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# Kinetics and Mechanism of the Homogeneous Oxidation of *n*-Butenes to Methyl Ethyl Ketone in a Solution of Mo–V–Phosphoric Heteropoly Acid in the Presence of Palladium Pyridine-2,6-Dicarboxylate

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**Abstract**—In catalytic two-step *n*-butene oxidation with dioxygen to methyl ethyl ketone, the first step is the oxidation of *n*-$C_4H_8$ with an aqueous solution of Mo–V–P heteropoly acid in the presence of Pd(II) complexes. The kinetics of *n*-butene oxidation with solutions of $H_7PV_4Mo_8O_{40}$ (HPA-4) in the presence of the Pd(II) dipicolinate complex $(H_2O)Pd^{II}(dipic)$ (**I**), where $dipic^{2-}$ is the tridentate ligand $2,6\text{-}NC_5H_3(COO^-)_2$, is studied. Calculation shows that, at the ratio $dipic^{2-} : Pd(II) = 1 : 1$, the ligand decreases the redox potential of the $Pd(II)/Pd_{met}$ system from 0.92 to 0.73–0.77, due to which Pd(II) is stabilized in reduced solutions of HPA-4. The reaction is first-order with respect to *n*-$C_4H_8$. Its order with respect to Pd(II) is slightly below unity, and its order with respect to HPA-4 is relatively low (~0.63). The activation energy of but-1-ene oxidation in the temperature range from 40 to 80°C is 49.0 kJ/mol, and that of the oxidation of but-2-ene is 55.6 kJ/mol. The mechanism of the reaction involving the *cis*-diaqua complex $[(H_2O)_2Pd^{II}(Hdipic)]^+$, which forms reversibly from complex **I**, is proposed. The reaction rate is shown to increase with an increase in the HPA-4 concentration due to an increase in the acidity of the solution.

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Methyl ethyl ketone (MEK, butan-2-one) finds wide use as a raw material for fine organic synthesis, as a solvent for paints, enamels, and resins, and as a dewaxing agent for lubricating oils. In industry MEK is produced from the *n*-butene fraction via one of the three-step technologies through butan-2-ol ether $CH_3CH(OSO_2OH)C_2H_5$ or $CH_3CH(OCOCH_3)C_2H_5$, which is subjected to hydrolysis to butan-2-ol, and the latter is dehydrated to MEK [1, 2]. These multistep technologies are energy-consuming and produce large amounts of acidic wastewater.

We have proposed a liquid-phase catalytic process for the production of MEK by direct oxidation of *n*-butenes with dioxygen via reaction (I) [3, 4].

$$n\text{-}C_4H_8 + \tfrac{1}{2}O_2 \xrightarrow{Pd+HPA} CH_3COC_2H_5. \qquad (I)$$

The homogeneous catalysts developed for this process are aqueous solutions (Pd + HPA), where HPA is the Keggin Mo–V–P heteropoly acid $H_{3+x}PMo_{12-x}V_xO_{40}$ [5, 6]. Such HPAs play the role of reversible oxidants in which the vanadium atoms undergo redox transformations vanadium(V) $\rightleftarrows$ vanadium(IV). The palladium concentration in these catalysts is (4–6) $\times 10^{-3}$ mol/l, and the HPA concentration is 0.1–0.3 mol/l. To provide explosion safety, process (**I**) is carried out in two steps in different reactors.

$$n\text{-}C_4H_8 + \tfrac{2}{m}HPA + H_2O \xrightarrow{Pd} CH_3COC_2H_5 + \tfrac{2}{m}H_mHPA, \qquad (II)$$

$$\tfrac{2}{m}H_mHPA + \tfrac{1}{2}O_2 \rightarrow \tfrac{2}{m}HPA + H_2O, \qquad (III)$$

where $H_mHPA$ ($H_{3+x+m}PMo_{12-x}V^{IV}_mV^{V}_{x-m}O_{40}$) is the reduced form of HPA, and $m = [V^{IV}]/[HPA]$ is the degree of reduction of HPA.

In step (II), which usually occurs at 40–70°C, vanadium(V) in the HPA solution oxidizes *n*-butene to MEK and is reduced to vanadium(IV). The resulting MEK is evaporated from the reduced catalyst Pd + $H_mHPA$ at 100°C, after which the catalyst is regenerated with dioxygen or air via reaction (III) at 140–145°C and a dioxygen pressure $P_{O_2}$ of about 3–4 atm [5]. Target reaction (II), the separation of the resulting MEK, and the catalyst regeneration step (III) constitute one technological cycle of reaction (I). The redox potential of the Pd + HPA solution decreases and its pH increases during reaction (II) [7, 8]. During reaction (III), these parameters return to their initial values. Therefore, reaction (II) followed by catalyst regeneration can be performed several times [9].

