Kinetics of Cyclohexene Oxidation by *p*-Quinones in Aqueous–Organic Solutions of Cationic Palladium(II) Complexes

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Abstract—A kinetic study of cyclohexene oxidation by *p*-quinones in water–acetonitrile solutions of cationic Pd(II) complexes has been carried out for the first time. The observed kinetic regularities (dependence of the initial rate on the $HClO_4$ and *p*-benzoquinone concentrations) and the shape of the kinetic curves differ radically from those for the chloride systems. The unsteady-state process can be described only under the assumption that complexes of reduced palladium species with quinones are catalytically active forms. The role of solvated palladiumcarbenium ions in particular steps of the mechanism is discussed.

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The discovery of catalytic systems based on palladium complexes and the oxidation of olefins into aldehydes and ketones [1, 2] (Wacker process) and into acetals, ketals, and enol esters [3, 4] in solutions of $PdCl_2$ and $CuCl_2$ stimulated studies aimed at modifying the catalytic systems and oxidation conditions in order to increase the rate and selectivity of the reactions, especially those of the syntheses of ketones from higher α-olefins, internal olefins, and cycloolefins. Aqueous–organic systems with dimethylfomamide (DMF), acetonitrile, and alcohols based on $PdCl_2$ with $CuCl_2$ ($CuCl_2$–O_2) or *p*-benzoquinone (BQ) as the oxidant were used [5, 6]. The reaction of ethylene with palladium sulfate and nitrate in acidic media was observed by Smidt et al. [7] as early as 1962. However, the non-chloride systems with quinones and heteropoly acids as oxidants were likely to be proposed and studied for the first time by Matveev and his colleagues [8–15]. The $PdSO_4$–H_2SO_4 ($HClO_4$)–H_2O–BQ systems are active in strongly acidic media (0.1–3.0 M $HClO_4$) at 20–30°C in ethylene and propylene oxidation, and the $PdSO_4$–HPA systems [12, 13] are active in the oxidation of ethylene and butylenes. These systems ($PdSO_4$, $Pd(OAc)_2$ with BQ or HPA) in aqueous–organic homogeneous [16–18] or two-phase [19] media turned out to be especially efficient in the case of higher olefins and cycloolefins. For instance, on passing from the Cl^- anion to the ClO_4^- anion in an acidic medium, the productivity of α-decene oxidation (mol l^{-1} h^{-1}) increases by a factor of about 24 at $[H^+] = 0.1$ mol/l and by a factor of ~60 at $[H^+] = 0.3$ mol/l [17]. In addition, the reactivity of lower olefins changes sharply. In the sulfate system under the same conditions, the oxidation rate of propylene exceeds that of ethylene by a factor of about 40 [15], whereas in the chloride system the ratio of these rates is 0.56 (Cl/Pd ≈ 20, $[HClO_4] = 1.0$ mol/l, 298 K) [20]. In the $Pd(OAc)_2$–DMF–water system, benzoquinone was also regenerated: hydroquinone was oxidized electrochemically [16] or via a reaction with oxygen catalyzed by the iron phthalocyaninate complex (PcFe) [21].

The following interesting hypotheses, which undoubtedly need experimental verification, have been suggested [10–15].

(1) The main state of palladium in the Pd^{2+}–H^+–BQ–H_2O catalytic system is represented by the reduced palladium species Pd(0) and Pd_2^{2+} stabilized by quinone and olefins. There is up to 2 mol of olefin (ethylene, propylene) per mole of palladium in the complex. The complex $Pd_2SO_4(BQ) \cdot 3H_2O$ was isolated [22], but its structure was not determined.

(2) The increase in the rate of olefin oxidation by quinones with an increase in the hydrogen ion concentration is explained by the fact that the slow step of this process, unlike the slow step in the chloride systems, is oxidation by quinone involving the proton of the π-complex $Pd(0)(BQ)(C_nH_{2n})_2$ or a Pd(I) π-complex, yielding a Pd(II) π-complex, for example,

$$Pd(BQ)(C_2H_4)_2 + H^+ \longrightarrow Pd(C_2H_4)_2(BQH)^+.$$
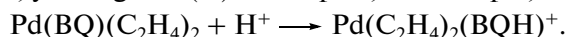
This π-complex decomposes rapidly under the action of a water molecule and a proton to $Pd(0)(C_2H_4)$, CH_3CHO, and BQH_2, probably through the formation of the hydroxyethyl–palladium (metallahydrin) intermediate that was proposed by Moiseev [4] and is now accepted by nearly all

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researchers. Some of the earlier observations [10–15] were confirmed by the study of aqueous–organic non-chloride systems in the oxidation of higher olefins by *p*-quinones [16–18, 21].

The main conclusions from these works are as follows:

(1) Evidently, it is Pd(II) cationic complexes that are the precursors of the catalytically active species in the process. It was shown that the reaction rate in these systems is independent of the nature of the anion in the palladium salt (SO_4^{2-}, NO_3^-, OAc^- [17]) in the presence of strong acids. Undoubtedly, the $Pd_3(OAc)_6$ trimer, reacting with a strong acid and acetonitrile, is converted into $Pd(CH_3CN)_{4-x} \cdot (H_2O)_x^{2+}$ complexes.

(2) In all of the "cationic" systems, the oxidation rate or the product yield increases over the same time as [H⁺] increases up to a constant (maximum) value. The acceleration of the reaction by strong acids due to the formation of palladium cationic complexes is also known for the oxidation of arenes by palladium acetate into biaryls in acetic acid [23–25].

It should be mentioned that the dependence of the olefin oxidation rate (*r*) on [H⁺] in aqueous chloride systems is not always described by the classical equation $r = a/[H^+]$ [4]. The zero order with respect to the acid concentration was observed for the oxidation of cyclohexene by *p*-benzoquinone in the $PdCl_2$–$LiCl$–$HClO_4$–H_2O system [20, 26]. The independence of the ethylene oxidation rate of [HCl] in the 0.5–2.0 mol/l range ([HCl + LiCl] = 5 mol/l) was observed in the $PdCl_2$–$HgCl_2$–$FeCl_3$ system at 90°C ($r = b + a/[H^+]$) [27]. Dependences on [H+] with an extremum were observed at Cl/Pd < 20 in the oxidation of *trans*-hex-2-ene [20], and the first-order reaction rate increased only in the [H⁺] range from 0.02 to 0.1 mol/l.

Estimation of the degree of hydrolysis of Pd^{2+} in water from the equilibrium constants of hydrolysis [28] shows that, for the largest known equilibrium constants (pK = 1.6), the degree of hydrolysis does not exceed 20% at [$HClO_4$] = 0.1 mol/l and [Pd] = 0.004 mol/l and decreases to 9% on going to an acid concentration of 0.2 mol/l. According to the presented estimates, if they are valid for the acetonitrile–water system, the influence of the acid concentration on the increase in the concentration of the palladium cation does not explain the approximately twofold increase in the rate of dec-1-ene oxidation in the [$HClO_4$] = 0.1–0.3 mol/l range [17]. The absence of an influence of the anion nature on the rate of olefin oxidation, mentioned above [17], may also indicate an insignificant contribution of the hydroxyl-containing palladium(II) complexes to the oxidation rate.

