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Ethylene and Cyclohexene Oxidation by *p*-Benzoquinone, Hydrogen Peroxide, and Oxygen in the Solutions of Cationic Pd(II) Complexes in Acetonitrile–Water and Ionic Liquid–Water Binary Solvents

G. E. Efremov[a], **E. A. Bovyrina**[a], **A. V. Podtyagina**[a], **I. V. Oshanina**[a], **and O. N. Temkin**[a], *
[a] *MIREA–RussianTechnological University (M.V. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119571 Russia*
**e-mail: olegtemkin@mail.ru*

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Abstract—Optimal conditions are selected for ethylene and cyclohexene oxidation reactions in the acetonitrile (AN)–water system in the presence of $Pd(AN)_x(H_2O)_{4-x}^{2+}$ complexes. It is shown that hydrogen peroxide oxidizes hydroquinone (QH_2) in acetonitrile solutions and in ionic liquids ($BMIM^+BF_4^-$, $BMIM^+PF_6^-$), and the rates of ethylene oxidation in the $BMIM^+PF_6^-$ ionic liquid in the presence of *p*-benzoquinone (Q) and hydroquinone are the same. It is shown that solid and soluble phthalocyanine iron complexes catalyze oxidation of olefins by oxygen in acidic acetonitrile media by converting *p*-benzoquinone to the third catalyst of the process. The apparent first-order rate constants of hydroquinone oxidation by oxygen are determined. The use of the $IL–H_2O–H_2SO_4$ system is found to be inappropriate for cyclohexanone synthesis because of the formation of byproducts of cyclohexene conversion.

Keywords: ethylene, cyclohexene, oxidation, acetonitrile, ionic liquids, *p*-benzoquinone, hydrogen peroxide, oxygen, cationic complexes, palladium

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INTRODUCTION

An interest in catalysis of olefin oxidation reactions by palladium cationic complexes has a number of reasons: the pronounced superelectrophilicity of cationic metal (Hg, Pt, Pd, Rh, and Au) complexes in various reactions [1–14], unusual kinetic behavior of palladium cationic complexes [7, 11, 15, 16] in the so-called Wacker oxidation of olefins [17, 18], and their high activity in cyclohexene (C_6H_{10}) oxidation to cyclohexanone ($C_6H_{10}O$) in aqueous–organic binary solvents [7, 11, 19, 20] compared to the processes in classical catalytic systems in the solution of palladium chloride complexes [21–23], which makes this process a promising technology for cyclohexanone synthesis

Earlier, in the Laboratory of Kinetics and Catalysis of the Chair of Chemistry and Technology of Basic Organic Synthesis at the Moscow Institute of Fine Chemical Technology, the following information on the acetonitrile (AN)–water system with *p*-benzoquinone (Q) oxidant was obtained:

1. The kinetics of cyclohexene oxidation in the $Pd(OAc)_2–HClO_4–LiClO_4–CH_3CN–H_2O$ system was studied and the kinetic model was proposed [11].

2. The process of formation of active $Pd(AN)_x(H_2O)_{4-x}^{2+}$ complexes was studied by NMR and electron spectroscopy [24].

3. A bimodal dependence of the initial rate of cyclohexene oxidation on the molar fraction of water (α_{H_2O}) has been determined [20] and phase equilibria in the cyclohexene–acetonitrile–water system was studied [20, 25].

4. Kinetic isotope effects were measured in the reactions of cyclohexene and ethylene oxidation in the $AN–H_2O/D_2O$ system [15] and in the reaction of ethylene oxidation in the $AN–H_2O–C_2H_4/C_2D_4$ system [16].

5. The kinetics of ethylene oxidation by *p*-benzoquinone was studied and the kinetic model was proposed based on the initial rates of the reaction [26].

p-Benzoquinone was used for the first time as a stoichiometric oxidant of olefins to carbonyl compounds in solutions of palladium chloride complexes by Moiseev and coworkers [18, 27]. *p*-Benzoquinone and sulfonaphthoquionone were also used in aqueous solutions of cationic palladium(II) complexes [28, 29] without additional stabilization of $Pd(H_2O)_4^{2+}$ by ligands. The use of quinones as stoichiometric oxidants in the solutions of cationic complexes in acidic media indicates the oxidation of palladium hydride complexes by quinones at the stage of Pd^{2+} regeneration or the stabilization of Pd^0 and Pd_2^{2+} complexes by coordinating quinines ($Pd(Q)^0$, $Pd(Q)_2^0$, and $Pd_2(Q)^{2+}$). In the interaction of these complexes with proton, Pd(II) is regenerated (see, e.g., [30]). The use of other stoichiometric oxidants in the reaction of olefin oxidation in the solutions of palladium complexes is known: H_2O_2, ROOH [31–33], and O_2 [34–37].

Oxygen as an oxidant for olefins and dienes in solutions of palladium complexes is used directly (e.g., [35]), with oxygen-activating catalysts (Co(II) complexes with various porphyrins [38]), or in the presence of a third catalyst: *p*-benzoquinone [6, 39–41]. The Co(II) [39–41] and Cu(II) [42, 43] complexes and Fe(II) phthalocyanine [6, 41] are used for the oxidation of hydroquinone (QH_2) by oxygen using hydroquinone as a component of the initial catalytic system. Hydroquinone is oxidized by oxygen in chloroform with catalysis by Co(II) and Mn(II) complexes with macrocyclic ligands [44]. The oxidation of hydroquinone by hydrogen peroxide in acetonitrile catalyzed by Cu(II), Fe(II), Co(II), and Mn(II) bromide complexes [45].

For further development of this field of olefin oxidation and the choice of binary solvents for carrying out the process of cyclohexene oxidation, it was necessary to check the possibility of using such oxidants as H_2O_2 and O_2 in strongly acidic media in the presence of palladium cationic complexes in aqueous–organic solvents and in the presence of catalysts for *p*-benzoquinone regeneration by hydroquinone oxidation with stoichiometric oxidants (H_2O_2 or O_2). Moreover, to solve a number of technological problems of the cyclohexene oxidation process, it was necessary to investigate the possibility of using ionic liquids (IL), which are used in oxidation processes [46–51], as ionic liquid–water binary solvents in the presence of palladium cationic complexes.