Reaction (II) is complicated and consists of steps (IIa) and (IIb). In the first of them, the Pd(II) complex oxidizes *n*-butene. In the second step, the complex of reduced Pd is oxidized with the vanadium-containing heteropoly acid:

$$n\text{-}C_4H_8 + Pd^{II} + H_2O \rightarrow CH_3COC_2H_5 + Pd^0, \quad \text{(IIa)}$$

$$Pd^0 + {}^2\!/\!_m\,HPA_{2V^V} \rightarrow Pd^{II} + {}^2\!/\!_m\,H_mHPA_{2V^{IV}}. \quad \text{(IIb)}$$

For reaction (II) to proceed rapidly and come to completion, it is necessary that the following relationship be valid for the potentials of the redox systems involved in this reaction:

$$E_{HPA/H_mHPA} > E_{Pd^{II}/Pd^0} > E^{O}_{MEK/n\text{-}C_4H_8}. \quad (1)$$

The value of $E^{O}_{MEK/n\text{-}C_4H_8}$ can easily be calculated using reference data [10]: $E_{HPA/H_mHPA}$ is constant and equal to 0.10 V. The values of $E_{HPA/H_mHPA}$ and $E_{Pd^{II}/Pd^0}$ can be varied. If $PdSO_4$, in which the anion $SO_4^{2-}$ forms an unstable complex with the cation $Pd^{2+}$ [11], that is a constituent of the catalyst, then palladium(II) in the initial catalyst solution exists mainly as the aqua complex $Pd^{2+} \cdot$ aq. In this case, the rate of reaction (II) at 40–70°C is nearly constant, and a dimeric redox system $Pd_2^{2+}/Pd_2^0$ having $E \approx 0.7$ V works in the catalyst [6]. However, in the MEK evaporation step, the vanadium(V) concentration in the solution of the reduced catalyst is insufficient for $Pd_2^0$ oxidation via reaction (IIb). Under these conditions, the dimeric complex $Pd_2^0$ can gradually polymerize to yield palladium metal, which will partially precipitate from the catalyst solution [12]. This will yield the well known system $Pd^{2+} \cdot aq/Pd_{met}$, which has the higher redox potential of $E^0 \approx 0.92$ V [13, 14].

Various methods for preventing this undesirable phenomenon were proposed. In particular, a small amount of HCl (up to $[Cl^-] \approx 0.035$ mol/l) was introduced into the catalyst [15], due to which the redox potential of the system $PdCl_4^{2-}/Pd_{met}$ decreased to ~0.70 V [16]. However, even the presence of this low concentration of chloride ions in the catalyst solution is undesirable, because the product undergoes partial chlorination and the selectivity of reaction (II) decreases [15]. For this reason, we have proposed to decrease the redox potential of the system $Pd^{II}/Pd^0$ by adding some pyridine derivatives to the catalyst composition [3]. Chlorine-containing organic compounds cannot form in the presence of pyridine derivatives.

It is known that the pyridine ring is very resistant to oxidants. However, pyridine itself and its alkyl derivatives readily form insoluble salts with heteropolyanions and, hence, these compounds are unsuitable as stabilizers of palladium in Pd + HPA solutions. Some pyridine derivatives containing acidic groups such as COOH or $SO_3H$ were chosen for the stabilization of Pd [3, 12]. These are 3-pyridinesulfonic acid and 2,6-pyridinedicarboxylic (dipicolinic) acid that form no insoluble salts with heteropoly anions. Dipicolinic acid $2,6\text{-}C_5H_3N(COOH)_2$, or $H_2$dipic, is stable, for example, in mixtures of dioxygen with ozone [18] and, hence, it will withstand the action of the severe $O_2$ atmosphere of reaction (III). $H_2$dipic and palladium(II) form the complexes $(H_2O)Pd^{II}$(dipic) (**I**) and $Pd^{II}(Hdipic)_2 \cdot 2H_2O$ [19]. However, only complex **I** is catalytically active in the oxidation of *n*-butenes [12]. It should be noted that dipicolinic acid is a rather accessible chemical, being an intermediate in the production of the drug Parmidinum [20].

In the present work, we have studied the kinetics of *n*-butene oxidation via reaction (II) in a solution of HPA-4 in the presence of dipicolinate complex **I** and made some conclusions about the mechanism of this reaction.

