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Catalytic Oxidation of Fe(II) Aqua Ions with Atmospheric Oxygen in the Presence of Pd(II) Tetraaqua Complex and an Aromatic Compound

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Abstract—The effect of a series of aromatic compounds (toluene, benzyl alcohol, benzonitrile, phenylacetonitrile, and *o*-cyanotoluene) in a concentration of 0.01 M on the oxidation of Fe(II) aqua ions with oxygen in the presence of Pd(II) tetraaqua complex at 25–70°C was revealed. In the presence of an aromatic compound, palladium black is not formed, which results in an increased yield of Fe(III) in the Pd-catalyzed oxidation of Fe(II) with oxygen in a perchloric acid medium. A scheme involving the formation of a complex of palladium species in an intermediate oxidation state with arene and molecular oxygen was suggested.

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We studied previously [1] the kinetics and mechanism of reaction (1) between the Pd(II) tetraaqua complex and Fe(II) aqua complex:

$$2[Fe(H_2O)_6]^{2+} + [Pd(H_2O)_4]^{2+} \longrightarrow 2[Fe(H_2O)_6]^{3+} + Pd(0). \qquad (1)$$

We found that the reaction is autocatalytic and occurs by the mechanism of one-electron transfer.

In an oxygen atmosphere [2], the catalytic oxidation of Fe(II) aqua complex with oxygen [reaction (2)] occurs concurrently with autocatalytic reaction (1):

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{[Pd]} 4Fe^{3+}_{aq} + 2H_2O. \qquad (2)$$

Reaction (2) is catalyzed by palladium species in an intermediate oxidation state, formed in the course of reaction (1). However, with increasing temperature the contribution of Pd-catalyzed reaction (2) to the formation of Fe(III) drastically decreases and becomes negligible at the temperatures exceeding 50°C. At elevated temperatures, active palladium species transform into low-active palladium black too rapidly to catalyze noticeably reaction (2) whose activation energy, according to [2], is lower than that of reaction (1).

Reaction (2) plays an important role in ensuring efficient catalytic oxidation of organic compounds in the system Pd(II)–Fe(III)/Fe(II)–oxygen in the absence of chloride ions [3]. This fact stimulates a search for conditions and substances that would stabilize catalytically active palladium species in the course of a catalytic process, preventing their transformation into low-active palladium black. The additive should not react with the starting aqua complexes of Pd(II) and Fe(II).

It is known that aromatic compounds form complexes with Pd in an intermediate oxidation state via the π-electron system of their rings [4, 5]. We showed [6] that small additions of aromatic compounds (acetophenone, benzonitrile, phenylacetonitrile) enhance the extent of oxidation of aliphatic alcohols in the catalytic system of Pd(II)–Fe(III) aqua complexes. Oxidation of alcohols with Fe(III) in the presence of Pd(II) tetraaqua complex results in the accumulation of Fe(II) aqua ions; when their critical concentration is reached, reaction (1) starts to rapidly develop. As a result, the catalytic cycle of the alcohol oxidation is broken because of formation of palladium black. In the absence of aromatic derivatives, this occurs at 30% conversion of Fe(III) to Fe(II). In the presence of, e.g., benzonitrile, the Fe(III) conversion reaches ~100%. The maximal rate of alcohol oxidation, however, is not influenced by the addition of an aromatic compound.

In this study we examined the catalytic oxidation of Fe(II) aqua ions with molecular oxygen in the presence of Pd(II) tetraaqua complex and aromatic compounds in aqueous solution.

Mixing of aqueous solutions of toluene, benzoic acid, benzyl alcohol, acetophenone, benzonitrile, phenylacetonitrile, or *o*-cyanotoluene of required concentrations with a solution of Pd(II) tetraaqua complex does not lead to the ligand substitution in the inner sphere of the starting Pd(II) complex. The UV spectra of these solutions exhibit a single absorption maximum at 380 nm characteristic of Pd(II) tetraaqua complex. In the examined temperature range, both in argon and oxygen atmosphere, these aromatic compounds undergo no transformations such as, e.g., Pd-catalyzed inner-sphere acid hydrolysis of nitriles.