EXPERIMENTAL

Materials

The following reagents were used in the work: acetonitrile CH_3CN (TU 2636-092-44493179-04, reagent grade, $\rho = 0.7828$ g/cm^3), perchloric acid $HClO_4$ (Acros-CAS, 70%), ethylene (GOST 25070-87), *p*-benzoquinone (Acros organics, 99%) (before experiments *p*-benzoquinone was sublimated) and nonaqueous lithium perchlorate $LiClO_4$ (TU 6-09-3360-73, reagent grade).

Palladium diacetate trimer $Pd_3(CH_3COO)_6$ was obtained by palladium black oxidation by concentrated nitric acid in glacial acetic acid [52, 53]. The trimeric crystal structure of the obtained palladium diacetate and the absence of impurities of the keto–polyform was confirmed by its good solubility in organic solvents [54]. H^1 NMR spectra of $Pd_3(CH_3COO)_6$ solutions in $CDCl_3$ confirmed the symmetrical structure of the molecule with six equivalent acetate groups and the absence of appreciable amounts of palladium nitrite complexes [55, 56].

Ionic liquids, butylmethylimidazolium tetrafluoroborate $BMIM^+BF_4^-$ (IL-1) with a concentration of >97% and butylmethylimidazolium hexafluorophosphate $BMIM^+PF_6^-$ (IL-2) with a concentration of >98.5% were produced by Merck, and triethylammonium triflate TEA^+Tf^- (IL-3) with a concentration of >99% was synthesized by us. The purity of ionic liquid was checked by ^1H, ^{13}C, and ^{19}F NMR methods.

Iron and cobalt phthalocyanine complexes (PcFe, PcCo, *PcFe and *PcCo, where *Pc is *tetra*-4-(*N*-dibutylsulfamoyl)phthalocyanine) were synthesized at NIOPIK State Scientific Center.

Experimental Procedure

Ethylene oxidation by *p*-benzoquinone and hydrogen peroxide, hydroquinone oxidation by oxygen, and cyclohexene oxidation by oxygen were carried out in a volumetric setup placed in a thermostatically controlled chamber. Experiments were carried out at 30°C in a reactor with a magnetic stirrer having a stirring rate of 1000–1500 rpm. The overall volume of solution in the reactor was ~10 mL. It was found that the reaction rate in a reactor with a magnetic stirrer does not depend on the volume of the solution in a range of 5–15 mL, which indicated the absence of diffusion limitations. The experimental procedure and catalysts preparation in the acetonitrile system is described in detail in [11, 26]. The procedure of catalyst preparation in ionic liquids is described below.

Analysis of Oxidation Products

The reaction products were analyzed by gas–liquid chromatography (GLC) and chromatography/mass spectrometry. In the case of the $AN–H_2O$ system, the acid was neutralized with sodium bicarbonate or potassium carbonate before analysis. In the case of ionic liquids, after neutralizing the acid, the products were extracted with diethyl ether or hexane. After purging from the ionic liquid with nitrogen, acetaldehyde was determined by the oxime method.

RESULTS AND DISCUSSION

Ethylene Oxidation in Binary Solvents

As noted above, olefins are rather efficiently oxidized by *p*-benzoquinone in the $AN–H_2O$ solutions in the presence of $Pd(AN)_x(H_2O)_{4-x}^{2+}$ palladium complexes. Thus, for instance, the turnover frequency

(TOF) of the catalyst in ethylene oxidation is approximately 130 times higher than in the solution of chloride complexes [15, 26]. The study of the formation of active cationic Pd(II) complexes showed [24] that three catalytic systems (III, IV, and V) may exist that differing in the distribution of complexes with different values of x (1, 2, and 3, respectively) in the initial $Pd(OAc)_2$–$HClO_4$–$LiClO_4$–AN–H_2O solution. System III was prepared after allowing to stay for 20 min a freshly prepared $Pd_3(OAc)_6$–AN solution with added acid and water. For the preparation of system IV, a $Pd_3(OAc)_6$–AN solution was allowed to stay for 7 days, and then perchloric acid and water were added to a portion of the solution and after 20 min were added into the reactor. To prepare system V, system IV (after adding the acid and water) was allowed to stay for seven more days. These three systems differ insignificantly in their catalytic activity in ethylene oxidation by p-benzoquinone at $\alpha_{H_2O} = 0.67$ molar fraction [26]. $LiClO_4$ was used to maintain the ionic strength of solution.

The study of the influence of the molar fraction of water in the AN–H_2O system on the initial rate of ethylene oxidation by p-benzoquinone showed the extremal dependences in an α_{H_2O} range of 0.2–0.3 molar fraction for catalytic systems III (Fig. 1) and IV (Fig. 2). Note that in the process of cyclohexene oxidation in system III [11, 20], a bimodal dependence of the initial rate on α_{H_2O} was obtained. As was shown by I.V. Martynov in his master's thesis (Moscow Technological University (Institute of Fine Chemical Technologies) 2016, unpublished data) and in [24], in system III in a range of 0.2–0.3 molar fraction of water, the sum of concentrations of $Pd(AN)_3(H_2O)^{2+}$ and $Pd(AN)_2(H_2O)_2^{2+}$ complexes is close to 99% of the overall palladium concentration. It is likely that the optimal concentration of the sum of active complexes in the less active system IV at a point of maximum is achieved with a lower molar fraction of water due to various processes occurring in the course of formation of these systems. In system III, water and acid react with the palladium acetate trimer, and in system IV they react with the acetonitrile complex of monomeric palladium acetate [24].

An increase in α_{H_2O} above 0.8 molar fraction leads to a significant decrease in the rate of ethylene oxidation by p-benzoquinone and to the instability of the catalytic system. In the range $\alpha_{H_2O} = 0.8$–0.93 molar fraction, palladium is partly reduced to the metal state during the process. These results point to the important role of acetonitrile as a ligand, which stabilizes reduced forms of palladium catalysts (Pd(0) and Pd(I)) in the solution. The specific role of acetonitrile can also be judged by comparing the activity of catalytic systems with various components of binary solvents (acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO)). In a system containing 5×10^{-4} M Pd, 0.2 M $HClO_4$, 0.2 M p-benzoquinone, 0.3 M $LiClO_4$, at $\alpha_{H_2O} = 0.67$ molar fraction, the rate of ethylene oxidation ($R_0(C_2H_4)$, mol L^{-1} min^{-1}) increases in the series DMF (0.74×10^{-3}) < DMSO (2.4×10^{-3}) < AN (5.5×10^{-3}).

