Russian Chemical Bulletin, International Edition, Vol. 56, No. 5, pp. 875—882, May, 2007

Kinetics and mechanism of catalytic oxidation of alcohols to carbonyl compounds with dioxygen in the Pd-containing aqua system

V. V. Potekhin

St. Petersburg State Technological Institute (Technical University),
26 Moskovsky prosp. 198013 St. Petersburg, Russian Federation.
Fax: +7 (812) 712 7791. E-mail: potechin@mail.admiral.ru

The oxidation of lower aliphatic alcohols C_1—C_4 with dioxygen to form the corresponding carbonyl compounds in the presence of the Pd^{II} tetraaqua complexes and Fe^{II}—Fe^{III} aqua ions in an aqueous medium was studied at 40—80 °C. The introduction of an aromatic compound (acetophenone, benzonitrile, phenylacetonitrile, *o*-cyanotoluene, nitrobenzene) and Fe^{II} aqua ion instead of the Fe^{III} aqua ion into the reaction system increases substantially the catalytic activity and the yield of the carbonyl compound. The key role of the Pd species in the intermediate oxidation state stabilized by the aromatic additive in the catalytic cycle of alcohol oxidation with dioxygen to the carbonyl compound was shown. An increase in the kinetic isotope effect with an increase in the temperature of methanol oxidation indicates a change in the rate-determining step of alcohol oxidation with dioxygen in the presence of Pd^{II}—Fe^{II}—Fe^{III} and the aromatic compound. At temperatures below 60 °C, the catalytically active palladium species are mainly formed upon the reduction of the Pd^{II} tetraaqua complex with the Fe^{II} aqua ion, whereas at higher temperatures the reaction between the alcohol and Pd^{II} predominates. The mechanism and kinetic equation of the process were proposed.

Key words: tetraaquapalladium(II) complex, iron(III)/(II), oxygen, oxidation of alcohols.

The catalytic oxidation of aliphatic alcohols C_1—C_4 to the corresponding carbonyl compounds in the presence of the Pd^{II} tetraaqua complex, Fe^{III}, and dioxygen in an aqueous medium has been studied earlier[1]

$$2\,R^1R^2CHOH + O_2 \xrightarrow{Pd^{II}—Fe^{III}} 2\,R^1R^2CO + 2\,H_2O. \qquad (1)$$

Based on the obtained kinetic regularities, we concluded that Pd^I species formed upon the reduction of the Pd^{II} tetraaqua complex with the substrate are involved in the catalytic reaction. In this case, the Pd^I species play both a positive role, providing selective conversion of alcohols to carbonyl compounds, and a negative role. The latter is related to a side reaction removing the Pd^I species from the catalytic cycle as inactive palladium black through the interaction between the Pd^{II} tetraaqua complex and Fe^{II} aqua ion.[2] The Fe^{II} ion is accumulated during reaction (1), because the oxidation of the Fe^{II} aqua ion to Fe^{III} with dioxygen in a perchloric acid medium occurs in low yield. Therefore, one can expect that in a wide temperature range under the conditions of quantitative oxidation of the Fe^{II} aqua ion with dioxygen in the presence of the Pd^{II} tetraaqua complex the yield of the carbonyl compounds upon alcohol oxidation in the Pd^{II}—Fe^{II}/Fe^{III}—O_2 system should increase.

A special role in the redox reactions involving Pd^{II} belongs to the aromatic derivatives[3—8] stabilizing the low-valent state of palladium. It has been shown[7,8] that the palladium species in an intermediate oxidation state act as the catalyst in the oxidation of the Fe^{II} aqua ion with dioxygen in the presence of the Pd^{II} tetraaqua complex. The activity of these species increases in the presence of additives of some aromatic compounds, in particular, aromatic nitriles. For instance, in the presence of benzonitrile, no precipitation of palladium black occurs and Fe^{II} is oxidized with dioxygen to Fe^{III}.[8]

This experimental fact can be used to determine the conditions providing an increase in the yield of carbonyl compounds and the selectivity of alcohol oxidation with dioxygen in the presence of the Pd^{II}—Fe^{III} aqua ions in an aqueous medium. At the same time, the additives of aromatic compounds in the catalytic system can suppress the side reaction between Pd^{II} and Fe^{II} with palladium black formation. In the present work we studied the Pd^{II}—$Fe^{II/III}$—PhX catalytic system (PhX is an aromatic compound) in the oxidation of alcohols C_1—C_4 with dioxygen.