## EXPERIMENTAL

Aqueous solutions (0.20 M) of the Keggin-type HPA $H_7PV_4Mo_8O_{40}$ (HPA-4) with $pH_0 \sim 0.45$ were synthesized from $V_2O_5$, $MoO_3$, $H_3PO_4$, and a cool 5% solution of $H_2O_2$ using the standard procedure [21]. The initial 30% $H_2O_2$ was special-purity grade, and the three other reactants were high-purity grade. Solutions with a lower HPA-4 concentration were prepared by dilution of the 0.20 M HPA-4 solution with water. The poorly water-soluble complex **I** was synthesized from $PdCl_2$ and dipicolinic acid (reagent grade) in a 0.2 M solution of $HNO_3$ [19]. The Pd + HPA-4 catalysts with a $Pd^{2+}$ content of $(2–15) \times 10^{-3}$ mol/l containing no foreign anions were prepared by introduction of various amounts of complex **I** into the HPA-4 solution. Note that the pH of the catalyst solution is determined by the pH of the corresponding HPA-4 solution [8], because the concentration of HPA-4 exceeds the concentration of complex **I** by more than one order of magnitude.

We used 99.6% but-1-ene (Budennovsk Chemical Industrial Complex, Russia) and 91–94% but-2-ene prepared by dehydration of butan-2-ol with $H_2SO_4$ [22]. Reaction (II) was carried out under atmospheric pressure at 40–80°C in a shaken temperature-controlled 170-ml glass reactor into which 40 ml of the catalyst was introduced. The process was conducted under kinetic control (400 reciprocations per minute). In experiments at temperatures above 70°C, the reactor was additionally attached to a temperature-controlled circulation device in which MEK vapor was absorbed with a 1.0 M aqueous solution of Girard's reagent $(C_5H_5N^+CH_2CONHNH_2 \cdots Cl^-)$ recrystallized from 2-methoxyethanol [23].

The solubility of *n*-butenes in the 0.20 M HPA-4 solution in the absence of the palladium(II) complexes was preliminarily determined. At 40°C, the solubility of but-1-ene was $1.65 \times 10^{-3}$ mol/l and that of but-2-ene was $1.50 \times 10^{-3}$ mol/l. At 70°C, their solubilities were $0.42 \times 10^{-3}$ and $0.39 \times 10^{-3}$ mol/l, respectively. The solubility of *n*-butenes in the 0.20 M HPA-4 solution at other temperatures (50, 60, and 80°C) was determined by interpolation or extrapolation.

Before each experiment, *n*-butene was passed (without bubbling) through the reactor with the catalyst (complex **I** + HPA-4) and also through the circulation device, if necessary. Thereafter, the reactor was connected to a burette filled with *n*-butene, and the first push of the shaken reactor was taken to be the initial point of the run.

The typical dependences of the *n*-butene volume absorbed by the **I** + HPA-4 solution on the reaction time at 70°C are presented in Fig. 1. The *n*-butene uptake rate gradually decreases during the run. The rate of reaction (II), $w_{\mathrm{II}}$, was estimated from the initial segments of $V_{\mathrm{C_4H_8}} = f(\tau)$ curves in the $0 \le m \le 1$ range and was expressed in units of (mol $C_4H_8$) $l^{-1}$ $min^{-1}$. Each run was repeated two or three times with a fresh portion of the catalyst, and the results obtained were used in the construction of the plots shown in Figs. 2–4.

In the runs in which the partial pressure of $C_4H_8$ ($P_{\mathrm{C_4H_8}}$) was varied, the reactor was blown with $C_4H_8$ + $N_2$ gas mixtures, and pure *n*-butene was supplied from the burette in the course of the reaction.

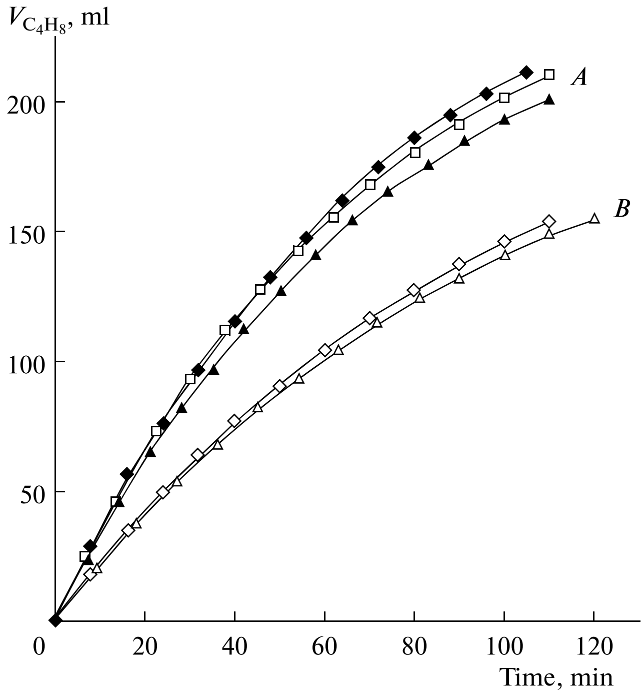

**Fig. 1.** But-1-ene uptake by solutions of the catalyst (complex **I** + HPA-4) at HPA-4 concentrations of (*A*) 0.20 and (*B*) 0.10 mol/l. Particular curves in groups *A* and *B* were obtained in the repeated runs with a fresh portion of the catalyst. Reaction conditions: 40 ml of the 0.008 mol/l $(H_2O)Pd^{II}$(dipic) + HPA-4 solution, 70°C, $P_{(\mathrm{C_4H_8+H_2O})} =$ 1 atm, and $P_{\mathrm{C_4H_8}} = 0.692$ atm.