When reaction (1) is performed in an inert atmosphere in the presence of an aromatic compound, the reaction rate constant decreases compared to the system containing no aromatic additive. The effect of toluene and acetophenone on the rate of reaction (1) is noticeable at low temperatures (40–50°C). At higher temperatures, palladium black precipitates quantitatively. The effect of aromatic nitriles is manifested in a wider temperature range. Table 1 shows by the example of benzonitrile (with other nitriles, the trend is similar) how the oxidizability of Fe(II) with Pd(II) tetraaqua complex varies with an increasing concentration of the aromatic compound. At the benzonitrile concentration exceeding 4 mM, the conversion becomes insignificant. At the same time, the effect of the aromatic nitrile, appreciable at low Fe(II) concentrations, fully disappears with an increase in the excess of Fe(II) relative to Pd(II) (last row in Table 1). Apparently, with an increase in the Fe(II) concentration, larger amount of the aromatic compound is required to inhibit autocatalytic reaction (1).

Increased concentrations of benzonitrile can also lead to transformations of the starting Pd(II) complex and, as a consequence, to the occurrence of other reactions.

The role of aromatic derivatives in autocatalytic reaction (1) in an argon atmosphere is comparable with the effect of a stopping reagent (inhibitor). In accordance with the mechanism of reaction (1) suggested in [1, 2], aromatic compounds presumably interact with an intermediate palladium species to form a complex slowly reacting with Fe(II). The formation of the complex depends on the concentration ratio of Fe(II) and aromatic compound. The higher the initial Fe(II) concentration, the higher the rate of its reaction with the intermediate Pd species compared to the complexation reaction, and hence the higher the rate of reaction (1). Therefore, at high Fe(II) concentrations, palladium black precipitates quantitatively. Under the conditions of the inhibited pathway of the autocatalytic development of reaction (1), when the rate of the reaction of intermediate palladium species with an aromatic compound prevails over the rate of their reduction with Fe(II), even minor amounts of Fe(III) accumulating at the beginning of the reaction start to inhibit the overall process. As we showed in [1], the rate of reaction (1) decreases with an increase in the initial Fe(III) concentration.

Table 1. Influence of benzonitrile concentration on reaction (1) in argon

PhCN, mM	Time, min	[Fe(III)], mM	[Pd(II)], mM
0	30	10	0
1	40	6	2
2	150	4	3
2[b]	150	3	1
2[c]	240	2	1.5
4	140	3	3.5
14	360	2	4
14[d]	40	10	0

[a] $[Pd(II)]_0$ 5, $[Fe(II)]_0$ 20 mM; $[HClO_4]$ 0.7 M; 65°C.

[b] $[Pd(II)]_0$ 2.5, [Fe(II)]0 20 mM.

[c] $[Pd(II)]_0$ 2.5, [Fe(II)]0 10 mM.

[d] [Pd(II)]0 5, [Fe(II)]0 60 mM.

It is important that the electronic properties of substituent X in the aromatic ring (X = CN or CH_2CN) do not exert an appreciable effect on the reaction course. This fact indicates that the electronic system of the aromatic ring is the decisive factor governing the effect of aromatic compounds on the rate of reaction (1). Furthermore, related aliphatic compounds, e.g., acetonitrile, exert no effect on reaction (1).

Our results suggest that a complex of palladium with an aromatic derivative, enriched with ring electrons, should exhibit reductive properties to a greater extent than oxidative properties, which should favor oxygen activation with this palladium complex.

Replacement of Ar by O_2 in the system Pd(II) tetraaqua complex–Fe(II) aqua complex–aromatic compound results in catalytic oxidation of Fe(II) with O_2 by reaction (2). It is important that Fe(II) is not oxidized with oxygen in the absence of Pd(II).

As expected, the rate of reaction (2) strongly depends on the aromatic compound concentration (Fig. 1).

Figure 1 shows the kinetic curves of oxygen uptake at different concentrations of benzonitrile in solution. With an increase in the benzonitrile concentration, the oxygen uptake rate increases; at benzonitrile concentrations exceeding 4 mM, no palladium black precipitates, as in the case of an inert atmosphere.

