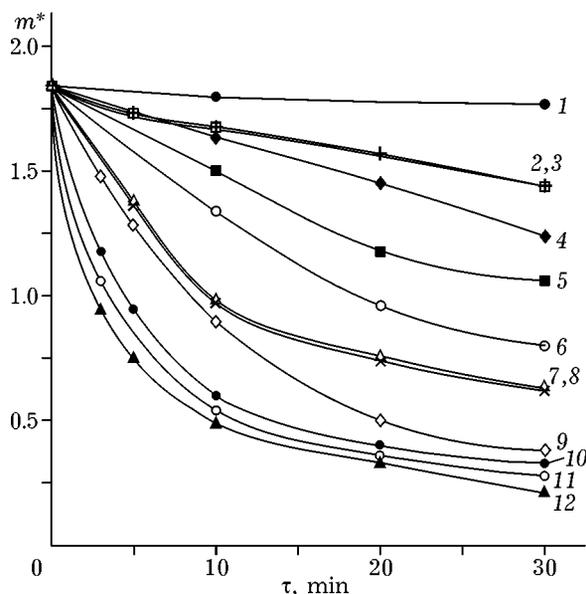


Fig. 4. Dependences of m^* on time of oxidation of 0.2 M H_m HPA-2 solution by oxygen at the different partial O_2 pressures for the constant temperatures ($m_r^* = 1.84$). $T = 353$ K: 1 - 1.0, 2 - 4.0, 3 - 8.0; $T = 393$ K: 4 - 0.5, 5 - 1.0, 6 - 2.0, 7 - 4.0, 8 - 8.0; $T = 433$ K: 9 - 0.5, 10 - 1.0, 11 - 2.0, 12 - 4.0.

At low temperatures (353–373 K), the reaction rate W_2 is practically constant in time. At higher temperatures (413–433 K), the values W_2 are large enough in the first 5–8 min and then they decrease.

The curves of $W_2 = f(m^*)$ relationship at various T values are presented in Fig. 3. As T increases from 353 to 433 K, the magnitude W_2 strongly rises for all values of m^* . In so doing the reaction rate W_2 at 433 K declines during the experiment by more than an order of magnitude (the curve 6); however, this reduction is not so significant at 393–413 K (the curves 4, 5). At $T < 373$ K, the values W_2 are very small, *i.e.* HPA-2 recovers too slowly.

The $m^* = f(t)$ relationship curves for various values of p_{O_2} are represented in Fig. 4. At 353 and 393 K the reaction rate increases with an increase in p_{O_2} from 1.0 to 4.0 atm, but its growth discontinues at $p_{O_2} > 4.0$ atm. At a temperature of 433 K the magnitude W_2 ceases to increase starting with $p_{O_2} = 1.0$ atm (compare the curves 9 and 10–12).

Figure 5 presents the curves of temperature dependence $\log W_2 = f(T^{-1})$ for the different values of m^* . The pressure p_{O_2} in these

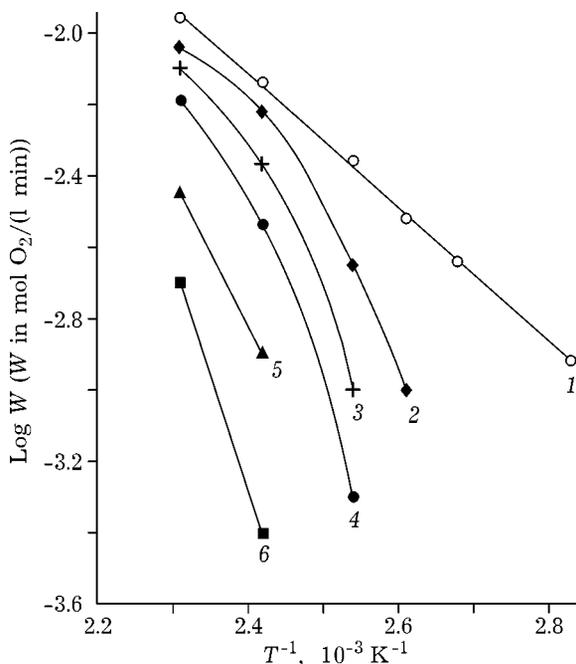


Fig. 5. The logarithmic rate of oxidation of 0.2 M H_m HPA-2 solution by oxygen *versus* the reciprocal absolute temperature at the different values of m^* : 1.7–1.8 (1), 0.9 (2), 0.8 (3), 0.7 (4), 0.6 (5), 0.5 (6). $m_r^* = 1.84$, $p_{O_2} = 4.0$ atm.