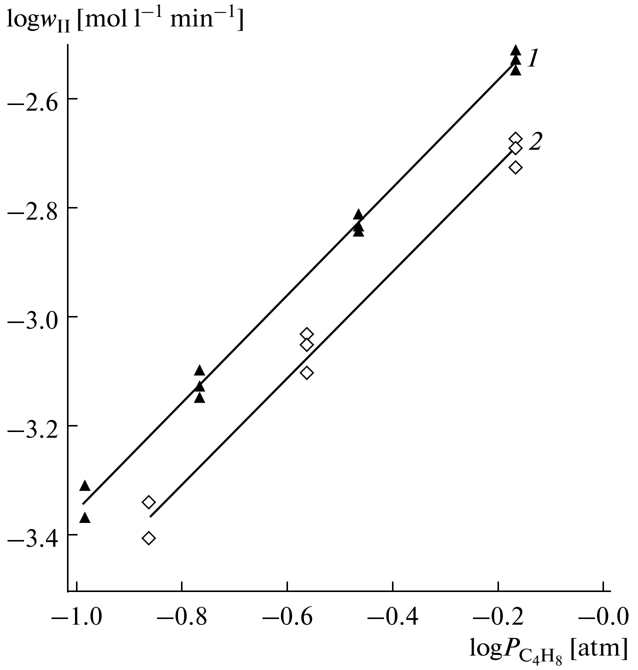

**Fig. 2.** Logarithmic plots of the oxidation rates of (*1*) but-1-ene and (*2*) but-2-ene versus the partial pressure. Reaction conditions: 40 ml of a 0.008 mol/l $(H_2O)Pd^{II}$(dipic) + HPA-4 solution, 70°C, and $P_{(\mathrm{C_4H_8+H_2O})} = 1$ atm, $P_{\mathrm{C_4H_8}} =$ 0.692 atm.

## RESULTS AND DISCUSSION

The logarithmic dependences of the rate of reaction (II) on the partial pressure of *n*-butenes in the presence of the catalytic system complex **I** + HPA-4 are shown in Fig. 2. It can be seen that, under all partial pressures of but-1-ene or but-2-ene, $w_{\mathrm{II}}$ is directly proportional to $P_{\mathrm{C_4H_8}}$.

The logarithmic dependences of $w_{\mathrm{II}}$ on the concentrations of complex **II** and HPA-4 are shown in Fig. 3. The apparent reaction order with respect to Pd is ~0.94. The dependence of $w_{\mathrm{II}}$ on the HPA-4 concentration is weaker: the apparent order is ~0.63.

The temperature dependences of $w_{\mathrm{II}}$ for the oxidation of both *n*-butenes are presented in the Arrhenius coordinates in Fig. 4. The rate $w_{\mathrm{II}}$ for but-2-ene at 40°C is lower than that for but-1-ene by approximately 1.75 times, whereas at 80°C it is lower by 1.25 times. In the range from 40 to 80°C, the apparent activation energy of but-1-ene oxidation is ~49.0 kJ/mol, while that of but-2-ene oxidation is ~55.6 kJ/mol.

The palladium complexes containing the dipicolinate anion $NC_5H_3(COO)_2^{2-}$ (**dipic**$^{2-}$), having two carboxylate groups $COO^-$, are important components of the catalyst [12]. In neutral and weakly acidic media, the dipic$^{2-}$ anion is a tridentate ligand and binds the $Pd^{2+}$ cation into the very strong monoaqua complex $(H_2O)Pd^{II}$(dipic) (**I**) [19]. It is reasonable to assume that the $COO^-$ groups of this ligand are partially protonated in the acidic medium, due to which the ligand becomes bidentate: $NC_5H_3(COOH)(COO^-)$ (**Hdipic**$^-$). In this case, complex **I** turns into the diaqua complex

$[(H_2O)_2Pd^{II}(Hdipic)]^+$ (**II**), in which $H_2O$ molecules are in *cis*-position to each other:

$$\underset{\mathbf{I}}{(H_2O)Pd^{II}\left[NC_5H_3(COO)_2\right]} + H^+ + H_2O \rightleftarrows \underset{\mathbf{II}}{(H_2O)_2Pd^{II}\left[NC_5H_3(COOH)(COO)\right]^+}. \quad \text{(IV)}$$

Since in the course of reaction (II) the concentration of $H^+$ ions in the HPA-4 solution decreases [8], equilibrium (IV) gradually shifts to the left.