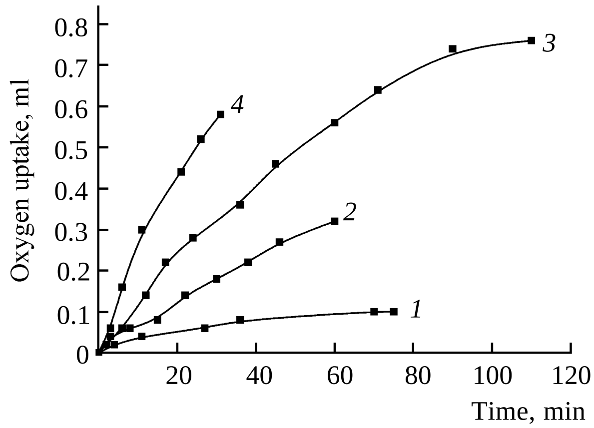


Fig. 1. Kinetic curves of oxygen uptake in reaction (2) at different PhCN concentrations. PhCN concentration, mM: (*1*) 0, (*2*) 2, (*3*) 4, and (*4*) 14; [Pd(II)] 5 and [Fe(II)] 20 mM; $P(O_2)$ 0.1 MPa; 65°C.

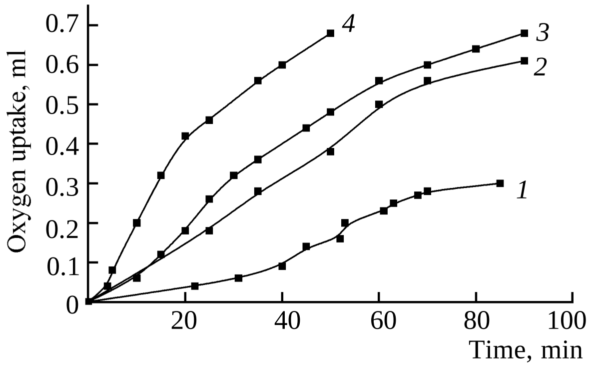


Fig. 2. Kinetic curves of oxygen uptake in reaction (2) at different oxygen pressures. $P(O_2)$, MPa: (*1*) 0.02, (*2*) 0.05, (*3*) 0.075, and (*4*) 0.1; [Pd(II)] 5, [Fe(II)] 20, and [PhCN] 14 mM; 65°C.

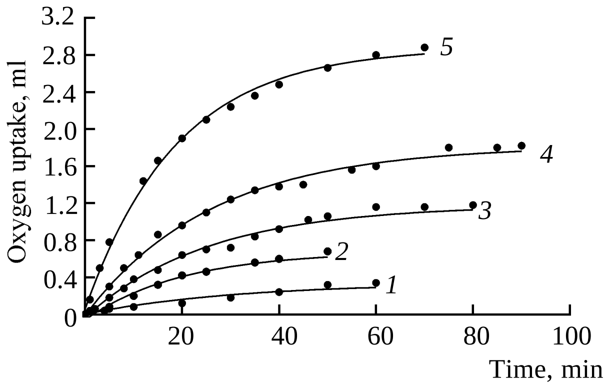


Fig. 3. Kinetic curves of oxygen uptake in reaction (2) at different Fe(II) concentrations. [Fe(II), mM: (*1*) 10, (*2*) 20, (*3*) 30, (*4*) 60, and (*5*) 100; [Pd(II)] 5 and [PhCN] 14 mM; $P(O_2)$ 0.1 MPa; 65°C.

The influence of the oxygen pressure and initial Fe(II) concentration on the rate of reaction (2) is shown in Figs. 2 and 3, respectively.

As compared to the system containing no aromatic additives [2], in which the reaction rate was maximal until Fe(II) was fully oxidized to Fe(III), in the presence of PhCN the reaction gradually decelerates with time.

No palladium black is formed during the reaction time in the examined range of initial concentrations of oxygen and Fe(II). The analytically determined concentrations of the substances after performing reaction (2) at different initial concentrations of the solution components are listed in Table 2.