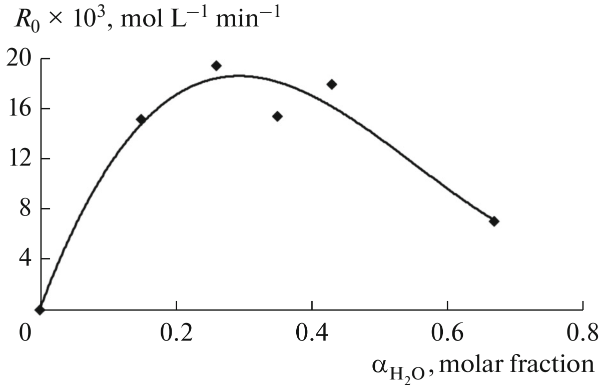

Fig. 1. Dependence of the initial reaction rate on the molar fraction of water in catalytic system III. $P_{C_2H_4} = 0.87$ atm, $[Pd]_\Sigma = 5.0 \times 10^{-4}$ mol/L, $[Q]_0 = 0.2$ mol/L, $[HClO_4] = 0.2$ mol/L, $[LiClO_4] = 0.3$ mol/L.

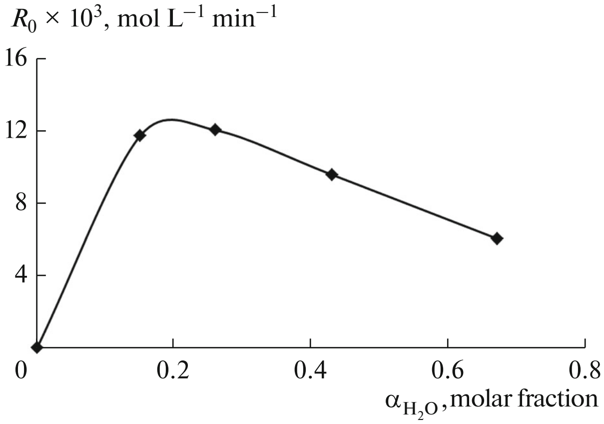

Fig. 2. Dependence of the initial reaction rate on the molar fraction of water in catalytic system IV. $P_{C_2H_4} = 0.87$ atm, $[Pd]_\Sigma = 5.0 \times 10^{-4}$ mol/L, $[Q]_0 = 0.2$ mol/L, $[HClO_4] = 0.2$ mol/L, $[LiClO_4] = 0.3$ mol/L.

The replacement of perchloric acid used in [11, 15, 16, 24] by H_2SO_4 with the same molar concentration leads to a decrease in the initial rate of ethylene oxidation by at most 12%. It was found earlier that, at $[H^+] > 0.2$ mol/L, the reaction rate remains almost constant up to $[H^+] = 0.5$ mol/L [26]. Experiments have also shown that there is a linear dependence of the initial oxidation rate on $[Pd]_\Sigma$ [26] and that its constancy is observed when hydroquinone is added to a

Table 1. Effect of [QH_2] on the rate of ethylene oxidation by *p*-benzoquinone

Run	[Q]	[QH_2]	$R_0(C_2H_4) \times 10^3$, mol L^{-1} min^{-1}
	mol/L		
1	2.0	–	5.33
2		0.06	5.34
3		0.10	5.67

$[Pd]_\Sigma = 5 \times 10^{-4}$ mol/L, [$HClO_4$] = 0.2 mol/L, [$LiClO_4$] = 0.3 mol/L, α_{H_2O} = 0.67 molar fraction.

Table 2. Activity of the catalytic systems in ionic liquids in ethylene oxidation by *p*-benzoquinone

Ionic liquid	α_{IL}	α_{H_2O}	α_{AN}	$R_0(C_2H_4) \times 10^3$, mol L^{-1} min^{-1}
	molar fraction			
$BMIM^+BF_4^-$	0.34	0.50	0.16	19.4
$BMIM^+PF_6^-$		0.49	0.17	3.2
TEA^+Tf^-		0.49	0.17	21.6

[Q] = 0.2 mol/L, $[Pd]_\Sigma = 2.5 \times 10^{-3}$ mol/L, [H_2SO_4] = 0.2 mol/L.

0.2 M *p*-benzoquinone solution (Table 1). The rate of ethylene oxidation remained constant when comparing experiments with 0.1 M *p*-benzoquinone (7.22×10^{-3} mol L^{-1} min^{-1}) and with [Q]/[QH_2] = 1 (7.21×10^{-3} mol L^{-1} min^{-1}).

Then, we studied the possibility of using hydrogen peroxide as a stoichiometric oxidant in binary solvents.

AN–H_2O system with H_2O_2. In the "standard" catalytic system with $[Pd]_\Sigma = 5 \times 10^{-4}$ mol/L and α_{H_2O} = 0.67 molar fraction at 30°C, neither hydrogen peroxide decomposition at its concentration of 0.3 mol/L nor ethylene consumption is observed. Only upon the addition of 0.2 M solution of *p*-benzoquinone (in 1 mL acetonitrile), the oxidation process begins but has a low rate (1.8×10^{-3} mol L^{-1} min^{-1}). To make the effect of *p*-benzoquinone addition more pronounced, the concentration of Pd(II) was increased by a factor of five to 2.5×10^{-3} mol/L and α_{H_2O} was increased to 0.93 molar fraction. Then, the rate of ethylene oxidation based on hydrogen peroxide increased from 0 to 2.25×10^{-4} mol L^{-1} min^{-1}. After adding *p*-benzoquinone (0.18 mol/L), the value R_0 drastically increased to 4.2×10^{-3} mol L^{-1} min^{-1}. An increase in [H_2O_2] to 1.07 mol/L at the same values of α_{H_2O} leads to an increase in the reaction rate in the presence of *p*-benzoquinone. The addition of *p*-benzoquinone (0.84×10^{-3} mol/L) leads to an increase in the rate by ~2 times, and with an increase in [$HClO_4$] to 1 mol/L, the reaction rate increases to 3.7×10^{-3} mol L^{-1} min^{-1}.