The redox potentials of the systems $(H_2O)Pd^{II}(dipic)/Pd_{met}$ and HPA-4/$H_m$HPA-4 should be used to determine the region of stability for the catalyst examined (Pd complex + HPA-4). The values of $E_{HPA\text{-}4/H_mHPA\text{-}4}$ were determined earlier [8], and the value of $E_{(H_2O)Pd(dipic)/Pd_{met}}$ can be calculated taking into account equilibria (V) and (VI):

$$\underset{\mathbf{I}}{(H_2O)Pd^{II}(dipic)} \xrightleftharpoons{K_C} Pd^{2+}\cdot aq + dipic^{2-}, \quad \text{(V)}$$

$$H_3dipic^+ \xrightleftharpoons[H^+]{K_1} H_2dipic^- \xrightleftharpoons[H^+]{K_2} Hdipic^- \xrightleftharpoons[H^+]{K_3} dipic^{2-}. \quad \text{(VI)}$$

In equilibrium (V) $K_C \approx 10^{-16}$ [24], and in equilibria (VI) $pK_1 = -1.05$, $pK_2 = 2.29$, and $pK_3 = 5.14$ [25]. For calculating $E_{Pd^{II}/Pd_{met}}$, one has to use material balances for palladium(II) (2) and for free (noncomplexed) dipicolinate anions (3) containing 0 to 3 protons:

$$\left[Pd^{II}\right]_\Sigma = \left[(H_2O)Pd^{II}(dipic)\right] + \left[Pd^{2+}\cdot aq\right] \approx \left[(H_2O)Pd^{II}(dipic)\right], \quad (2)$$

$$[dipic]_\Sigma = \left[dipic^{2-}\right] + \left[Hdipic^-\right] + [H_2dipic] + \left[H_3dipic^+\right] \approx \left[Hdipic^-\right] + [H_2dipic]. \quad (3)$$

The concentration of free $Pd^{2+}\cdot aq$ ions at $K_C \approx 10^{-16}$ is negligibly low and, hence, can be neglected in Eq. (2). In addition, in the pH 0.5–2.2 range the terms $[dipic^{2-}]$ and $[H_3dipic^+]$ in equilibria (VI) can be neglected. Under these conditions, the $Hdipic^-$ ion should be the dominant form of free dipicolinate. Since complex **I** is very stable, the noncomplexed species $Pd^{2+}\cdot aq$, $Hdipic^-$, and $H_2dipic$ are present in very low concentrations in the solution of complex **I**. They are interrelated by the material balance equation

$$\left[Pd^{2+}\cdot aq\right] = [dipic]_\Sigma \approx \left[Hdipic^-\right] + [H_2dipic]. \quad (4)$$

Taking into account the equilibrium between $Hdipic^-$ and $H_2dipic$, we obtain the equation

$$\left[Pd^{2+}\cdot aq\right] \approx \left[Hdipic^-\right]\left(1 + \left[H^+\right]K_2^{-1}\right). \quad (5)$$

At pH ≤ 2.2, there are almost no nonprotonated ions $dipic^{2-}$ in the catalyst solution, and equilibrium (V) is then transformed into (VII):

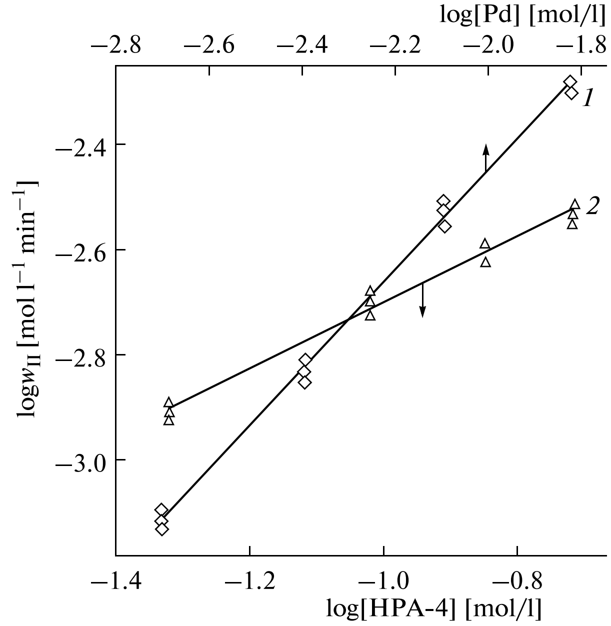

**Fig. 3.** Logarithmic plots of the oxidation rate of but-1-ene versus the concentrations of (*1*) complex **I** and (*2*) HPA-4. Reaction conditions: 40 ml of a 0.008 mol/l $(H_2O)Pd^{II}(dipic)$ + HPA-4 solution, 70°C, and $P_{C_4H_8}$ = 0.692 atm.