Experimental

The Pd^{II} tetraaqua complex was synthesized according to an earlier described procedure.[9] Alcohols (reagent grade) were used. The initial aromatic compounds (benzonitrile, phenylacetonitrile, acetophenone, *o*-cyanotoluene, and nitrobenzene) were

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 842—848, May, 2007.

1066-5285/07/5605-0875 © 2007 Springer Science+Business Media, Inc.

purchased from Aldrich. The aromatic compounds were used as 0.02—0.04 *M* aqueous solutions corresponding to their limiting solubility in water. To obtain specified concentrations of substances, a calculated amount of a solution of the Pd^{II} tetraaqua complex and oxidized alcohol were added to an aqueous solution of the aromatic compound. The Fe^{III} ion was introduced into the reaction by adding a solution of $Fe_2(SO_4)_3 \cdot 9H_2O$ in perchloric acid. A specified concentration of Fe^{II} in the reaction mixture was created by the dissolution of a weighed sample of Moore´s salt. In all runs, the volume of the reaction solution was 10 mL, and the concentration of perchloric acid was 0.7 mol L^{-1}.

The reaction was carried out using a volumetric setup and a temperature-controlled reactor of the "catalytic duck" type at 40—80 °C, and the amount of consumed dioxygen was measured at a constant pressure of 0.1 MPa. In preliminary experiments we determined the shaking frequency above which the reaction rate remained unchanged, *i.e.*, the kinetic regime was provided. The partial oxygen pressure was varied by dilution of oxygen with argon.

The concentration of Pd^{II} was measured spectrophotometrically from the intensity of the green color of the complex formed by the addition of excess Sn^{II} chloride solution to the analyzed sample.[10] The concentration of Fe^{III} was determined by spectrophotometry as a complex with sulfosalicylic acid.[11]

The amount of formaldehyde formed was measured spectrophotometrically in the presence of chromotropic acid sodium salt.[12] The concentrations of other carbonyl compounds were determined by the gravimetrically from the formation of hydrazone with a solution of 2,4-dinitrophenylhydrazone.

The conversion products of the aromatic compounds were analyzed by LC-MS (Agilent 6890/5973 Network, HP-5 Crosslinked 5% PH Siloxane column with a length of 100 m). The organic substances were extracted from the reaction solution with chlorobenzene that, as found for model systems, completely extracts aromatic compounds from an aqueous solution. In the case of benzonitrile calibration was used.

Results and Discussion

The kinetic curves of oxygen absorption during methanol oxidation in the system of Pd^{II}—Fe^{III} aqua ions in the presence of some aromatic compounds are shown in Fig. 1.

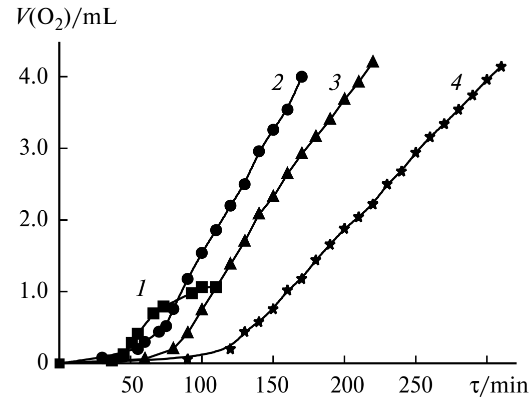

Fig. 1. Effect of the aromatic additives ([PhX] = 12 mmol L^{-1}) on the rate of methanol oxidation with dioxygen: *1*, no arene additive; *2*, benzonitrile; *3*, acetophenone; *4*, nitrobenzene; $[Pd^{II}]_0$ = 5 mmol L^{-1}, $[Fe^{III}]_0$ = 30 mmol L^{-1}, [MeOH] = 4 mol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}, 65 °C; hereinafter $V(O_2)$ is the volume of absorbed oxygen.

In all cases, the induction period caused by the formation (accumulation) of an active species followed by the region of the developed reaction in which the rate of oxygen absorption is maximum and constant, are observed. As should be expected, in the presence of an aromatic compound, the duration of the developed reaction of alcohol oxidation is much higher than that in the solution containing no additive. In the latter case, the reaction is rapidly retarded (see Fig. 1, curve *1*) because of the reduction of Pd^{II} to Pd^0 and precipitation of palladium black. In the case of the arene-containing additive (benzonitrile, acetophenone, nitrobenzene), no Pd reduction occurs in the solution.