Thus, the rate of ethylene oxidation by hydrogen peroxide in the absence of *p*-benzoquinone is approximately 18 times lower than the rate with its presence (α_{H_2O} = 0.93 molar fraction) and increases with an increase in [H_2O_2], [$HClO_4$], and α_{H_2O}. The interaction of hydrogen peroxide with acetonitrile is likely to retard the oxidation process or the acetonitrile complex of Pd(0) is oxidized by hydrogen peroxide more slowly. An increase in α_{H_2O} leads to a higher rate of oxidation by hydrogen peroxide and a slower rate of oxidation with added *p*-benzoquinone.

Then, we checked the possibility of hydrogen peroxide to oxidize ethylene in the acetonitrile system in the presence of hydroquinone. Under these conditions ethylene proved to be oxidized at a rate $R_0(C_2H_4) = 1.0 \times 10^{-3}$ mol L^{-1} min^{-1}.

[QH_2]	[H_2O_2]	[Pd]	[H_2SO_4]	α_{H_2O}, molar fraction	$R_0(C_2H_4) \times 10^3$, mol L^{-1} min^{-1}
mol/L					
0.1	0.3	0.005	1.0	0.67	1.03

Because hydrogen peroxide almost does not oxidize ethylene in the absence of *p*-benzoquinone, a noticeable rate of ethylene oxidation in this experiment points to the ability of hydrogen peroxide to oxidize hydroquinone without additional catalysts.

Ionic liquid–H_2O systems. We also used ionic liquids used in oxidative catalysis, including Wacker oxidation [47]: $BMIM^+BF_4^-$ (IL-1), $BMIM^+PF_6^-$ (IL-2), and TEA^+Tf^- (IL-3). According to our and other [49] data, IL-1 can be well mixed with water to form homogeneous systems up to 76% H_2O. Table 2 shows the activity of the catalytic system in a ionic liquid in the reaction of ethylene oxidation by *p*-benzoquinone with a catalyst added to the ionic liquid in 1 mL acetonitrile at V_Σ = 10 mL.

Ionic liquid–H_2O systems with H_2O_2. At [H_2O_2] = 1.2 mol/L and [H_2SO_4] = 0.2 mol/L, the process of ethylene oxidation by hydrogen peroxide in IL-2 begins in the absence of *p*-benzoquinone. At the tenth minute, it stops, and only after adding 0.1 M of the *p*-benzoquinone solution, ethylene is consumed at a rate of 1.1×10^{-3} mol L^{-1} min^{-1}, which is approximately 3 times lower than without hydrogen peroxide. An increase in [H_2SO_4] to 1 mol/L when hydrogen peroxide and *p*-benzoquinone are used together lead to an increase in the rate of oxidation to 3.6×10^{-3} mol L^{-1} min^{-1}. Under the same conditions in IL-1, $R_0(C_2H_4)$ is 5.3×10^{-3} mol L^{-1} min^{-1}.

The use of hydrogen peroxide with hydroquinone additives showed that hydroquinone is rapidly oxidized by hydrogen peroxide in IL-2, because the rates of ethylene oxidation almost coincide (with 0.1 M hydroquinone ($R_0(C_2H_4) = 2.4 \times 10^{-3}$ mol L^{-1} min^{-1} and with 0.1 M *p*-benzoquinone ($R_0(C_2H_4) = 3.0 \times 10^{-3}$ mol L^{-1} min^{-1}) (Fig. 3). An increase in $[Pd]_\Sigma$ in the ionic liquid leads to a proportional increase in the rate R_0, and a five-fold increase in $[H_2SO_4]$ in IL-2 containing hydrogen peroxide and hydroquinone increases approximately five times the rate of ethylene oxidation. Note that, in the presence of hydrogen peroxide in the ionic liquid, the kinetic curves do not have any pronounced fast and slow segments that are characteristic of reactions with the participation of quinones in acetonitrile systems [11, 15, 26].

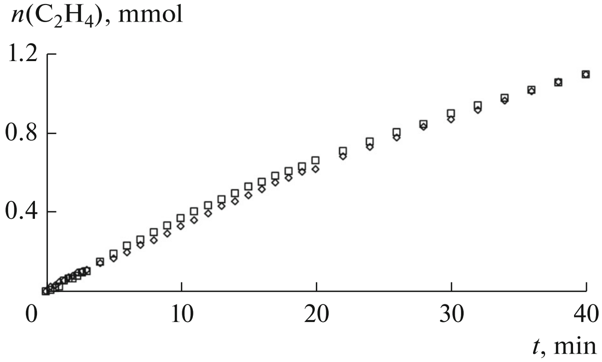

Fig. 3. Dependence of the amount of ethylene absorbed on time in the presence of *p*-benzoquinone (□, 0.1 mol/L) or hydroquinone (◇, 0.1 mol/L). $[Pd^{2+}] = 2.5 \times 10^{-3}$ mol/L, $[H_2O_2] = 1.2$ mol/L, $[H_2SO_4] = 1$ mol/L, $\alpha_{H_2O} = 0.46$ molar fraction, $\alpha_{AN} = 0.20$ molar fraction, $\alpha_{IL\text{-}2} = 0.34$ molar fraction.

Catalyst preparation for systems containing a ionic liquid. In the course of studying the oxidation process in ionic liquids, a question arose of the procedure for catalyst preparation. Earlier, catalytic systems III and IV were prepared with acetonitrile. The reactor was charged with 1 mL of $Pd(OAc)_2$ solution with an acid in acetonitrile. When working with ionic liquids, the catalysts were prepared in 1 mL of acetonitrile, in acetic acid (AA), and in a ionic liquid (a weighed sample of palladium acetate was dissolved in a portion of acetic acid, perchloric or sulfuric acid was added, and the solution was allowed to stay for 20 min. Alternatively, 0.5 mL of water and 0.6 mL of 92% sulfuric acid were added to 2 mL $BMIM^+BF_4^-$, and the solution was allowed to stay for 20 min. Experiments showed that the best procedure is the variant with acetonitrile (Table 3).