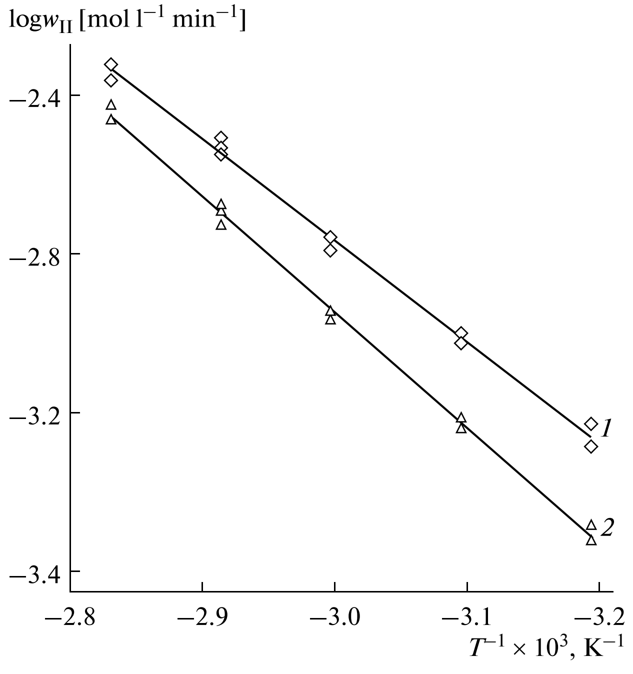

**Fig. 4.** Dependences of logarithms of the oxidation rates of (*1*) but-1-ene and (*2*) but-2-ene on the inverse reaction temperature. Reaction conditions: 40 ml of a 0.008 mol/l $(H_2O)Pd^{II}(dipic)$ + 0.20 mol/l HPA-4 solution, 70°C, and the pressure $P_{C_4H_8}$ was reduced to 0.692 atm.

Calculation of the concentration of free $Pd^{2+} \cdot aq$ ions and the oxidation potential $E$ of complex $(H_2O)Pd(dipic)$ in acidic media

| Conditions | | Results of calculation | |
|---|---|---|---|
| $[Pd^{II}]_\Sigma \times 10^3$, mol/l | pH | $[Pd^{2+}] \times 10^6$, mol/l | $E$, V |
| 8.0 | 0.50 | 14.87 | 0.775 |
| 8.0 | 0.85 | 6.68 | 0.765 |
| 8.0 | 1.20 | 3.04 | 0.757 |
| 8.0 | 1.50 | 1.59 | 0.749 |
| 8.0 | 1.85 | 0.765 | 0.739 |
| 8.0 | 2.20 | 0.394 | 0.731 |
| 4.0 | 1.50 | 1.36 | 0.744 |
| 15.0 | 1.50 | 2.72 | 0.753 |

$$(H_2O)Pd^{II}(dipic) + H^+ \xrightleftharpoons{K_\Sigma} Pd^{2+} \cdot aq + Hdipic^-, \quad \text{(VII)}$$

where $$K_\Sigma = \frac{[Pd^{2+} \cdot aq][Hdipic^-]}{[H^+][(H_2O)Pd^{II}(dipic)]} = \frac{K_C}{K_3}. \quad (6)$$

Expressing $[Hdipic^-]$ from Eq. (6), we obtain

$$[Hdipic^-] = \frac{K_C}{K_3} \frac{[H^+][Pd^{II}_\Sigma]}{[Pd^{2+} \cdot aq]}. \quad (7)$$

Substituting $[Hdipic^-]$ from Eq. (7) into Eq. (5), we have

$$[Pd^{2+} \cdot aq] = \frac{K_C [H^+][Pd^{II}]}{K_3 [Pd^{2+} \cdot aq]}\left(1 + \frac{[H^+]}{K_2}\right). \quad (8)$$

Finally, combining both terms containing $[Pd^{2+} \cdot aq]$ on the left-hand side of Eq. (8) and taking the square root of $[Pd^{2+} \cdot aq]^2$, we obtain

$$[Pd^{2+} \cdot aq] = \sqrt{\frac{K_C [H^+](K_2 + [H^+])[Pd^{II}]}{K_2 K_3}}. \quad (9)$$

The concentrations of free $Pd^{2+} \cdot aq$ ions calculated via Eq. (9) are given in the table. It can be seen that the concentration of $Pd^{2+} \cdot aq$ ions decreases with an increasing in pH of the solution of complex **I**, indicating some strengthening of complex **I**. Using the calculated values of $[Pd^{2+} \cdot aq]$, one can calculate the redox potentials $E_{Pd^{II}/Pd_{met}}$ in solutions of complex **I** using Nernst's equation (10) [26]:

$$E_{Pd^{II}/Pd_{met}} = E^\circ_{Pd^{2+} \cdot aq/Pd_{met}} + \frac{RT}{nF} \ln[Pd^{2+} \cdot aq]. \quad (10)$$