In our previous study [2] we experimentally determined the difference between the activation energies of reactions (1) and (2), $E_{a(1)}$ and $E_{a(2)}$, respectively.

$$E_{a(1)} - E_{a(2)} - \Delta H^0 = 50\ \text{kJ}\,\text{mol}^{-1}. \qquad (3)$$

Here ΔH^0 is the enthalpy of complexation of Pd species in the intermediate oxidation state with O_2. In [2], experimental determination of $E_{a(2)}$ was impossible because of a decrease in the contribution of Pd-catalyzed reaction (2) to the formation of Fe(III) with increasing temperature. At the same time, the quantity $E_{a(1)}$ in an inert atmosphere was determined: 52.4 ± 5.1 kJ mol^{-1}.

In the examined system in the presence of an aromatic compound, the Pd(II) concentration does not appreciably change in the course of the process, and reaction (2) is quantitative; therefore, the temperature dependence of the rate of reaction (2), as we found in this study, follows the Arrhenius law with the activation energy $E_{a(2)}$ 31.7 ± 3.2 kJ mol^{-1}.

Assuming that the palladium complex with an aromatic compound makes equal contributions to the energy parameters of reactions (1) and (2), we can consider Eq. (3) to be valid for the arene-containing system also. Substituting the values found for the activation energy, we obtain the enthalpy of palladium complexation with oxygen ΔH^0 29.3 kJ mol^{-1}, which is comparable with the enthalpies of complexation of platinum group metals in low valence states with molecular oxygen (12–47 kJ mol^{-1} depending on the ligand surrounding [7]).

According to the stoichiometry of reaction (2), the ratio between Fe(III) and oxygen should be 4. Table 2 shows that actually the ratio is close to the stoichiometric value only at high Fe(II) concentrations and low partial pressures of oxygen. In the other cases, this ratio varies from 2 to 3. This fact suggests that O_2

not only oxidizes Fe(II) but also participates in concurrent reactions. One of possible pathways of oxygen consumption is the oxidation of the aromatic derivative. Participation of oxygen in the oxidation of arene is obvious, since in the absence of organic additives the $[O_2]/[Fe(III)]$ ratio is always 4.

Indeed, in the presence of toluene and benzyl alcohol we detected products of their oxidation: benzyl alcohol and benzaldehyde, respectively. In solutions containing benzonitrile or phenylacetonitrile, a decrease in the nitrile concentration by the end of the reaction was proved by gas chromatography–mass spectrometry (Table 2). Furthermore, dark brown precipitates formed in reaction solutions containing aromatic nitriles. Analysis showed that these precipitates were Pd(II) complexes containing no perchlorate or sulfate [in the case when Pd(II) tetraaqua complex was taken in a sulfuric acid solution] anions. The positive charge of Pd(II) is compensated by an inner-sphere ligand formed by oxidation of the starting aromatic nitrile.

Some assumptions concerning the ligand surrounding were made from the IR spectra.

One of possible transformation pathways of aromatic nitriles is hydrolysis. However, we found no bands characteristic of the carboxy group in the IR spectra. Instead, we observed bands of the coordinated nitrile group (2370–2240 cm^{-1}) and strong bands at ~1600 cm^{-1}. The latter bands belong to the skeleton vibrations of the aromatic ring with a substituent is conjugated with the ring. The band at 2262 cm^{-1} in the case of PhCN corresponds to ν(CN) for the coordinated nitrile group in a Pd(II) complex of the $[Pd(PhCN)_2X_2]$ type [8]. It should be noted that in such complexes the band at ~1600 cm^{-1} is weak. The doublet at 2367, 2336 cm^{-1} (m), strongly shifted toward higher frequencies, also characterizes the stretching vibrations of the coordinated nitrile group. The set of bands in the region characteristic of the coordinated CN group suggests simultaneous coordination to Pd(II) of both unchanged benzonitrile and its oxidation products.

Introduction of methyl group into the *o*-position of benzonitrile does not significantly alter the spectrum. When reaction (2) is performed in the presence of 12 mM *o*-cyanotoluene {[Pd(II)] 5, [Fe(III)] 20 mM, 65°C}, the $Fe(III)/O_2$ ratio was also 2. The IR spectrum of the precipitate formed in the process contained a band at 2264 cm^{-1}, corresponding to the coordinated nitrile group, and a broad medium-intensity band with a maximum at 1555 cm^{-1}.