All these observations [6, 10–18, 21] and especially the change in the relative reactivity of the ethylene/propylene pair [15] suggest that oxidation via mechanisms different from the classical mechanism substantiated by Moiseev [4, 29] takes place in the

non-chloride aqueous–organic and aqueous systems. Now the likelihood of catalysis of oxidation processes by complexes of reduced palladium species with quinones (Q) is doubtless [30]. For instance, Pd(I) carbonyl complexes catalyze the oxidative carbonylation of alcohols to dialkyl oxalates [31, 32] and Pd(0) complexes catalyze the oxidative dehydrogenation of olefins [33] and the oxidative carbonylation of alkynes at the C–H bond [34, 35]. Interesting information on the mechanism of action of palladium dications in aqueous acidic media was provided by the study of their reduction by alcohols and Fe(II) ions and their catalytic effect in alcohol oxidation by oxygen [36–39]. π-Allyl complexes and products of the allylic oxidation of olefins [40] were observed in the oxidation of olefins and cycloolefins substituted at the double bond by palladium(II) cations in water.

The purpose of the present work is to carry out a kinetic analysis of olefin oxidation by quinones under conditions of the existence of palladium cationic complexes using cyclohexene oxidation in aqueous–organic media as an example and to find approaches to the elucidation of the mechanism of this reaction and of the chemical and kinetic functions of *p*-quinones [30].

EXPERIMENTAL

Kinetic experiments were carried out in a solution 10 ml in volume in a temperature-controlled (23°C) sealed reactor equipped with a magnetic stirrer. The reactor was charged with a palladium salt (palladium acetate), *p*-benzoquinone (or another quinone), and 6 ml of an acetonitrile–water (7 : 1 vol/vol) mixture as the solvent. Next, the necessary amount of perchloric acid in the solvent (2 ml) was introduced. The reactor was blown with nitrogen (500 ml, measured with a burette) and sealed, and the solution was stirred magnetically for 20 min. The necessary amounts of the substrate (cyclohexene) and the reference substance (methyl ethyl ketone) were dissolved in the solvent (2 ml), and the resulting solution was analyzed by GLC. After that, the solution was syringed into the reactor. The moment of injection of the solution of the substrate was taken to be the onset of the reaction. The first sample for GLC analysis was taken with a microsyringe after 1 min. Thereafter, the reaction mixture was sampled at 6-min intervals during the experiment.

GLC analysis was carried out on an LKhM-8MD chromatograph (thermal-conductivity detector, column length of 1 m, Porapak Q as the adsorbent, helium as the carrier gas (1.7 l/h), injection port temperature of 250°C, oven temperature of 200°C, detector temperature of 180°C, detector current of 150 mA) for determination of cyclohexene, another LKhM-8MD chromatograph (thermal-conductivity detector, column length of 3 m, Apiezon as the adsorbent, helium as the carrier gas (1.35 l/h), injection port tem-

perature of 240°C, oven temperature of 150°C, detector temperature of 220°C, detector current of 140 mA for the determination of cyclohexanone, and a Tsvet chromatograph (flame-ionization detector, column length of 3 m, 10% PPMS-4/Polikhrom I phase, air (0.33 l/h), hydrogen (0.03 l/h), helium (1.2 l/h), injection port temperature of 300°C, oven temperature of 100°C). The composition of the liquid phase after the run was determined by chromatography coupled with mass spectrometry on an Agilent Technologies 6890 N gas chromatograph (United States) equipped with an Agilent Technologies 5973 mass detector (capillary column HP-1; polymethylsiloxane active phase; column length of 50 m; inner diameter of 0.32 m; 0.51-μm-thick phase layer; helium as the carrier gas (1 ml/min); flow ratio of 100 : 1; temperature-programmed heating of the columns: isotherm at 50°C (5 min), heating rate 15 K/min (12 min), isotherm at 230°C (5 min); sample size of 0.2 μl).

Specimens for high-resolution transmission electron microscopy (HRTEM) on a JEOL JEM 2100 instrument were prepared as follows. Magnesium oxide was deposited onto the copper grid of the detector. For this purpose, the grid was held for 2−5 s in the white smoke of burning magnesium. Next, the solution to be examined was sprayed as a mist onto the grid using an ultrasonic disperser or a sprayer. The analyzed samples were compared with those obtained by spraying solutions of nanoclusters (giant palladium clusters [41] kindly presented by I.P. Stolyarov) in acetonitrile.

Distilled cyclohexene (reagent grade, Acrosorganics), acetonitrile (reagent grade), freshly sublimated *p*-benzoquinone, and palladium acetate synthesized according to a known procedure [42] were used.

The program for solving the direct problem of chemical kinetics in a closed well-stirred reactor [43] uses the STIFF subprogram [44] recompiled for an ATX computer (Fortran 95 language) for numerical integration of systems of ordinary differential equations. The program for numerical estimation of the parameters of a given kinetic model [43] uses the method of configurations in the minimization of the deviation of calculated responses from the measured values. This method is among the direct extremum seeking methods; that is, it requires no calculation of derivatives of the objective function of the sought parameters. Since the values of the sought parameters differ strongly in their order of magnitude, they were varied in the logarithmic field. The increment was changed automatically during the search in such a way that the maximum convergence rate was ensured along with the required accuracy. The objective function, a measure of the deviation of a model from experimental data, was the squared difference between the calculated and measured responses (current concentrations of the substrate in the reaction mixture) averaged over the entire data array. Particular runs were compared in terms of the sum of the squares of these deviations. Note that the root-mean-square deviation of the sub-
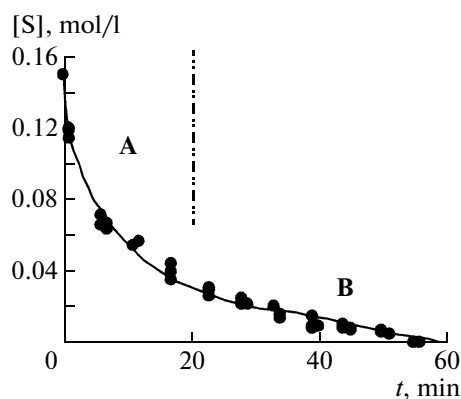
Fig. 1. Time dependence of the cyclohexene concentration [S]. The data reproducibility in four experiments is demonstrated. $[Pd]_0 = 0.004$ mol/l, $[BQ]_0 = 0.2$ mol/l, $[HClO_4] = 0.2$ mol/l.

strate concentration calculated using the optimum model from the experimental concentration was somewhat larger than 4 mmol/l, which is close to the experimental error (Fig. 1).

RESULTS AND DISCUSSION

The study of reaction (I) involving BQ and other quinones (Q),

$$C_6H_{10} + H_2O + Q \longrightarrow C_6H_{10}O + QH_2 \qquad (I)$$

in the $Pd(OAc)_2-HClO_4-CH_3CN-H_2O$ system showed [45][1] that, in the ranges of Pd(II) concentrations from 0.001 to 0.005 mol/l and $HClO_4$ concentrations from 0.1−0.5 mol/l at an acetonitrile to water molar ratio of 2.4 (used earlier [16−18]) and temperatures of 20−25°C, the substrate disappearance kinetics is well reproducible (Fig. 1). Cyclohexene (S) is oxidized to cyclohexanone (P) with high selectivity (95−100%). Among the by-products, we identified 2-cyclohexen-1-ol and 2-cyclohexen-1-one. When the quinone is absent or deficient, palladium black or palladium mirror forms and benzene and cyclohexane appear among the products. At a $Pd(OAc)_2$ concentration of 0.05 mol/l, the proportion of 2-cyclohexen-1-one reaches 13%. The study of the $Pd(OAc)_2$ (0.05 mol/l)−$HClO_4$ (0.2 mol/l)−BQ (0.2 mol/l)−S (0.06 mol/l)−CH_3CN-H_2O mixture showed that the $Pd(OAc)_2-CH_3CN-H_2O$ system is quite stable both in the absence and in the presence of the acid. The $Pd(OAc)_2-BQ$ system without the acid and substrate does not yield palladium black. In the $Pd(OAc)_2-HClO_4-S$ system, the solution rapidly turns colorless and palladium black, cyclohexanone, and benzene form. Cyclohexanone is almost nonoxidizable in the $Pd(OAc)_2-HClO_4$ system.