When methanol is oxidized in the presence of the arene-containing additives, the number of formaldehyde formed and the conversion of Fe^{III} increase (Table 1).

As can be seen from the data in Table 1, the amount of the aromatic derivative introduced into the reaction solu-

Table 1. Effect of the aromatic compounds (PhX) on the oxidation rate of methanol[a]

PhX	τ^b	t^c	$[Fe^{III}]$	$[Pd^{II}]$	$[O_2]^d$	[HCHO]	$w_{max}(O_2) \cdot 10^6$ /mol L^{-1} s^{-1}
	min		mmol L^{-1}				
No additives	40	100	27	0	5.75	18	2
PhCN	60	170	10	4.6	18.8	48	2.6
$PhCH_2CN$	65	170	10	4.6	18.8	48	2.6
$PhC(O)CH_3$	70	200	10	4.2	19.1	49	2.2
$PhNO_2$	121 (60)[e]	300	7	4.6	16	44	1.6 (2.3)[e]

[a] $[Pd^{II}]_0$ = 5 mmol L^{-1}, $[Fe^{III}]_0$ = 30 mmol L^{-1}, [PhX] = 12 mmol L^{-1}, [MeOH] = 4 mmol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}, 65 °C.

[b] Induction period.

[c] Reaction duration.

[d] Concentration of reacted oxygen.

[e] $[PhNO_2]$ = 5 mmol L^{-1}.

tion exerts no substantial effect on the rate of the developed reaction. However, the induction period changes: it increases with the introduction of the additive and has the maximum duration in the case of nitrobenzene. A decrease in the initial nitrobenzene concentration in the reaction mixture decreases the induction period, which is probably caused by the oxidation properties of nitrobenzene, because no such effect is observed for other aromatic derivatives.

For all the aromatic compounds used, there is some critical concentration, ~3 mmol L^{-1}, below which alcohol is oxidized in the same way as in the absence of an additive.

The effect of the aromatic compounds on the Pd-catalyzed oxidation of alcohols in argon has been reported earlier.[6] The determining role of the benzene ring rather than the electronic properties of the functional group of the substituent in the aromatic ring was shown.[6] It is most likely that the mechanisms of the influence of the arene compounds in the alcohol oxidation and the oxidation of Fe^{II} aqua ion with dioxygen in the presence of the Pd^{II} tetraaqua complex have a common feature: the active form of an intermediate palladium species is stabilized and its transformation into palladium black is suppressed.

Based on the results of several studies,[1,2,6–8,13,14] we can assume that the oxidation of alcohols with dioxygen in the catalytic Pd^{II}—Fe^{III} aqua ions system in the presence of the PhX aromatic compounds includes the following steps:

$$\mathrm{R^1R^2CHOH + [Pd(H_2O)_4]^{2+} \longrightarrow [R^1R^2C(OH)Pd(H_2O)_3]^+ + H_3O^+}, \tag{2}$$

$$\mathrm{[R^1R^2C(OH)Pd(H_2O)_3]^+ \longrightarrow R^1R^2CO + Pd^0 + H_3O^+}, \tag{3}$$

$$\mathrm{[R^1R^2C(OH)Pd(H_2O)_3]^+ + Fe^{3+}_{aq} \longrightarrow R^1R^2CO + Pd^+_{aq} + Fe^{2+}_{aq} + H_3O^+}, \tag{4}$$

$$\mathrm{Pd^+_{aq} + Fe^{3+}_{aq} \rightleftharpoons Pd^{2+}_{aq} + Fe^{2+}_{aq}}, \tag{5}$$

$$\mathrm{[R^1R^2C(OH)Pd(H_2O)_3]^+ + Pd^{2+}_{aq} \longrightarrow Pd_2{}^{2+} + R^1R^2CO + H_3O^+}, \tag{6}$$

$$\mathrm{Pd_2{}^{2+} + PhX \rightleftharpoons \underset{\mathbf{I}}{[Pd_2(PhX)]^{2+}}}, \tag{7}$$

$$\mathrm{\underset{\mathbf{II}}{[Pd_2(PhX)]^{2+}} + O_2 \rightleftharpoons [Pd_2(PhX)(O_2)]^{2+}}, \tag{8}$$