experiments has been chosen to be equal to 4.0 atm, since at $p_{O_2} > 4.0$ atm, the reaction rate becomes independent of p_{O_2} at all studied temperatures. It has been demonstrated that when $m^* > 1.7$ –1.8, the dependences $\log W_2 = f(T^{-1})$ are linear, the observed activation energy E_a^{obs} is constant and equal to 36 kJ/mol. As m^* decreases, the magnitude E_a^{obs} increases and becomes a variable. Accordingly, in the case $m^* = 0.9$, this magnitude is 36 kJ/mol at 413 $\leq T \leq 433$ K and increases up to 96 kJ/mol at 383 $\leq T \leq 393$ K. At further decrease of m^* , the value E_a^{obs} quickly rises at any temperature. For example, at $m^* = 0.5$ it is equal to 132 kJ/mol in the range 413–433 K.

It has been demonstrated in special experiments that with rise in temperature to 463 K the concentrated (0.2–0.4 M) HPA-2 solutions remain homogeneous both in the reduced and in the oxidized state. Hence, the HPA-2 solutions are distinguished from vanadium-rich HPA- x solutions in their *high thermal stability*.

Of interest is the dependence $m^* = f(t)$, which has been studied at $T = 433$ K and $p_{O_2} =$

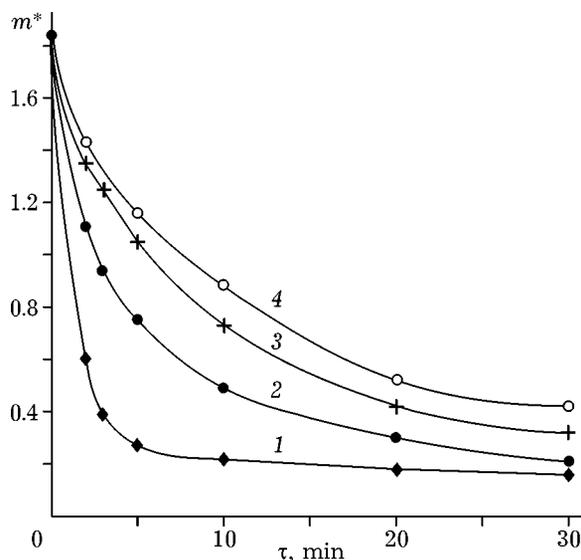


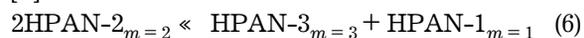
Fig. 6. Dependences of m^* magnitude on time for the reaction (2) at different concentrations of $H_m\text{HPA-2}$ solution, M: 1 - 0.1, 2 - 0.2, 3 - 0.3, 4 - 0.4. $T = 433\text{ K}$, $m_r^* = 1.84$; $p_{O_2} = 4.0\text{ atm}$.

4 atm at various concentrations of $H_m\text{HPA-2}$ (Fig. 6). With an increase in $[H_m\text{HPA-2}]$, the magnitude m_i^* grows. For instance, when $\tau = 30\text{ min}$, for $[H_m\text{HPA-2}] = 0.1\text{ M}$ $m_i^* = 0.16$, for $[H_m\text{HPA-2}] = 0.2\text{ M}$ $m_i^* = 0.21$, for 0.3 M $m_i^* = 0.32$, and for 0.4 M $m_i^* = 0.42$. With increasing concentration of $H_m\text{HPA-2}$, the initial magnitudes Dm^*/Dt drop.