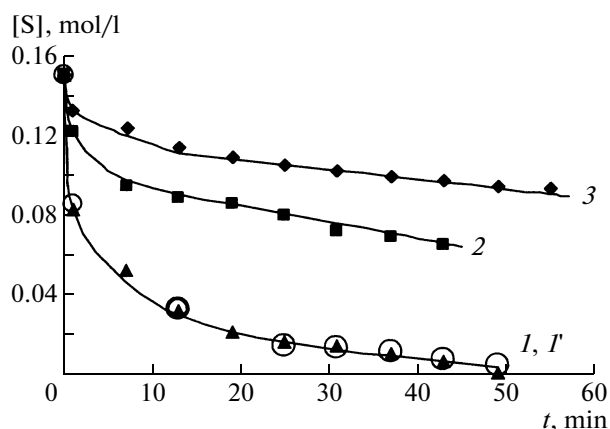
[1] E.A. Sudachenko took part in the preliminary experiments.

[S], mol/l

Fig. 2. Kinetics of cyclohexene disappearance at different $[Pd]_0$ values of (*1*) 0.004 (*1'* is a replica of *1*), (*2*) 0.002, and (*3*) 0.0015 mol/l; $[BQ]_0 = 0.4$ mol/l, $[HClO_4] = 0.2$ mol/l.

A kinetic analysis showed that the kinetic curves have two characteristic parts (Figs. 1, 2) under nearly all conditions. The rapid decrease in the reaction rate with time, depending on $[Pd]_0$, $[S]_0$, $[H^+]_0$, and $[Q]_0$, is observed in the region **A**. In the region **B**, the rate changes insignificantly with time as the substrate concentration ([S]) decreases, being almost independent (in a certain concentration range) of the initial concentrations of the reactants and catalyst (Fig. 3).

Under conditions of a 2.6-fold excess of quinone over the substrate and a constant acid concentration, the dependences are not described by simple kinetic laws (1) and (2) with respect to [S]:

$$-d[S]/dt = k[S]^n, \qquad (1)$$

$$-d[S]/dt = k[S]^n/(1 + k_1[S]^m), \qquad (2)$$

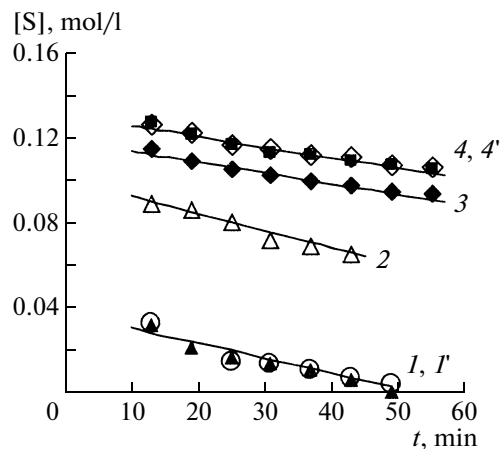which are characteristic of processes involving a single form of the active species. The best description

(in terms of the sum of squared deviations between the experimental and calculated [S] values (SS)) of region **A** using Eq. (1) is attained at $n = 2$.

In the case of the model described by law (2), the best combination of the n and m values is $n = 2$ and $m = 0.2$. The introduction of the quinone concentration ($[Q] = a + [S]$, where $a = [Q]_0 - [S]_0$) into Eqs. (1) and (2), which yielded

$$-d[S]/dt = k[S]^n[Q]^m = k[S]^n(a + [S])^m, \qquad (3)$$

$$-d[S]/dt = k[S]^n(a + [S])/(1 + k_1[S]^m) \qquad (4)$$

improved the description of the curves by Eq. (3) for the experiments presented in Fig. 1 at $n = 1$ and $m = 1$ ($a = 0.05$). However, the best description (in terms of SS) of experiments at $a = 0.25$ ($n = 2$. $m = 1$) is at variance with the run of the kinetic curves in Fig. 2. This situation is not improved by passing to Eq. (4). It follows from these results that several forms of active species are involved in the process.

The next stage of the work was to determine the dependences of the initial rates (region **A**) on the initial concentrations of H^+ and BQ. The dependence of r_0 on $[H^+]_0$ (Fig. 4) was obtained at a constant ionic strength of $[HClO_4] + [LiClO_4] = 0.7$ mol/l. In full agreement with the literature [17], the initial reaction rate r_0 is zero at $[H^+] = 0$ and increases with an increase in $[H^+]_0$, passing through a weak maximum at $[H^+] = 0.4–0.5$ mol/l. In the region **B**, the rate r_B remains almost unchanged with time and is independent of $[H^+]_0$. The initial oxidation rate increases with an increase in the benzoquinone concentration to approximately $[BQ]_0 = 0.4$ mol/l and then passes through a maximum (Fig. 5). As in the experimental series with $[H^+]_0$, the rate r_B in the region **B** is almost independent of $[BQ]_0$. Since the initial rate depends explicitly on the benzoquinone concentration, we studied the influence of the nature of the *p*-quinone on
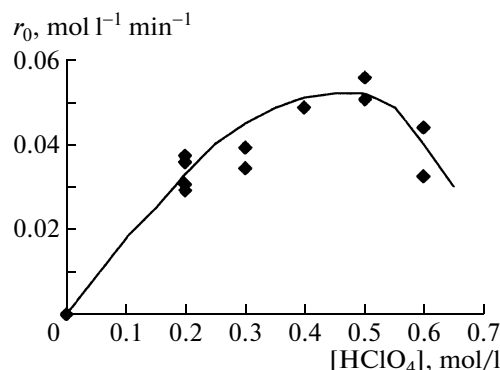

Fig. 3. Kinetics of cyclohexene disappearance in the region **B** at different $[Pd]_0$ value of (*1*) 0.004 (*1'* is a replica of *1*), (*2*) 0.002, (*3*) 0.0015, (*4*) 0.001 (*4'* is a replica of *4*) mol/l; $[BQ]_0 = 0.4$ mol/l, $[HClO_4] = 0.2$ mol/l.

Fig. 4. Dependence of the initial oxidation rate (r_0) on $[H^+]_0$ at a constant ionic strength of $[HClO_4] + [LiClO_4] = 0.7$ mol/l, $[Pd]_0 = 0.004$ mol/l, $[BQ]_0 = 0.2$ mol/l, and $[S]_0 = 0.15$ mol/l.
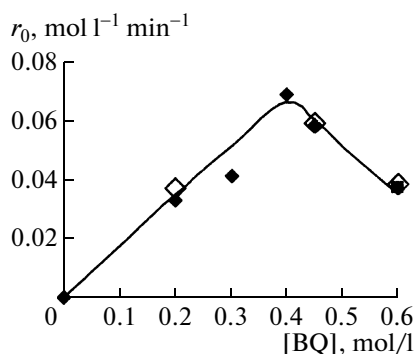
Fig. 5. Dependence of the initial oxidation rate on the *p*-benzoquinone concentration; $[Pd]_0 = 0.004$ mol/l, $[HClO_4] = 0.2$ mol/l, $[S]_0 = 0.15$ mol/l.