Acetaldehyde purging with nitrogen at 40–60°C from IL-1 with $[H_2SO_4] = 0.3$ mol/L, $[QH_2] = 0.3$ mol/L, and $[H_2O_2] = 4.8$ mol/L for 2 h led us to obtain 70% acetaldehyde based on consumed ethylene and a small amount of CH_3COOH with a selectivity of ~8%. Interestingly, in IL-3 without Pd(II) at $\alpha_{H_2O} = 0.56$ molar fraction and $[H_2SO_4] = 1$ mol/L, ethylene is consumed at a low rate (0.3 mmol for 140 min) to form a small amount of ethanol.

Choice of Conditions for Hydroquinone Oxidation by Oxygen in the AN–H_2O System

Solid $PcFe_{solid}$, $PcCo_{solid}$ and soluble $^*PcFe_{soluble}$, $^*PcCo_{soluble}$ compounds and $Cu(OAc)_2$ at $P_{O_2} = 0.87$ atm (30°C) in solutions with $\alpha_{H_2O} = 0.67$ molar fraction at the concentrations of reagents $Pd(OAc)_2$ (5×10^{-4} mol/L), $HClO_4$ (0.1 mol/L), and hydroquinone (0.2 mol/L) were used as catalysts for hydroquinone oxidation. Hydroquinone is oxidized by oxygen at a noticeable rate ($R_0(O_2) = (5.0–5.76) \times 10^{-3}$ mol L^{-1} min^{-1}) only at high concentrations of $PcFe_{solid}$ (0.035–0.07 mol/L). When studying the activity of $^*PcFe_{soluble,}$ it was found that the presence of $Pd(OAc)_2$ in a concentration of 5×10^{-4} mol/L has almost no effect on the rate of hydroquinone oxidation ($R_0(O_2) = (2.4–2.9) \times 10^{-3}$ mol L^{-1} min^{-1}). In the case of cobalt catalysts $PcCo_{solid}$ and $^*PcCo_{soluble}$ an order of magnitude lower oxidation rate (3.9×10^{-4} mol L^{-1} min^{-1}) was obtained only at a higher concentration of these catalysts (0.07 mol/L), although catalysis by porphyrin and salen complexes of Co(II) is known. It is also known that $Cu(OAc)_2$ catalyzes hydroquinone oxidation by oxygen in CH_3COOH (50°C) [42] and in acetonitrile [43]. The process in acetonitrile at 25°C occurs very slowly (72 h with a quinone yield of 50%), and only at a pressure of $P_{O_2} = 6–8$ atm, the process is fast and selective. Even under these conditions, $CuSO_4$ in acetonitrile does not catalyze hydroquinone oxidation [43].

Catalysis by copper acetate was tested at $\alpha_{H_2O} = 0.67$ molar fraction with perchloric (0.3 mol/L) and acetic (0.35 mol/L) acids. In both cases, oxygen consumption was not observed for 1 h. Meantime, it is known that $Cu_2(OAc)_4 \cdot 2H_2O$ rapidly oxidizes hydroquinone in ethanol with the complex formation of a

Table 3. Comparison of the methods for the preparation of catalytic systems in IL-1 in ethylene oxidation by hydrogen peroxide

Catalyst preparation procedure	Component	α_{H_2O}	$\alpha_{IL\text{-}1}$	$R_0(C_2H_4) \times 10^3$, mol L^{-1} min^{-1}
	molar fraction			
Acetonitrile	0.19 (AN)	0.43	0.38	4.42
Acetic Acid	0.17 (AA)	0.46	0.37	2.47
Ionic liquid	–	0.66	0.34	1.24

$[H_2O_2] = 1.2$ mol/L, $[QH_2] = 0.1$ mol/L, $[Pd]_\Sigma = 2.5 \times 10^{-3}$ mol/L, $[H_2SO_4] = 1$ mol/L.

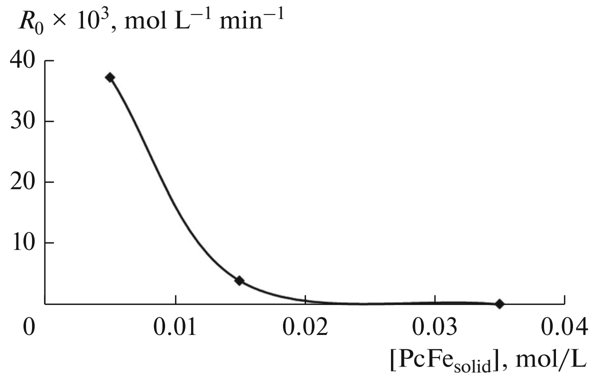

Fig. 4. Dependence of the initial rate of ethylene oxidation reaction on the concentration of solid iron phthalocyanine. $[Pd]_\Sigma = 5 \times 10^{-3}$ mol/L, $[Q] = 0.1$ mol/L, $[HClO_4] = 0.2$ mol/L, $\alpha_{H_2O} = 0.67$ molar fraction, $\alpha_{AN} = 0.33$ molar fraction, $V_\Sigma = 10$ mL.

$Cu^I(OAc)$ with *p*-benzoquinone $[Cu^I_2(syn\text{-}\mu_2\text{-}\eta^2\eta^2\text{-}Q)(OAc)_2]$, in which the Cu–Cu distance is very short (2.73 Å) [57]. In the experiments with perchloric acid in the presence of Pd(II) cationic complexes, Cu(II) will also exist in $Cu(ClO_4)_2$ and $CuSO_4$ forms, which are cationic.

The absence of the catalytic effect in the reaction of hydroquinone oxidation in acetonitrile by oxygen in this case is probably associated with very high stability constants of acetonitrile complexes of Cu(I)–$Cu(AN)_2^+$ and $Cu(AN)_4^+$ in organic solvents [58] reaching 10^4–10^6. This is reflected in the value of the oxidation potential of the Cu^{2+}/Cu^+ pair in acetonitrile, which is 1.21 V relative to the standard hydrogen electrode [59] (compared to 0.15 V in water). For the above reasons, Cu(I) acetonitrile complexes are poorly oxidized by oxygen, which leads to the absence of catalysis in the reaction of hydroquinone oxidation.