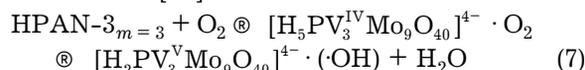
Early works [23, 24] that dealt with the study of $H_m\text{HPA-}x$ oxidation by oxygen have been made *under model conditions* ($[H_m\text{HPA-}x]$ from 0.035 to 0.1 M, buffer solutions with pH ~ 3 , $T < 307\text{ K}$). It has been demonstrated that the mechanism of HPAN- x_m ($H_{x+m-1}PV_m^IVV_{x-m}^VMo_{12-x}O_{40}^{4-}$) anion oxidation is complex and includes formation of $[HPAN-x_m \cdot O_2]$ intermediate active complexes (IAC), in which HPAN- x_m anion contains no less than three atoms of vanadium (IV). By virtue of the fact that the values of m^* are always < 2 in $H_m\text{HPA-2}$ solutions, the formation of HPAN- $x_m \cdot 3$ anions is rather problematic. For instance, *two consecutive reactions of disproportionation* are essential for HPAN- $x_m \cdot 3$ anions to be formed:

1) disproportionation of HPAN- $2_{m=1}$ anion with respect to vanadium (IV) and (V) to form HPAN- $2_{m=2}$ anion [23]:
 $2\text{HPAN-}2_{m=1} \ll \text{HPAN-}2_{m=2} + \text{HPAN-}2_{m=0}$ (5)

2) the subsequent disproportionation of HPAN- $2_{m=2}$ anion with respect to vanadium and molybdenum to form HPAN- $3_{m=3}$ anion [6]:



Formation and disintegration of IAC of composition $[HPAN-3_{m=3} \cdot O_2]$ attended with the reduction of coordinated O_2 molecule occurs by the scheme [23]



It is our belief that the second stage (reaction (6)) is displaced to the left even at high values of m^* , because it is endothermic. Therefore, the formation of HPAN- $3_{m=3}$ anion that is active with respect to oxygen occurs at this stage to only a small degree and the reaction (6) controls the reaction (2) throughout the whole interval of m^* values.

Carrying out the reaction (2) at high temperatures ($\sim 413\text{--}433\text{ K}$) makes it possible to *surmount an endothermic barrier* (see $m^*(T)$ values at the page 47) and to increase W_2 dramatically *at any values of m^** . Hence it follows that high enough concentration of $[HPAN-3_{m=3} \cdot O_2]$ IAC, which represents the site of vanadium (IV) oxidation to vanadium (V), can be provided *only at high temperatures and high O_2 pressure*.

With decrease of m^* in the course of the reaction (2), the concentration of IAC decreases at the expense of not only the equilibrium (6), but also endothermic equilibrium (5) shifted to the left. In so doing the endothermic effect of an overall reaction (2) increases which has been experimentally revealed by us in [21].

The stages (5) and (6) are characterized by the (meanwhile unknown) magnitudes of enthalpy $-DH_{4r}$ and $-DH_{5r}$. The equilibrium states for these stages depend on the values of m^* and on the temperature of the reaction (2). With decreasing m^* , the combined contribution of enthalpies of endothermic stages (5) and (6) to an enthalpy of the reaction (2) steadily grows. The observed activation energy of the reaction (2) rises in comparison to the true activation energy of IAC disintegration in accord with the scheme (7) by the value of the sum of enthalpy contributions of the stages (5) and (6). Growth of E_a^{obs} occurs for the most part due to an

increase of the stage (5) contribution, because it is the equilibrium of this stage that will be displaced to a greater extent.

It is obviously important to compare the reaction rates among themselves at various H_m HPA-2 concentrations. However, it is difficult to make such a comparison correctly, since with increasing concentration of H_m HPA-2 solutions the concentration of H^+ ions strongly increases as well, thus inhibiting the recovery of HPA-2 by oxygen.

CONCLUSION

The possibility in principle for deep oxidation of H_m HPA-2 solutions under a pressure of oxygen up to 8 atm at elevated temperatures (~413–433 K) to recover HPA-2 was shown for the first time. The obtained results make it possible to recommend HPA-2 solutions as the *reversibly reacting oxidizers* instead of such irreversible oxidizers as CrO_3 or $KMnO_4$. High stability of the concentrated HPA-2 solutions provides a reliable guarantee that it will be possible to create on their basis the new ecologically feasible technologies for catalytic oxidation of various substrates by oxygen.

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