Fig. 6. Influence of the nature of *p*-quinone on the cyclohexene disappearance kinetics: (*1*) 2,6-di(*tert*-butyl)-*p*-benzoquinone, (*2*) trimethyl-*p*-benzoquinone, and (*3*) *p*-benzoquinone. $[Pd]_0 = 0.004$ mol/l, $[HClO_4] = 0.2$ mol/l, $[Q]_0 = 0.2$ mol/l.

the rate of reaction (I). When trimethyl-*p*-benzoquinone and 2,6-di(*tert*-butyl)-*p*-benzoquinone were used, the catalytic oxidation process was observed, but the rate of oxidation by quinones containing electron-donating substituents was considerably lower (Fig. 6). The other quinones (anthraquinone-2,6-disulfonic acid, 2,3-dichloro-1,4-naphthaquinone, anthraquinone, and tetrachloro-*p*-benzoquinone) are very poorly soluble in the acetonitrile–water mixture.

The shape of the kinetic curves, an analysis of the reaction order with respect to [S], and the dependences of the initial rates on $[H^+]_0$, $[BQ]_0$, and the nature of *p*-quinones are in accord with the conclusions from the works on ethylene and propylene oxidation in aqueous solutions of cationic palladium(II) complexes [14, 15] and suggest that the mechanism of reaction (I) in the system examined is not defined by the classical sequence of steps of the so-called Wacker process [4]:

$$Pd(II) \xrightarrow[-P]{S, H_2O} Pd(0) \xrightarrow[-BQH_2]{BQ, H^+} Pd(II). \qquad (II)$$
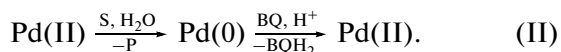
If this one-route mechanism is modified by the introduction of BQ into the substrate conversion step,

$$Pd(II) \xleftarrow{S} Pd(II)S \xrightarrow[P]{BQ, H_2O} Pd(0)BQ \xrightarrow[-BQH_2]{H^+} Pd(II), (III)$$
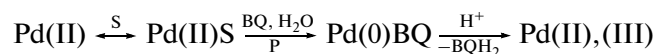
the kinetic equation obtained under the quasi-steady-state conditions with respect to the Pd(0)BQ intermediate with allowance made for the participation of all palladium species in the material balance will not agree with the partial dependences $[S]–t$, $r_t–[S]$ (the order with respect to the substrate decreases with a decrease in its concentration), $r_0–[BQ]_0$, and $r_0–[H^+]_0$. The independence of r_0 on $[BQ]_0$ is observed at the zero order with respect to the substrate, whereas the first order with respect to $[BQ]_0$ is obtained at the zero order with respect to $[H^+]$ and when the order
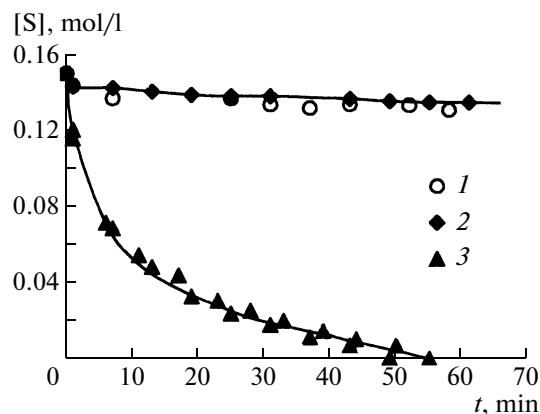
with respect to $[S]_0$ is below unity. An analysis of the unsteady-state model (against eight experiments) showed the high inaccuracy of the description, and reaction scheme (III) does not describe the run of the kinetic curves either: the regions **A** and **B** are absent, and the dependences on the palladium concentration are described inadequately. An analysis of reaction scheme (III) also confirms the assumption that several forms of palladium, namely, Pd(II) and Pd(0), Pd(II) and Pd(I), Pd(I) and Pd(0), or all the three forms of the complexes contribute to the rate of substrate disappearance in the multiroute reaction.

Under conditions of the formation of several active species from the precursors and catalysis by the most active species, the initial reaction rates in the region **A** cannot correspond to the kinetics of a quasi-steady-state process. Note that the condition for applicability
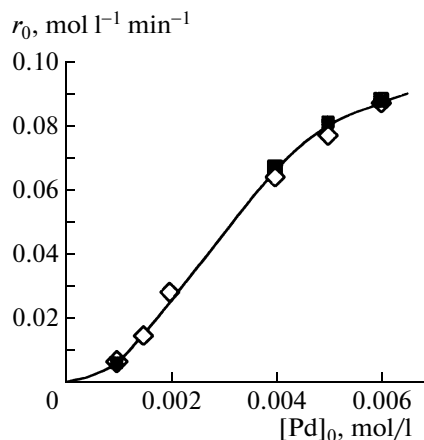

Fig. 7. Dependence of the initial oxidation rate on $[Pd]_0$ at $[BQ]_0 = 0.004$ mol/l, $[HClO_4] = 0.2$ mol/l, and $[S]_0 = 0.15$ mol/l.
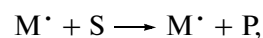
of quasi-steady-state treatment to homogeneous processes ($[S]_0/[Pd]_0 \geq 15$ [30]) in the concentration ranges examined is not satisfied at conversions higher than 60–80%.

It follows from the analysis of the kinetic curves for various $[Pd]_0$ values (Fig. 2) that the initial rate is a complicated function of $[Pd]_0$ represented by an S-shaped curve in the concentration range from 0.001 to 0.006 mol/l (Fig. 7), second-order with respect to $[Pd]_0$ in the 0–0.002 mol/l range. The reaction rate for the oxidation of the substrate S in the region **B** is almost independent of $[Pd]_0$ (Fig. 3).
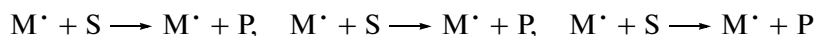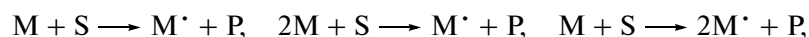
The weak dependence of r_0 on $[Pd]_0$ in the region **B**, some darkening of the solution during the reaction, and the known facts of catalysis by nanoparticles and colloids in homogeneous systems [30], in combination with published data [36–39] on the appearance of colloidal palladium in aqueous cationic systems with such reducing agents as alcohols and olefins and on the catalysis of oxidation reactions of these substrates by colloidal palladium, suggest that the solution examined contains nanoclusters that are inactive in catalysis, are stabilized by BQ and the substrate, and are in equilibrium with the active monomeric and dimeric molecular complexes of Pd(0) or Pd_2^{2+}, respectively. In this case, the concentration of the active complexes can change little with the initial metal concentration ($[M]_0$) [30]. A TEM study of the reaction solutions showed, however, that the solutions do not contain particles larger than 1 nm. The particles of the "giant cluster" of Pd [41] 26.0 ± 3.5 Å in size are clearly seen in the TEM images.