When carrying out the process of ethylene oxidation by *p*-benzoquinone (0.1 mol/L) under standard conditions with $[Pd]_\Sigma = 5 \times 10^{-4}$ mol/L, we found that the presence of solid iron phthalocyanine $PcFe_{solid}$ (0.035 mol/L) completely inhibits the oxidation process. It turned out that only an increase in the Pd(II) concentration by an order of magnitude and a decrease in the amount of $PcFe_{solid}$ lead to the oxidation of ethylene with initial rates $R_0(C_2H_4)$ shown in Fig. 4. At a zero concentration of $PcFe_{solid}$, the rate of ethylene oxidation by *p*-benzoquinone at this composition of the catalytic system is ~72×10^{-3} mol L^{-1} min^{-1}. It also turned out that the rate of oxidation $R_0(O_2)$ of formed hydroquinone by oxygen (in a concentration of 0.1 mol/L) in the presence of $PcFe_{solid}$ decreases with an increase in the ratio $[Fe]/[Pd] > 3$. Of possible explanations for the $PcFe_{solid}$ inhibition of ethylene oxidation by *p*-benzoquinone, the most likely is the adsorption of cationic Pd(II) complexes on the surface of iron phthalocyanine, which prevents the activation and oxidation of ethylene by palladium. The reasons for the inhibition of O_2 activation on the active centers of the $PcFe_{solid}$ surface with an increase in its amount are not yet clear. Interestingly, the inhibition of ethylene oxidation by the possible interaction of Pd(II) with iron phthalocyanine also occurs in the case of soluble $^*PcFe_{soluble}$ (Fig. 5a), but in the solution of this complex, the process of hydroquinone oxidation occurs predictably faster with increasing concentration of $^*PcFe_{soluble}$ (Fig. 5b).

Table 4. Effect of [PcFe$_{solid}$] on the process of cyclohexene oxidation by oxygen

Run	$[C_6H_{10}]$	$[QH_2]$	[Q]	[PcFe$_{solid}$]	$R_0(O_2) \times 10^3$, mol L^{-1} min^{-1}
	mol/L				
4	0.16	0.2	–	0.035 (purified)	3.73
5		–	0.2		–

$[Pd]_\Sigma = 5 \times 10^{-4}$ mol/L, $[HClO_4] = 0.1$ mol/L, $\alpha_{H_2O} = 0.32$ molar fraction.

In the system with $^*PcFe_{soluble}$ at $[Pd]_\Sigma = 5 \times 10^{-3}$ mol/L, $[Q] = 0.1$ mol/L and $[H_2SO_4] = 0.2$ mol/L, it was found that, with an increase in [Fe]/[Pd] from 3 to 7, the amount of absorbed ethylene is higher than stoichiometric based on *p*-benzoquinone by a factor of ~1.3. Using GLC analysis, we found that, in addition to acetaldehyde, a mixture of three isomeric linear butenes are formed.

A similar inhibition by $PcFe_{solid}$ of olefin oxidation was noted also in the oxidation of cyclohexene by *p*-benzoquinone in the presence of $PcFe_{solid}$ purified by washing with water on filter (Table 4) at a low concentration of Pd(II) when hydroquinone almost does not form at a ratio [Fe]/[Pd] of 70 (run 5), but added hydroquinone (run 4) is oxidized by oxygen.

Only an increase in the Pd(II) concentration by an order of magnitude, as in the case of ethylene, led to the oxidation of cyclohexene to cyclohexanone, the appearance of hydroquinone, and its oxidation by oxygen (Table 5). The average productivity with respect to cyclohexanone during the time of a run in runs 6 and 8 was 0.23–0.26 mol L^{-1} min^{-1}.

A kinetic study of hydroquinone oxidation in the AN–H_2O system by oxygen showed that the reaction is described by the first order in hydroquinone both in the presence of solid $PcFe_{solid}$ and soluble $^*PcFe_{soluble}$ iron phthalocyanine (Table 6).

A decrease in the rate constant in runs 9 and 10 has no explanation either. The oxidation of hydroquinone by oxygen in the presence of $PcFe_{solid}$ (0.035 mol/L) also occurs in IL-1 ($\alpha_{H_2O} = 0.57$ molar fraction, $\alpha_{AN} =$

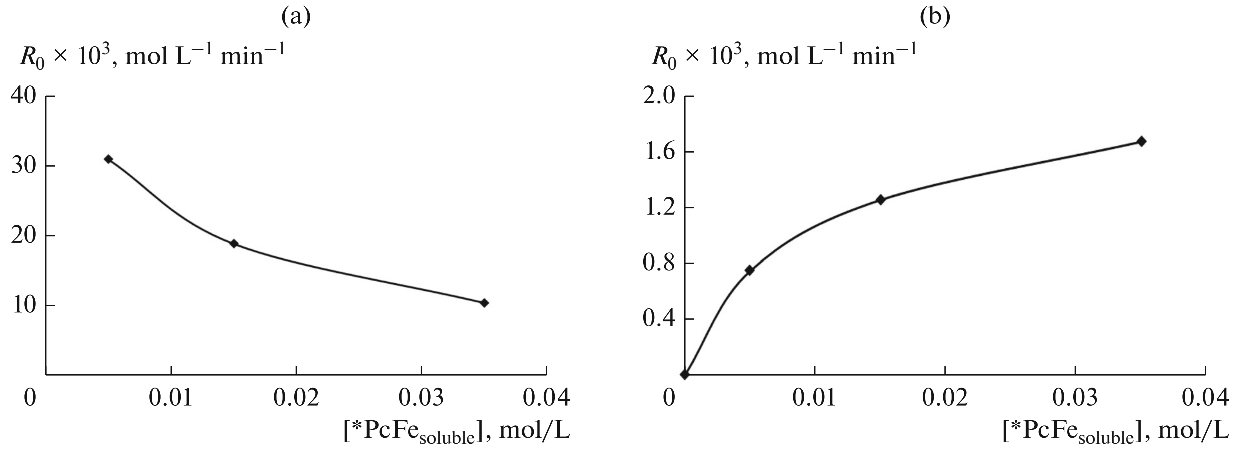

Fig. 5. Dependence of the initial rate of oxidation of (a) ethylene and (b) hydroquinone on the concentration of soluble iron phthalocyanine. $[Pd]_\Sigma = 5 \times 10^{-3}$ mol/L, [Q] = 0.1 mol/L, $[HClO_4] = 0.2$ mol/L, $\alpha_{H_2O} = 0.67$ molar fraction, $\alpha_{AN} = 0.33$ molar fraction, $V_\Sigma = 10$ mL.