$$\mathrm{[Pd_2(PhX)(O_2)]^{2+} + R^1R^2CHOH \xrightarrow{+\,2\,H^+} R^1R^2CO + 2\,Pd^{2+} + PhX + 2\,H_2O}, \tag{9}$$

$$\mathrm{[Pd_2(PhX)(O_2)]^{2+} + 2\,Fe^{2+}_{aq} \xrightarrow{+\,2\,H^+} 2\,Pd^{2+}_{aq} + 2\,Fe^{3+}_{aq} + PhX + 2\,H_2O}, \tag{10}$$

$$\mathrm{Pd_2{}^{2+} + R^1R^2CHOH \longrightarrow R^1R^2CO + 2\,Pd^0 + 2\,H^+}, \tag{11}$$

$$\mathrm{Pd_2{}^{2+} + 2\,Fe^{2+}_{aq} \longrightarrow 2\,Pd^0 + 2\,Fe^{3+}_{aq}}, \tag{12}$$

$$\mathrm{Pd^{2+} + Fe^{2+}_{aq} \rightleftharpoons Pd^+ + Fe^{3+}_{aq}}, \tag{13}$$

$$\mathrm{Pd^+ + Fe^{2+}_{aq} \longrightarrow Pd^0 + Fe^{3+}_{aq}}, \tag{14}$$

$$\mathrm{Pd^0 + Pd^{2+}_{aq} \rightleftharpoons Pd_2{}^{2+}}. \tag{15}$$

The main reactions proceeding *via* parallel routes can be distinguished from an array of steps (2)—(15). Reactions (2), (4), (5) and (2), (6)—(10) compose the catalytic cycle of alcohol oxidation with iron(III) and dioxygen, respectively, and reactions (3) and (11)—(14) producing palladium black refers to chain termination in the cycle of the Pd-catalyzed alcohol transformation into the carbonyl compound.

Note that the palladium complex with dioxygen is also formed by the reaction of dioxygen with the $Pd_2{}^{2+}$ species containing no coordinated aromatic ligand. However, the data on the kinetics of alcohol oxidation with dioxygen in the absence of PhX suggest that in this case the reactions producing palladium black (reactions (11) and (15)) proceed more rapidly than the formation of the palladium complex with the active dioxygen. Therefore, alcohol oxidation with dioxygen in the presence of the Pd^{II}—Fe^{III} aqua ions but without an aromatic additive is characterized by a considerably lower number of catalytic cycles (2.5 with respect to Pd^{II}) compared to the system containing the PhX additive (more than 60).

The key role in the mechanism (see reactions (2)—(15)) belongs to the palladium species in the intermediate oxidation state (Pd^I) and the $Pd_2{}^{2+}$ clusters. The formation of the cluster palladium species during aliphatic alcohol oxidation with the Pd^{II} tetraaqua complex was proved by UV spectrophotometry from the appearance of an absorption band with a maximum at 312 or 316 nm, depending on the nature of alcohol.[13]

The $Pd_2{}^{2+}$ species manifest the enhanced reactivity toward dioxygen. It has previously been found[2] that the Fe^{III} aqua ion does not oxidize the cluster palladium but has a substantial effect on the step of their formation. In excess Fe^{III} aqua ion over Pd^{II}, no cluster palladium species are formed in concentrations sufficient for the progress of reactions (7)—(10) until the rate of Fe^{III} consumption in reaction (4) becomes lower than the rate of reaction (6). This time determines the induction period in the kinetic curves of oxygen absorption. Therefore, the duration of the induction period of alcohol oxidation with dioxygen in the presence of the Pd^{II}—Fe^{III} aqua ions elongates with an increase in the initial concentration of the Fe^{III} aqua ion.

The duration of the induction period (τ) for methanol oxidation with dioxygen ($[Pd^{II}]_0$ = 5 mmol L^{-1}, [MeOH] = 4 mol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}, [PhCN] = 12 mmol L^{-1}, 65 °C) at different initial concentrations of Fe^{III} is presented below.

$[Fe^{III}]_0$/mmol L^{-1}	10	20	30
τ/min	20	40	60

On going of the process from the induction period to the developed reaction of alcohol oxidation with dioxygen, a certain ratio of concentrations of the formed Fe^{II} and unreacted Fe^{III} is established in the reaction solution. When the initial Fe^{III} concentration is 30 mmol L^{-1}, the solution at the end of the induction period contains the Fe^{II} aqua ion in a concentration of 20 mmol L^{-1} corresponding to the 2 : 1 ratio. It is most likely that this ratio is close to equilibrium value because it remains unchanged until the rate of oxygen consumption is constant.