An analysis of very simple unsteady-state models with one active catalyst species, $M^\cdot$, and the precursor M (one catalytic route), in which the rates of catalytic cycles on various catalyst species were defined as the rate of the first, irreversible step, ignoring the fast conversion of the intermediates, for example,

$$M^\cdot + S \longrightarrow M^\cdot + P,$$

showed that models **1.30**–**1.50**

$$M + S \longrightarrow M^\cdot + P, \quad 2M + S \longrightarrow M^\cdot + P, \quad M + S \longrightarrow 2M^\cdot + P,$$

$$M^\cdot + S \longrightarrow M^\cdot + P, \quad M^\cdot + S \longrightarrow M^\cdot + P, \quad M^\cdot + S \longrightarrow M^\cdot + P$$
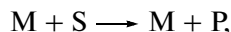
1.30 **1.40** **1.50**

do not fit the experimental data for [BQ] = 0.4 mol/l (Fig. 2). The symbol M in model **1.50** designates the Pd_2^{2+}-type dimeric complex forming immediately from Pd^{2+}.

The introduction of a catalytic cycle for the species M,

$$M + S \longrightarrow M + P,$$

into these models (models **1.3**–**1.5**), i.e., the appearance of the second catalytic route, substantially improves the description of the curves presented in Fig. 2 (in terms of the average sum of the squared deviations SS (given in parentheses) for particular experiments with the number of measurements in each entry taken into account), models **1.3** and **1.5** being preferable: **1.3** (0.236×10^{-4}) $\approx$ **1.5** (0.23×10^{-4}) < **1.4** (0.86×10^{-4}). In all models, there is fast conversion of M into $M^\cdot$ at the beginning of the region **A**. Modification of models **1.3**–**1.5** by the introduction of the reversible step of intermediate formation,

$$M^\cdot + S \longleftrightarrow MS^\cdot,$$
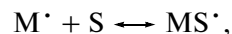
provided a very insignificant improvement to the description of the experiment. Models **1.3**–**1.5** can be clearly visualized by representing the catalytic cycles as a loop in a graph, for instance,

1.3 **1.4** **1.5**
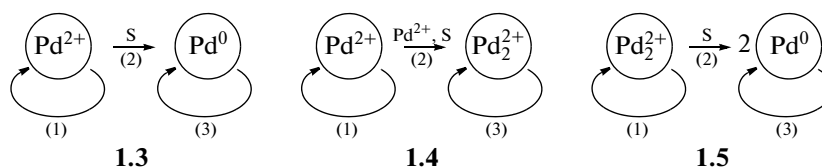
To take into account the variation of the quinone concentration with time, the quinone concentration [Q] was introduced into the equations for the rates of several steps of kinetic models **1.3**–**1.5**, and the model series **1.3M2**–**1.5M2** was thus obtained:

The schemes:

$$\mathrm{Pd^{2+}} \xrightarrow{\ S\ } \mathrm{X_1} \xrightarrow[-P]{\ Q\ } \mathrm{Pd^0Q} \xrightarrow{\ S\ } \mathrm{X_2}$$

with P, Q cycles — **1.3M2**

$$\mathrm{Pd^{2+}} \xrightarrow{\ S\ } \mathrm{X_1} \xrightarrow[-P]{\ Pd^{2+},\,Q\ } \mathrm{Pd_2Q^{2+}} \xrightarrow{\ S\ } \mathrm{X_2}$$

with P, Q cycles — **1.4M2**

$$\mathrm{Pd_2Q^{2+}} \xrightarrow{\ S\ } \mathrm{X_1} \xrightarrow[-P]{\ Q\ } 2\,\mathrm{Pd^0Q} \xrightarrow{\ S\ } \mathrm{X_2}$$

with P, Q cycles — **1.5M2**

$$2\,\mathrm{Pd^{2+}} \xrightarrow[-P]{\ S,\,Q\ } \mathrm{Pd_2Q^{2+}} \xrightarrow{\ S\ } \mathrm{X_1} \xrightarrow[-P]{\ Q\ } 2\,\mathrm{Pd^0Q} \xrightarrow{\ S\ } \mathrm{X_2}$$

with P, Q cycles — **1.5M3**
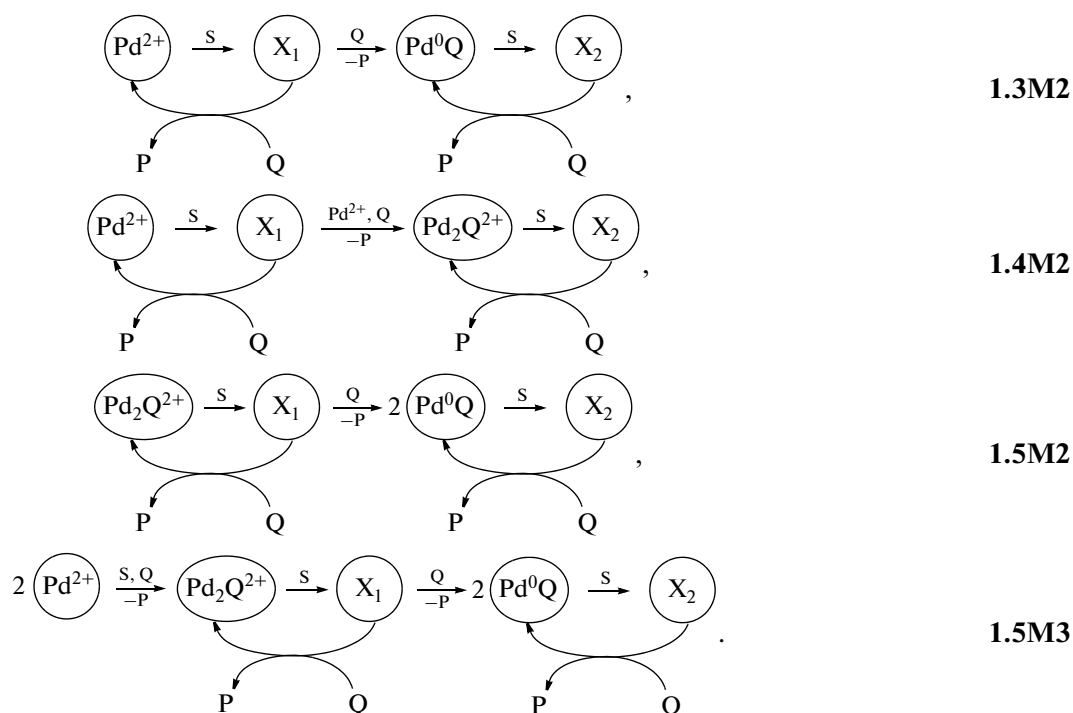
Model **1.5M3** includes irreversible $[\mathrm{Pd_2Q}]^{2+}$ formation from $\mathrm{Pd^{2+}}$. Passing to these models noticeably improved the description of the experimental curves for different values of $[\mathrm{Pd}]_0$ and $[\mathrm{Q}]_0$. According to the SS values (in parentheses), the models are arranged in the following order:

1.5M3 (0.05×10^{-4}) < **1.3M2** (0.12×10^{-4})

< **1.5M2** (0.66×10^{-4}) < **1.4M2** (1.0×10^{-4}).

Almost the same order of models,

1.5M3 (0.67×10^{-4}) < **1.3M2** (1.43×10^{-4})

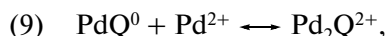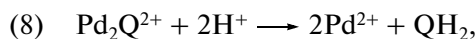$\approx$ **1.5M2** (1.44×10^{-4}) < **1.4M2** (1.79×10^{-4})

was obtained in terms of the sums of squared deviations calculated for all experiments with one set of rate constants, nonlinear model **1.5M3** being preferable.