Assuming that one of the benzonitrile oxidation products is *o*-cyanophenol, we performed the reaction of *o*-cyanophenol with the Pd(II) tetraaqua complex in an oxygen atmosphere in the absence of Fe(II). As a result, we obtained a dark brown complex which exhibited the same solubility as the complexes described above. Its IR spectrum contained a strong band of the coordinated nitrile group at 2270 cm^{-1} (2240 cm^{-1} for the free ligand) and a strong doublet at about 1600 cm^{-1}.

Table 2. Analytically determined concentrations of substances after performing reaction (2) in the presence of PhCN under different initial conditions[a]

Oxygen pressure, MPa	$[Fe(II)]_0$, mM	$\Delta[O_2]$, mM	[Fe(III)], mM	$[Fe(III)]/\Delta[O_2]$	Δ[PhCN], mM
0.02	20	1.3	5.1	3.9	–
0.05	20	3	7	2.3	–
0.075	20	3	7.3	2.4	–
0.1	20	3	7	2.3	6
0.1	10	1.4	4	2.8	3
0.1	30	6	12	2	–
0.1	60	8	16	2	12
0.1[b]	100	12	40	3.3	24

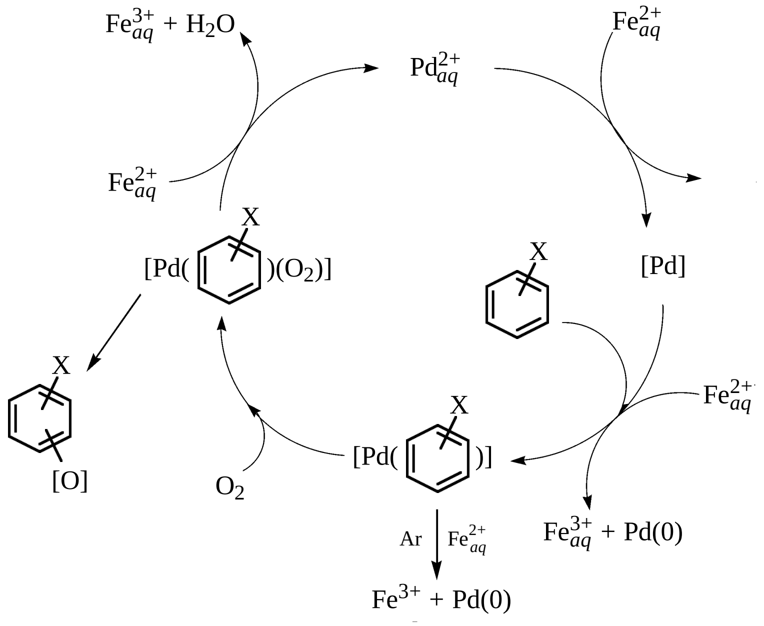
[a] [Pd(II)]0 5 mM, $[HClO_4]$ 0.7 M, [PhCN] 14 mM, 65°C, 90 min.

[b] [PhCN] 0.03 M.

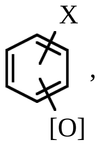
Indirect indications that possible hydroxylation products of the aromatic nitrile form a complex with Pd(II) were obtained in the following model reaction. A well-known procedure for preparing phenols involves hydroxylation of aromatic ring with Fenton’s reagent [9]. To a solution obtained after the catalytic decomposition of hydrogen peroxide in the system containing Fe(II)/Fe(III) aqua ions and benzonitrile, we added Pd(II) aqua complex; in so doing, a precipitate formed. Comparison of its IR spectrum with that of the complex obtained from reaction (2) performed in the presence of benzonitrile shows that the organic ligands are similar.

Oxidation of an aromatic C–H bond with oxygen complexes of d metals is well known. It is believed that the oxidation mechanism does not involve generation of radical species in the bulk of solution and the oxidation occurs heterolytically, inside the complex, with molecular oxygen activated by coordination to the *d* metal [10].

Our results suggest the following pathways of the catalytic oxidation of Fe(II) in Ar and O_2 atmospheres:



[Pd], palladium species in intermediate oxidation state;



, oxidation product of the aromatic compound.