For the valence transition $Pd(II)/Pd_{met}$, $n = 2$. At 25°C Eq. (10) simplifies to

$$E_{Pd^{II}/Pd_{met}} = E^\circ_{Pd^{2+} \cdot aq/Pd_{met}} + 0.02955 \log[Pd^{2+} \cdot aq]. \quad (11)$$

The results of calculation of $E_{Pd^{II}/Pd_{met}}$ are also given in the table. It can be seen that the potential $E_{Pd^{II}/Pd_{met}}$ decreases by 0.044 V as the pH of the solution increases from 0.50 to 2.20. Nevertheless, at any pH values the calculated values of $E_{Pd^{II}/Pd_{met}}$ for the Pd(II) dipicolinate complexes are much smaller than the known value $E^\circ_{Pd^{2+} \cdot aq/Pd_{met}} = 0.92$ V [14].

It was found earlier that the redox potentials $E$ and pH of the HPA-4 solutions depend on the degree of their reduction, $m$, which increases in the course of reaction (II) [7, 8]. Using the published data [8], we have plotted $E$ for the homogeneous catalysts (**I** + HPA-4 complex) against their pH at 25°C and various HPA-4 concentrations. It follows from Fig. 5, where the arrow shows the direction of the shifts in $E$ and pH during reaction (II), that the catalysts remain homogeneous in the region above the $E_{Pd^{II}/Pd_{met}} = f(pH)$ curve, according to inequality (1). But they become unstable and begin to precipitate $Pd_{met}$ in the region under this curve. So, the acceptable lower boundary of the potential $E$ of the reduced catalyst based on the 0.2 M HPA-4 solution is ~0.75 V. This corresponds to $m \approx 2$, i.e., to the reduction of approximately 50% of the vanadium(V) in the HPA-4 solution to vanadium(IV) [8]. Further reduction of the catalyst can result in the precipitation of the metallic phase, which will decrease the activity of the catalyst in the next cycle of reaction (I).

In our work [12], we began to study the problem of palladium stabilization in the Pd + HPA catalytic solutions. The palladium concentration in the reduced solutions (complex **I** + HPA-5) was determined by our extraction colorimetric method using an α-benzil dioxime solution. It proved that palladium(II) is retained in the solution of the catalyst based on HPA-5 until the reduction of ~60% of the vanadium(V) to vanadium(VI). Thus, the regions of stability of palladium in solutions of the homogeneous catalysts based on HPA-4 and HPA-5 coincide rather closely.

Thus, the ligands $dipic^{2-}$ and $Hdipic^-$ indeed stabilize Pd(II) in the catalyst solution due to the strong decrease in the redox potential of the $(H_2O)Pd^{II}(dipic)/Pd_{met}$ system compared to the $Pd^{2+} \cdot aq/Pd_{met}$ system. According to our data, the increase in temperature to ~90°C does not appreciably shift the redox potentials of the HPA-4/$H_m$HPA-4 system. This provides good reason to believe that the region of stability for the Pd + HPA catalysts at elevated temperatures will not differ substantially from the region of their stability at room temperature.

It seems likely that just complex **II**, not complex **I**, exhibits some catalytic activity in reaction (II). In complex **I**, only one coordination site is occupied by a water molecule. But complex **II** formed from complex **I** contains two $H_2O$ molecules, and one of them can readily be replaced by an *n*-butene molecule to form the mixed *cis*-complex $[(H_2O)(n\text{-butene})Pd^{II}(Hdipic)]^+$ (**III**):

$$\underset{\textbf{II}}{(H_2O)_2Pd^{II}(Hdipic)^+} + n\text{-butene} \rightleftarrows \underset{\textbf{III}}{(H_2O)(n\text{-butene})Pd^{II}(Hdipic)^+} + H_2O. \qquad \text{(VIII)}$$

It is assumed that the further transformations of complex **III** are analogous to the transformations of complex $(H_2O)(olefin)PdCl_2$, which was described many times as an intermediate in the oxidation of olefins with palladium(II) chloride complexes [27, 28]. These transformations lead to the complex $Pd^0(H_2dipic)$ (**IV**) and the target product (MEK). It is assumed that the $Pd^0...N$ bond in complex **IV** is retained, but $Pd^0$–OCOR bonds are absent [12]. Complex **IV** is then oxidized to the initial complex **I** by vanadium(V) contained in the HPA-4 solution. Thus, one turnover of palladium in the catalyst composition is completed. Then all steps of reaction (II) are repeated, and the HPA-4 solution is gradually reduced. Equilibrium (IV) is gradually shifted to the left, and the concentration of reactive complex **II** decreases, inducing a decrease in the reaction rate $w_{II}$.