An analysis of simple models **1.3–1.5** and **1.3M2–1.5M3** shows that, if in the region **A** the species M is rapidly converted into the species M˙, then, after the consumption of the substrate and the addition of a new portion of cyclohexene, it is to be expected that the process will be repeated at the rate corresponding to the activity of the species M˙, for which the rate constants are 10–100 times lower than those for the species M. It turned out that the addition of the substrate at the end of the reaction results in an almost complete reproduction of the initial curve, whereas the addition of the substrate in the 8th or 20th minute changes the shape of the curve, reproducing the shape of some portion of the initial curve. It follows from these data that, during the process, the species M˙ is converted back into the species M, and both species coexist in different ratios throughout the process. In view of these observations, the steps in which M˙ is converted into M, i.e., the processes of oxidation by quinones and a proton of the complexes in the lower oxidation states to the complexes in the higher oxidation state (e.g., $\mathrm{Pd^{2+}}$), should be introduced into the next generations of the kinetic models. The introduction of these steps will result in the appearance of three-route mechanisms; for instance, model **1.5M3** will transform into model **3.1.5M3**:

$$2\,\mathrm{Pd^{2+}} \xleftarrow{\ (7)\ }$$
$$\Big\downarrow{\scriptstyle S,\,Q \atop -P}\ (1)$$
$$\mathrm{Pd_2Q^{2+}} \xrightarrow[(2)]{\ S\ } \mathrm{X_1} \xrightarrow[(4)]{\ Q \atop -P} 2\,\mathrm{Pd^0Q} \xrightarrow[(5)]{\ S\ } \mathrm{X_2}$$

with (3) P, Q and (6) P, Q cycles — **3.1.5M3**
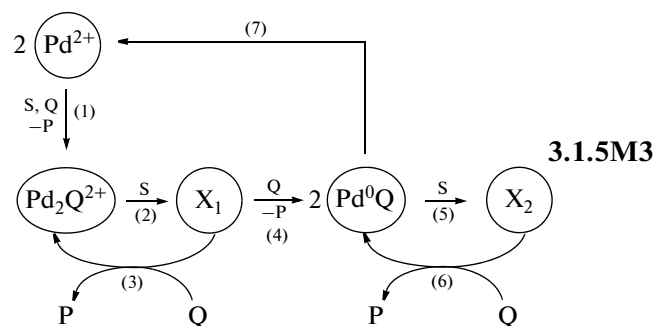
Model **3.1.5M3** describes the effect of substrate addition but does not completely reproduce the shape of the kinetic curve in the region **B** and its character upon the introduction of a new portion of the substrate after the complete consumption of the initial portion. For this reason, the oxidation steps $\mathrm{Pd(I)} \longrightarrow \mathrm{Pd(II)}$ and $\mathrm{Pd(0)} \longrightarrow \mathrm{Pd(I)}$ were additionally introduced into model **3.1.5M3**,

$$(8)\quad \mathrm{Pd_2Q^{2+}} + 2\mathrm{H^+} \longrightarrow 2\mathrm{Pd^{2+}} + \mathrm{QH_2},$$

$$(9)\quad \mathrm{PdQ^0} + \mathrm{Pd^{2+}} \longleftrightarrow \mathrm{Pd_2Q^{2+}},$$
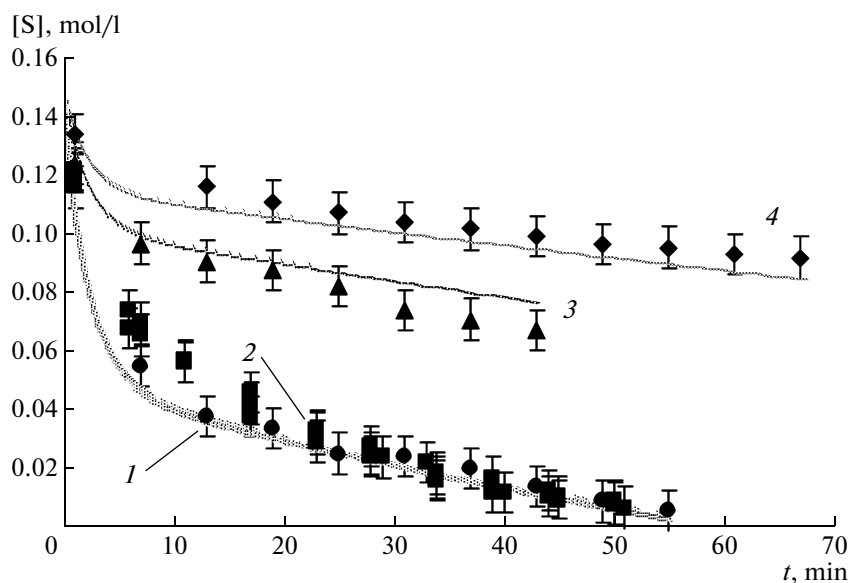
[S], mol/l

Fig. 8. Kinetics of cyclohexene disappearance at different initial concentrations of palladium and *p*-benzoquinone: $[Pd]_0 = ($*1*$)$ 0.004, (*3*) 0.002, and (*4*) 0.0015 mol/l; $[BQ]_0 = 0.4$ and (*2*) 0.004 mol/l; $[BQ]_0 = 0.2$ mol/l, $[HClO_4] = 0.2$ mol/l.

taking into account that step (9) (Pd(I) disproportion-ation) is reversible, and model **4.1.5M3** was obtained. The five-route mechanism of cyclohexene oxidation (model **4.1.5M3**) provides a satisfactory description of both regions of the curves (**A** and **B**) for different con-ditions (Fig. 8) and for experiments with the initial and added substrate at high benzoquinone concentrations (Fig. 9). The SS value is 0.17×10^{-4}, i.e., 4.1 mmol/l, which is close to the experimental error. Step (9) turned out to be close to equilibrium at all reaction times, with an equilibrium constant of 3.6×10^4 l/mol (in the computation variant presented). A similar dis-proportionation reaction, but without a revere pro-cess, was proposed for the reduction of palladium(II) complexes with hydrogen [46].

The results of determination of the rate constants of the reaction steps, the rates of these steps, and the concentrations of the intermediates in the framework of model **4.1.5M3** and the performed computation suggest the following:

(1) Step (8) nearly does not contribute to the change in the Pd(I) concentration, and the rate of the reaction via route P1 (steps (1) and (8)) is the lowest.

(2) In the region **A**, at the first moments of the reac-tion, the entire Pd(II) is rapidly converted into Pd(0) through Pd(I), and the high rate of substrate disap-pearance in the first 5 min is mainly due to the rate of routes P2 (steps (2) and (3)) and P3 (steps (5) and (6)), the contribution of route P2 being strongly predomi-nant. The maximum contribution to the reaction rate is made by routes P4 (steps (1), (2), (4), and (7)) and P5 (steps (1), (7), and (−9)).

(3) In the region **B**, the greater part of the palla-dium exists in the form of PdQ^0 and a smaller part exists in the form of X_1. The rates of routes P2 and P3

in this part of the curve have the same order, but r_{P2} is higher than r_{P3} by a factor of 2−3.

(4) After the substrate is consumed (73rd minute), more than a half of the palladium still remains in the form of Pd(0), and it is on these Pd(0) and Pd(I) forms that the process resumes upon substrate addition. If the substrate is not added in the 73rd minute, then, according to the kinetic model, by the 90th minute nearly all of the Pd will have been convert into Pd(II), and in the 76th minute it will exist mainly in the form of Pd(I).