0.22 molar fraction, $\alpha_{IL\text{-}1} = 0.21$ molar fraction) at the rate $R_0(O_2) = 2.3 \times 10^{-3}$ mol L^{-1} min^{-1} and $k = 27.7 \times 10^{-3}$ s^{-1}.

Cyclohexene Oxidation in Binary Solvents

Using the results of the study of ethylene and hydroquinone oxidation in the AN–H_2O and ionic liquid–H_2O systems, we chose the conditions for the reaction of cyclohexene oxidation.

AN–H_2O system with *p*-benzoquinone. The study of phase equilibria in the ternary AN–H_2O–C_6H_{10} system [20, 25] showed (Fig. 6) the presence of domains of three-phase (I) and two-phase (II) exfoliation and a homogeneous domain (III). This made it possible to choose the compositions of solutions in the homogeneous and two-phase domains for carrying out the reaction of cyclohexene oxidation by *p*-benzoquinone. In the homogeneous domain at α_{H_2O} = 0.3 molar fraction and $[C_6H_{10}]_0 = 0.15$–0.16 mol/L in the $Pd(OAc)_2$ (4×10^{-3} mol/L)–$HClO_4$ (0.2 mol/L)–Q(0.2 mol/L) system at 30°C, we obtained the following results (Table 7).

The process selectivity to cyclohexanone in two runs is 93%. The transition to the two-phase domain (II) to solutions with α_{H_2O} = 0.26 molar fraction, $\alpha_{AN} = 0.64$ molar fraction, $\alpha_{C6H10} = 0.1$ molar fraction and $\alpha_{H_2O} = 0.8$ molar fraction, $\alpha_{AN} = 0.08$ molar fraction, $\alpha_{C6H10} = 0.12$ molar fraction (shaken reactor) is accompanied by a drastic decrease in the selectivity to cyclohexanone to 45% in the first domain (α_{H_2O} = 0.26, point 1) and 10% in the second domain (α_{H_2O} = 0.8, point 2). In these systems, high-boiling products of probable cyclohexene oligomerization in addition to cyclohexene and cyclohexanone appeared in the chromatograms [2]. Thus, transition to heterogeneous systems with high concentrations of cyclohexene leads to its side transformations in solutions containing an acid and Pd^{2+}.

It was shown above (Table 5) that cyclohexene can be oxidized by oxygen in the AN–H_2O system in the presence of solid iron phthalocyaninate and *p*-benzoquinone:

$$C_6H_{10} + ½\, O_2 = C_6H_{10}O.$$

Table 5. Cyclohexene oxidation by oxygen in the presence of PcFe$_{\text{solid}}$

Run	$[C_6H_{10}]$	[PcFe $_{\text{solid}}$]	$R_0(O_2) \times 10^3$, mol L^{-1} min^{-1}	Time of a run, min	Absorbed O_2	Oxidized QH_2	$[C_6H_{10}O]$ (after a run), mol/L	$C_6H_{10}O$ yield, %
	mol/L				mmol			
6	0.16	0.01	0.85	40	0.13	0.26	0.091	57
7	0.16	0.005	1.26	90	0.28	0.57	0.085	53
8	0.16	0.0025	0.66	40	0.12	0.23	0.104	65

$[Pd]_\Sigma = 5 \times 10^{-3}$ mol/L, [Q] = 0.1 mol/L, $[HClO_4] = 0.2$ mol/L, $\alpha_{H_2O} = 0.32$ molar fraction, $\alpha_{AN} = 0.68$ molar fraction, $V_\Sigma = 10$ mL.

Table 6. Rate constant of hydroquinone oxidation by oxygen in the presence of PcFe catalysts

Run	PcFe	$[Pd]_\Sigma$	$k \times 10^3$, s^{-1}
	mol/L		
9	0.005 (solid)	0.005	9.8
10	0.015 (solid)	0.005	4.8
11	0.005 (soluble)	0.005	8.1
12	0.015 (soluble)	0.005	12.3
13	0.035 (soluble)	0.005	15.3

Table 7. Changes in the concentrations of cyclohexene and cyclohexanone in the course of experiments

Run	*t*, min	$[C_6H_{10}]$	$[C_6H_{10}O]$
		mol/L	
14	0	0.153	0
	1	0.091	0.043
	30	0	0.124
	60	0	0.137
15	0	0.154	0
	1	0.100	0.077
	45	0	0.154
	–	–	–

As a result, for liquid–liquid equilibria in the AN–H_2O–C_6H_{10}–$C_6H_{10}O$ system, it was found [60] that the homogeneous system can be separated into components by extractive distillation. To simplify the technology of separation of cyclohexanone, it is advisable to expand the set of organic high-boiling solvents for aqueous–organic systems.

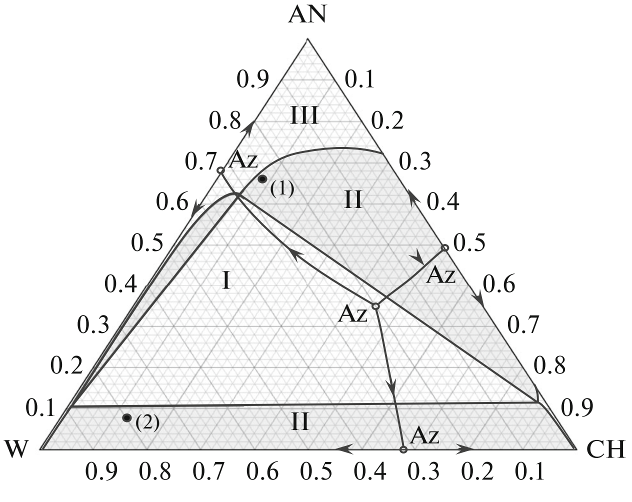

Fig. 6. A diagram of phase equilibrium of the ternary system water (W)–acetonitrile (AN)–cyclohexene (C_6H_{10}), containing the domains of three-phase (I) and two-phase (II) (shaded) exfoliation and homogeneous domain (III), and the arrangement of the chosen points of the composition (1) and (2) [25]. Az is azeotrope.