For the oxidation of but-2-ene, the rate $w_{II}$ is lower than that for the oxidation of but-1-ene. It can be assumed that this is due to the lesser shift of equilibrium (VIII) to the right for the formation of mixed complex **III** with but-2-ene than for the formation of the analogous complex with but-1-ene.

In the presence of the Pd(II) chloride complexes, the rate of reaction (II) decreases with an increase in the acidity of the solution [27]. However, in the presence of complex **I**, this reaction is accelerated with an increase in the acidity of the HPA-4 solution (Fig. 3). This fact can be explained by the shift of equilibrium (IV) to the right with an increase in the concentration of the bidentate ligand $Hdipic^-$. A similar acceleration was earlier observed for the oxidation of allyl alcohol by a complex Pd(II) with diethylenetetramine, $H_2NCH_2CH_2NHCH_2CH_2NH_2$ [29]. When this solution is acidified, the tridentate ligand is also partially protonated forming the respective bidentate ligand $H_3N^+CH_2CH_2NHCH_2CH_2NH_2$, which has only two $Pd\cdots N$ bonds with palladium(II).

In the present work, the reaction order with respect to HPA-4 is 0.63; i.e., it differs from the zero order, which was observed in the presence of the dinuclear complex $Pd_2^{2+}$ [30]. This complex did not contain any ligands whose composition would change depending on the acidity of the medium. Hence, the composition of this complex remained invariable in the wide medium acidity range from pH –0.34 to pH 0.81. Due to this, the rate of alkene oxidation in the catalytic system $Pd_2^{2+}$ + HPA did not depend on the acidity of the medium [6]. Therefore, the dependence of $w_{II}$ on the HPA-4 concentration observed in the present study is only seeming. This dependence can be explained by a change in the concentration of the active complex **II** at different acidities of the HPA-4 solutions.

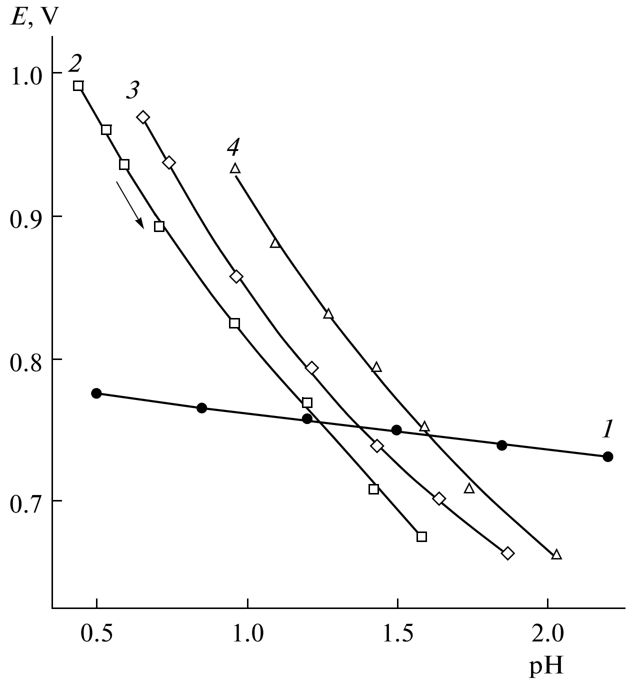

**Fig. 5.** Region of stability for solutions of the reduced homogeneous catalysts (complex **I** + HPA-4) at various pH values at 25°C: (*1*) complex **I** in a concentration of 0.008 mol/l and (*2–4*) HPA-4 in concentrations of (*2*) 0.20, (*3*) 0.10, and (*4*) 0.05 mol/l.

In recent years, we have developed methods for the synthesis of modified non-Keggin-type Mo–V–phosphoric HPA solutions [31] that possess enhanced thermal stability. The initial pH values of these solutions are below zero. Probably, enhanced concentrations of the reactive palladium(II) dipicolinate complexes can be achieved in the catalysts based on these solutions.

Thus, in the present work we have shown that the equilibrium mixture of dipicolinate complexes **I** and **II** is generated, if dipicolinate ion is used for stabilization of Pd(II) in the aqueous solution of Pd(II) + HPA-4 that is our homogeneous catalyst. In the course of reaction (II), the concentration of the reactive complex **II** in the mixture decreases due to an increase in pH during the reduction of the catalyst solution. It was found earlier that all changes in the physicochemical properties of solutions of Mo–V–P HPA during redox reactions (II) and (III) are reversible [9]. Therefore, the pH of the catalyst solution regenerated via reaction (III) will be the same as the pH of the initial solution. Hence, the initial rate of reaction (II) with the regenerated catalyst should be equally high. Thus, the oxidation of *n*-butenes in reaction (II) and the subsequent regeneration of the catalyst can be carried out several times with the retention of homogeneity of the catalytic system $(H_2O)Pd^{II}(dipic)$ + HPA-4.

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