(5) The region **B** of the kinetic curve for the sub-strate indicates a nearly constant reaction rate in spite of the substrate concentration [S] decreasing with time (Figs. 2, 3). This is due to the fact that the increase in the univalent palladium concentration is approximately in inverse proportion to [S], owing to which the rate of the main route, including steps (2) and (3), remains almost unchanged. The contribution from this route is great (more than 80%);

(6) An increase in the total catalyst concentration from 0.0015 to 0.004 mol/l does not result in a propor-tional increase in the reaction rate (Fig. 3). However, the main reason for this behavior is that, in the region **B** of the kinetic curve, the low substrate con-centration corresponds to the high catalyst concentra-tion and vice versa.

Thus, in the framework of the model considered, the initial palladium(II) participates mainly in the for-mation of the Pd(0) and Pd(I) complexes, including those resulting from step (9). It should be noted that simpler models do not fit the observed kinetics.

For further discrimination of the kinetic models, it is necessary to analyze hypotheses about the

mechanisms of olefin oxidation involving possible Pd^{2+}, Pd_2^{2+}, and Pd^0 complexes in order to establish theoretically possible ways of kinetic coupling between the intermediates and routes with the quinone, acid, substrate, and palladium concentrations taken into account.

In the catalytic system under study, the main ligands stabilizing the palladium complexes in different oxidation states are acetonitrile, quinones, and olefins. The cationic complexes $[Pd(CH_3CN)_4]^{2+}$ and $[Pd_2(CH_3CN)_6]^{2+}$ are known [47]. The complex $Pd_2SO_4(BQ)$ was described [22]. The following complexes were synthesized and characterized: LPdQ [48] (L = 1,5-cyclooctadiene, Q = various *p*-quinones), $[L_2Pd(\eta^2\text{-}Q)]_2(QH_2) \cdot MeOH$, and $L_2Pd_2(\mu\text{-}\eta^2\text{-},\eta^2\text{-}Q)_2 \cdot MeOH$ [34, 35] (L = PPh₃, Q = *p*-benzoquinone). Thus, palladium can be in the oxidation states (II), (I), and (0) during the oxidation of cyclohexene (and other olefins) in the $CH_3CN–H_2O–H^+–Q$ system.

Various functions of *p*-quinones in the oxidation reactions catalyzed by Pd(II) and Pd(I) complexes were analyzed [49]. In the framework of the classical mechanism [4], but involving the intermediate resulting from the *trans*-addition of a water molecule to the π-complex of olefin with Pd^{2+} (protonated olefin palladiumhydrin compound, e.g., $\sim PdCH_2CH_2OH_2^+$), let

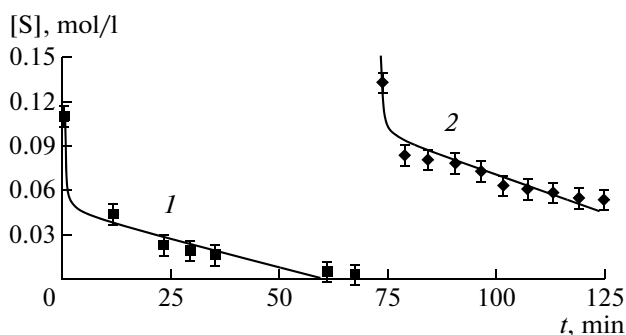**Fig. 9.** Comparison of the kinetic curves recorded before and after the addition of the substrate: $[Pd]_0 = 0.004$ mol/l, $[BQ]_0 = (I)$ 1.05 and (*2*) 0.85 mol/l, $[HClO_4] = 0.2$ mol/l.

us consider, in greater detail, the probable mechanisms of oxidation (using ethylene as an example) in solutions of Pd^{2+}, Pd_2^{2+}, and Pd(0) complexes, taking into account some earlier hypotheses [10–15].
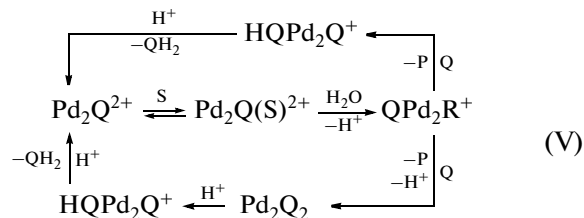
Active Species $Pd^{2+}(S–C_2H_4)$

The two routes leading to $[Pd_2Q]^{2+}$ from the Pd^{2+} precursor are shown in reaction scheme (IV).

$$\text{(IV)}$$
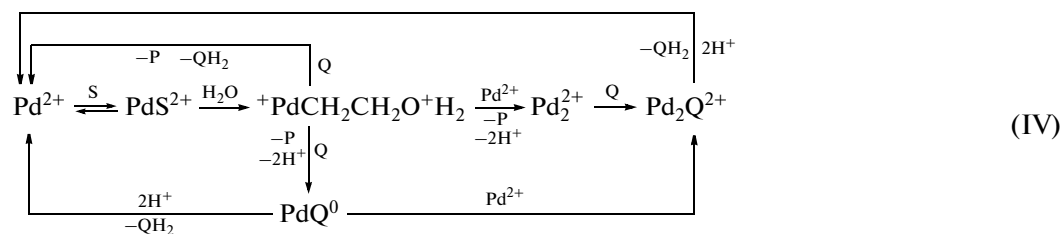
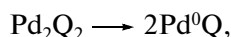### *Active Species $[Pd_2Q]^{2+}$*

Two routes seem likely to involve the active complex $[Pd_2Q]^{2+}$:

$$\text{(V)}$$

R = CH_2CH_2OH.

The dissociation of the Pd_2Q_2 complex can result in the Pd^0Q complex,

$$Pd_2Q_2 \longrightarrow 2Pd^0Q,$$

forming an additional link between reactions (IV) and (V).

Active Species Pd^0Q

$$\text{(VI)}$$
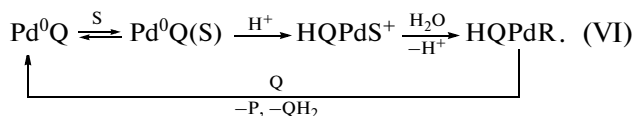
Reaction schemes (IV)–(VI) show that independent catalytic cycles are possible on the Pd^0Q and $[Pd_2Q]^{2+}$ complexes and three of the four linearly independent routes associated with Pd^{2+} according to scheme (IV) are related to the formation of the Pd^0Q or $[Pd_2Q]^{2+}$ intermediates and differ slightly from the classical mechanism of the Wacker process. Both the quadratic-law dependences with respect to the concentration $[PdCl_4]^{2-}$ and the formation of palladium complexes in the oxidation state (I) were established by the study of the kinetics of olefin oxidation in chloride systems [4]. Only one route in this scheme, with

the intermediate compound $^+PdCH_2CH_2O^+H_2$, can proceed through intermediates specific, to a greater extent, to $[PdL_4]^{2+}$, although the formation of intermediates of this type cannot be excluded in the case of Pd_2^{2+} or protonated Pd^0Q.

Reaction schemes (IV) and (V) contain routes in which no changes occur in the oxidation state of palladium in the intermediates; i.e., the so-called concerted mechanism (term used in classical oxidation catalysis) occurs, with electrons transferred from the substrates (organic ligands) to the oxidant through the metal atom (G.K. Boreskov, K.B. Yatsimirskii). For the oxidation of carbon oxide by p-quinones catalyzed by the palladium complexes, this mechanism was suggested for the first time by Gololodov [50, 51].