Oxidation of Fe(II) with the palladium oxygen complex is a multistep process involving formation of intermediate reduced oxygen species whose oxidative power is higher than that of molecular oxygen. The aromatic compound may be oxidized specifically with these oxygen species.

In the oxidation of Fe(II) aqua ions with oxygen in the presence of Pd(II) tetraaqua complex and an aromatic compound, both Fe(II) and organic compound are subject to oxidation. Both reactions are catalyzed by an oxygen complex of palladium in an intermediate oxidation state, stabilized by the aromatic compound. The major role is played by reaction (1) generating catalytically active palladium species. The oxidation products of the aromatic compound form a complex with Pd(II), which decreases the concentration of Pd(II) tetraaqua complex in solution and hence the reaction rate, which can be seen in the kinetic curves. The higher the Fe(II) concentration, the lower the contribution of oxygen to the oxidation of the organic compound.

EXPERIMENTAL

The Pd(II) tetraaqua complex was prepared according to [11]. Aromatic derivatives (toluene, benzyl alcohol, benzonitrile, phenylacetonitrile, *o*-cyanotoluene) were used as 0.02 M aqueous solutions (0.01 M for toluene). To an aqueous solution of an aromatic compound we added a solution of Pd(II) tetraaqua complex in an amount required to obtain the desired concentrations. The reaction mixture was prepared by dissolving a weighed portion of Mohr's salt in a solution of Pd(II) tetraaqua complex containing an aromatic compound. The Fe(II) concentration was varied from 0.01 to 0.1 M. The $HClO_4$ concentration was 0.7 M in all the cases.

The reaction kinetics in an Ar atmosphere was monitored by variation of the Fe(III) concentration, which was determined spectrophotometrically with sulfosalicylic acid [12]. The kinetics of Fe(II) oxidation with oxygen was monitored by the O_2 uptake on a volumetric installation in a temperature-controlled shaken reactor at 25–70°C. The reaction rate was independent of the shaking frequency. The reaction solution volume was 10 ml in all the experiments. The oxygen partial pressure was varied by dilution of oxygen with argon.

The Pd(II) concentration was determined spectrophotometrically by the intensity of the green color of the complex formed on adding excess $SnCl_2$ solution to the sample being analyzed [13].

The transformation products of aromatic compounds were analyzed qualitatively and quantitatively by gas chromatography–mass spectrometry (Agilent 6890/5973 Network 1000 × 250 × 5). After the reaction completion, organic substances were extracted with chlorobenzene, which quantitatively recovers these aromatic compounds from aqueous solution, as shown for model systems. In the case of benzonitrile, a calibration was made.

Precipitates formed by the reaction in oxygen in the presence of an aromatic nitrile followed by cooling with ice were filtered off, repeatedly washed with ether, and dried in a desiccator over P_2O_5. The resulting compounds were dark brown substances containing Pd(II), soluble in hydrochloric acid and insoluble in alcohols, acetone, acetonitrile, acetic acid, chlorinated methanes, benzene, and dioxane but partially soluble in pyridine and dimethyl sulfoxide. However, the solution concentrations were insufficient for obtaining satisfactory NMR spectra. Therefore, it was impossible to characterize the complexes by NMR spectroscopy.

The IR spectra were recorded on an FSM-1201 Fourier IR spectrometer (KBr pellets). IR spectra of complexes, ν, cm^{-1}: from benzonitrile, 3050 (CH), doublet 2367 + 2336 m, 2262 w (CN), 1598–1562 (Ar), 733, 698 (Ar–H); from phenylacetonitrile, 2958, 2925 (CH_2), doublet 2359 + 2341 m, 2221 w (CN), 1588 s, 738, 696 (Ar–H); from *o*-cyanotoluene, 2925 (CH_3), 2264 m (CN), 1555 s (Ar), 765 (Ar–H); *o*-cyanophenol, 2240 m (CN), doublet 1600 + 1580 s (Ar), 754 (Ar–H); after hydroxylation of benzonitrile, 2963 (CH), doublet 2367 + 2336 m, 2262 w (CN), 1607 s (Ar); after hydroxylation of phenylacetonitrile, 2970, 2925 (CH_2), doublet 2359 + 2341 m, 2221 s (CN), 1623 s (Ar).

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