Ionic liquid–H_2O system in cyclohexene oxidation. Unlike ethylene oxidation, cyclohexene oxidation in systems with a ionic liquid is not as efficient and selective. For example, in the case of IL-1, cyclohexene is converted in the presence of sulfuric acid without palladium acetate to form high boiling oligomers. At the same time, cyclohexanone, introduced into a solution containing palladium cationic complexes, does not transform within 1 h. In the system with IL-3, cyclohexene is almost not oxidized by *p*-benzoquinone for 30 min: in the extract (diethyl ether), ~96% of the initial cyclohexene is found. The oxidation of cyclohexene by oxygen in IL-1 in the presence of hydroquinone and $PcFe_{solid}$ for 2 h led to the complete conversion of cyclohexene, but the yields of cyclohexanone and cyclohexanol, which is the product of cyclohexene hydration were low: 5.5%. It was found by chromatography/mass spectrometry that the extract of diethyl ether contains 2-cyclohexen-1-ol, 2-cyclohexen-1-one, benzene, unsaturated products of cyclohexene oligomerization (dodecane and others), and the products of oligomer oxidation (hexadecenoic, octadecenoic and other acids). Apparently, the stronger acidic properties of IL-1 with 0.2 M H_2SO_4 lead to the catalysis of nonoxidative reactions: cyclohexene oligomerization and its hydration. The addition of $PcFe_{solid}$ is likely to favor the side conversions of cyclohexene. As noted above, the formation of butenes from ethylene was also detected in the acetonitrile system when carrying out the reaction in the presence of $PcFe_{solid}$.

The transition to two-phase systems in the case of IL-1 and IL-2 under conditions of increasing concentrations of cyclohexene in the catalytic system leads to a decrease in the cyclohexanone selectivity to 10–30% in cyclohexene oxidation by *p*-benzoquinone.

It follows from the results obtained that the studied ionic liquid are not suitable media for cyclohexene oxidation. It is possible that ionic liquids with less pronounced acidic properties [49] will be more suitable as components of binary solvents for this reaction catalyzed by cationic palladium complexes.

CONCLUSIONS

A study of ethylene oxidation by *p*-benzoquinone in the AN–H_2O system in the presence of cationic palladium complexes showed that the optimal conditions at 30°C are $\alpha_{H_2O} = 0.3$ molar fraction, $[H_2SO_4] = 0.2$ mol/L, $[Q] = 0.1–0.2$ mol/L at $P_{C_2H_4} = 0.8–0.9$ atm. The selectivity to acetaldehyde is at least 95%. It is shown that the rate of ethylene oxidation by hydrogen peroxide in this system is very low and increases about

10 times only when *p*-benzoquinone is added to the solution.

It is reasonable to carry out cyclohexene oxidation by *p*-benzoquinone under homogeneous conditions at $\alpha_{H_2O} = 0.3$ molar fraction (and at 0.6–0.7 molar fraction), $[H_2SO_4] = 0.2$ mol/L, $[Q] = 0.1$ mol/L, and $[C_6H_{10}] < 0.2$ mol/L. The selectivity to cyclohexanone reaches 93%.

Comparison of the activity of catalytic systems in cyclohexene oxidation in binary solvents (with cationic palladium complexes) with aqueous or aqueous–organic catalytic systems based on Pd(II) chloride complexes with quinone and $CuCl_2$ as oxidants is very complicated. Comparison of TOF values for different catalytic systems is correct only at the same substrate concentrations and, of course, at the same orders in a substrate and a catalyst (using $[M]_\Sigma$; for a review, see [61]). It is especially difficult to judge the orders of magnitude of activity values when determining the TOF from the initial reaction rates in the case of different kinetic models [11] with different structures of the apparent rate constants. According to [7], the transition to cationic Pd(II) complexes in acidic solutions in a binary AN–H_2O solvent accelerates the oxidation process of cyclohexene by ~50 times compared with all known systems. Unfortunately, we do not know from that work how this value was obtained. If we assume the first order in cyclohexene, data presented in [7] can be used to estimate the apparent rate constant ($k \approx 0.08$ min^{-1}) and calculate the TOF for $[C_6H_{10}] = 0.16$ mol/L and $[Pd]_\Sigma = 5 \times 10^{-3}$ mol/L. We get TOF = 2.56 min^{-1}. Based on [11, 20] and our work, the values of TOF in the AN–H_2O system (based on the initial rates) are within the range 9–25 min^{-1} (30°C). In solutions of palladium chloride complexes at [Cl]/[Pd] = 19.2 with the same oxidant (*p*-benzoquinone), TOF = $(0.6–4.3) \times 10^{-3}$ min^{-1} [22] (25°C). In an ethanol solution of $PdCl_2$ and $CuCl_2 \cdot 2H_2O$ [23] at 60°C, TOF = 0.3 min^{-1}.

Ethylene oxidation by *p*-benzoquinone in IL-1, IL-2, and IL-3 effectively occurs with rates close to those in the AN–H_2O system. The rate of ethylene oxidation with hydrogen peroxide is much higher than in the acetonitrile system. It is also shown that, in ionic liquids, hydroquinone is oxidized by hydrogen peroxide to quinone, and the rates are almost the same when either *p*-benzoquinone or hydroquinone is added. It is found that in the presence of a catalyst that activates oxygen ($PcFe_{solid}$), hydroquinone is oxidized by oxygen in the AN–H_2O and ionic liquid–H_2O systems with *p*-benzoquinone conversion into a third catalyst of olefin oxidation (Pd^{2+}–Q–PcFe) in accordance with literature data [6, 39–41].

The apparent first-order rate constants in the oxidation of hydroquinone with oxygen are determined. The high concentrations of PcFe (solid and soluble) at [PcFe]/[Pd] > 3–7 lead to the retardation if ethylene and cyclohexene oxidation.

Ionic liquids used by us prove to be inappropriate media for cyclohexene oxidation in the presence of sulfuric acid. Thus, in IL-1, cyclohexene is converted into byproducts of nonoxidative and oxidative types even at $[Pd]_\Sigma = 0.01$ mol/L, and in IL-3, the oxidation process almost does not occur at 25°C.

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