The cationic character of the initial complex $[Pd(CH_3CN)_4]^{2+}$ or $[Pd(CH_3CN)_{4-x}(H_2O)_x]^{2+}$ and, hence, the carbocationic character of the primary π-complex make it possible to consider other mechanisms of olefin oxidation including solvated metal carbenium ions (protonated olefin metalhydrin intermediates) and specific, to a greater extent, to $[PdL_4]^{2+}$ in aqueous solutions. Assumptions about the formation of such ions were made previously for the reactions involving the trimer $Pd_3(OAc)_6$ in acetic acid, namely, the oxidative dimerization [52, 53] and the oxidation esterification of olefins [54–56] (Moiseev reaction). The formation of products of the allyl and, first of all, homoallyl acetoxylation of α-olefins and cyclohexene in acetic acid (in the latter case) [54–57] and of allyl esters in the oxidation of cyclododecatriene in methanol [58] agrees with these assumptions, as well as with the formation of the π-allyl complexes and products of the allyl oxidation of cyclohexene and other olefins in aqueous solutions [40].

Similar regularities were observed earlier in the reactions of the Hg^{2+} ion [59–63], another strong electrophile, particularly in the selective formation of acrolein from propylene in acid solutions of mercury(II) perchlorate [63]. The mechanisms involving mercurycarbenium ions and vinyl mercury intermediates formed from olefins in acetonitrile solutions were also discussed [64–66]. The reversible absorption of ethylene by mercury(II) perchlorate in aqueous solutions of perchloric acid with an equilibrium constant of 1.5×10^4 l/mol at 298°C, independent of the H^+ concentration, is likely due to the formation of the solvated mercurycarbenium ion $^+HgCH_2CH_2OH_2^+$ rather than a π-complex, contrary to what was believed previously [66].

Thus, the conversions of the metalcarbenium ion solvated by the water molecule give rise to a mechanism similar to the classical oxidation mechanism [4] (reaction scheme (IV)) and to the π-allylic, vinylic, and even carbenic mechanisms of olefin oxidation by p-quinones in acid solutions of cationic palladium(II) complexes (Scheme). In solvated metal carbenium ions **1**, both hydride shifts, namely, 2–1 and 1–2, are likely. These shifts result in cyclohexanone via the formation of intermediate hydroxycarbenium ion **2** (classical demetallation mechanism [4]) or Pd^{2+} carbene complex **3**, respectively. The mechanism including the *anti*-addition of a water molecule to the π-complex involving intermediates **1** and **2** is likely to occur in the oxidation of cyclohexene in solutions of palladium(II) chloride complexes [20, 26] (see the discussion of the *syn*-addition of Pd–OH to olefin and the *anti*-addition of a water molecule to the π-complex in the review dedicated to the 50th anniversary of the development of the Wacker process [67]). The deprotonation of **1** from positions 1 or 3 affords vinyl (**4**) or allyl (**5**) compounds, respectively. The conversions of **4** (probably, through the carbene η^2-vinyl derivative) and **5** (through cyclohexenol **6**) also can result in cyclohexanone. Another very probable mechanism of the formation of **6** is the β-elimination of PdH^+ from positions 1–6 of intermediate **1**. The route involving the β-elimination of PdH^+ from positions 1 and 2 of intermediate **1** to form the intermediate π-complex of PdH^+ with the derivative of vinyl alcohol **8** and the isomerization of **1** to **9**, which was discussed for the Wacker process [4, 68], is possible for **1** in the case of the *trans*-addition of a water molecule to the π-complex of cyclohexene with Pd^{2+}. The 3–2 shift of the hydride ion in intermediate **1** can yield the 3-cyclohexen-1-ol homoallyl oxidation products, which have not been observed yet in aqueous acid solutions. However, the mechanism of the positional isomerization of **7**, including the conversions of the π-complex of **7** with PdH^+, can also result in such products. The decomposition of intermediates **1**, **3**, **4**, and **5** in the presence of p-quinones and an acid can yield Pd^{2+} without the participation of the intermediate complex Pd^0Q or $[Pd_2Q]^{2+}$; i.e., the route involving only the Pd(II) compounds can appear (see reaction scheme (IV)).

The possibility of these mechanisms taking place in olefin oxidation into saturated ketones requires serious experimental proofs. However, the theoretical probability of these mechanisms makes it possible to introduce internal catalytic cycles associated with Pd^{2+} into the analyzed hypotheses involving the palladium(I) and palladium(0) complexes.

To discriminate possible hypotheses as to the reaction mechanism, it is necessary to additionally study the composition of the isotopomers of the cyclohexene oxidation products, the kinetic isotope effects, the dependences of the initial rates on $[H^+]$ and the initial substrate concentration at different benzoquinone concentrations, the influence of acetonitrile on the hydrolysis of Pd^{2+}, the nature of the palladium complexes in solution (using electronic and NMR spectroscopy), and the influence of the mole fraction of water in the binary solvent on the rate and selectivity of the process. It is also required to elucidate the routes of the transformation of cyclohexenol and allyl alcohol
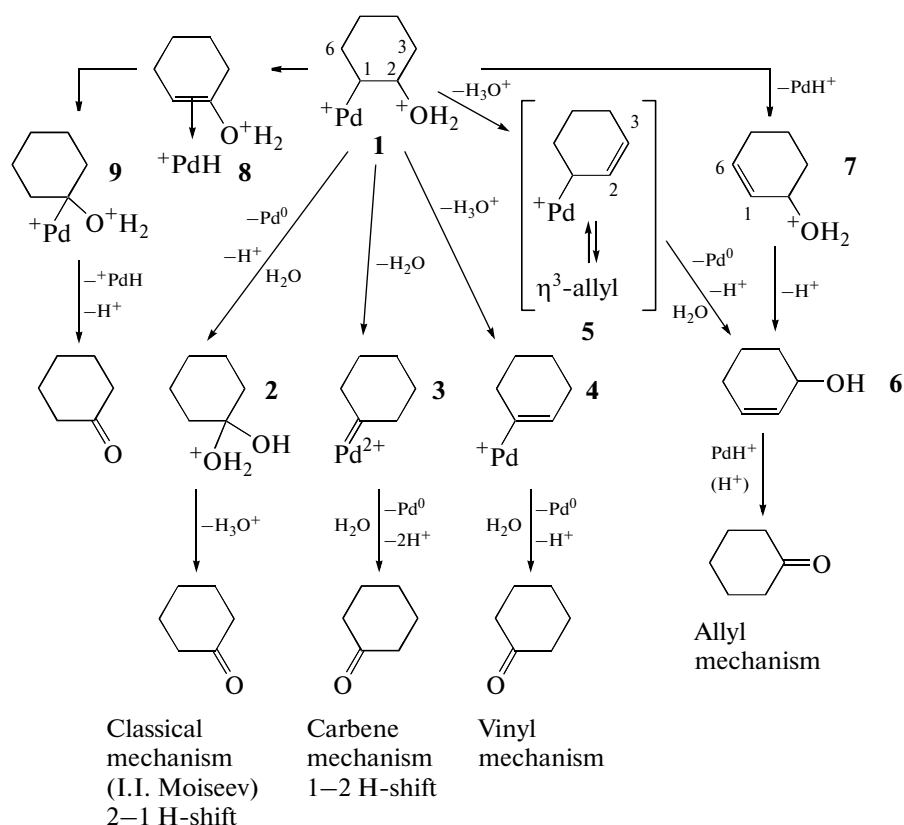
Scheme. Mechanisms of olefin oxidation by *p*-quinones in solutions of cationic palladium(II) complexes.

under the conditions of cyclohexene oxidation, because the formation of propionaldehyde was observed upon allyl alcohol oxidation by palladium chloride [69].

ACKNOWLEDGMENTS

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