If the initial reaction solution contains the Fe^{II} and Fe^{III} aqua ions in concentrations of 20 and 10 mmol L^{-1}, respectively, methanol oxidation with dioxygen has a considerably shorter induction period (Fig. 2).

It should be mentioned that if the catalytic alcohol oxidation with dioxygen is related to the formation of palladium cluster species, then the introduction of a reducing agent into the reaction solution should shorten the induction period.

The formation of the cluster palladium species is a result of reduction of the Pd^{II} tetraaqua complex with the initial organic substrate and also with the Fe^{II} aqua ion (see reactions (13)—(15)).[2] Therefore, for the combined addition of the Fe^{II} and Fe^{III} aqua ions in the presence of the aromatic compounds, one can expect a decrease in the induction period (see Fig. 2). However, this explanation can be unconvincing, because the decrease in the initial concentration of the Fe^{III} aqua ion itself shortens the induction period (see above). In addition, the Fe^{III} ion has an effect on the rate of the reaction between the Pd^{II} and Fe^{II} aqua ions, which decreases with an increase in the initial concentration of $Fe^{III}{}_{aq}$ due to reversible reaction (13).[2] If this suggestion is valid, the increase in the rate of formation of the active $Pd_2{}^{2+}$ species and, correspondingly, shortening of the induction period are possible when the Fe^{II} aqua ion is introduced in the absence of the Fe^{III} aqua ion in the initial reaction solution of alcohol oxidation with dioxygen.

Indeed, the addition of the Fe^{II} aqua ion to the reaction solution in the absence of Fe^{III} results in the disappearance of the induction period (Fig. 3).

If the solution contains no aromatic compound, palladium black precipitates immediately due to the reaction between the Pd^{II} and Fe^{II} aqua ions.

When alcohol is oxidized with dioxygen in the presence of the Pd^{II}—Fe^{II} aqua ions, palladium black is completely formed in the presence of all aromatic compounds used, except for aromatic nitrile such as benzonitrile. At the same time, in excess Fe^{III} aqua ion, all studied aromatic additives exert a similar effect. Therefore, we studied the effect of the Fe^{II} aqua ion on the rate of reaction (1) in the presence of benzonitrile.

The rate of oxygen consumption is constant and slightly changes with the variation of the initial Fe^{II} concentration in a range of 5—60 mmol L^{-1}. The material balance of methanol oxidation and the reaction rates under different initial conditions are given in Table 2.

The data in Table 2 show that the rate of oxygen consumption in the catalytic system containing the Fe^{II} aqua ion in the initial solution instead of Fe^{III}, under other equivalent conditions, is higher than that in the catalytic system prepared with the Fe^{III} aqua ion (see Table 1): $3.6 \cdot 10^{-6}$ and $2.6 \cdot 10^{-6}$ mol L^{-} s^{-1}, respectively. This suggests that the rate increase is caused by the con-

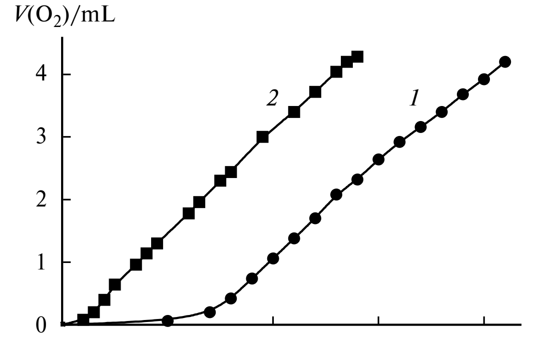

Fig. 2. Effect of Fe^{II} on methanol oxidation in the Pd^{II}—Fe^{III} system: *1*, $[Fe^{III}]_0$ = 30 mmol L^{-1}, $[Fe^{II}]_0$ = 0; *2*, $[Fe^{III}]_0$ = 10 mmol L^{-1}, $[Fe^{II}]_0$ = 20 mmol L^{-1}; $[Pd^{II}]_0$ = 5 mmol L^{-1}, [MeOH] = 4 mol L^{-1}, [PhCN] = 12 mmol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}, 65 °C.

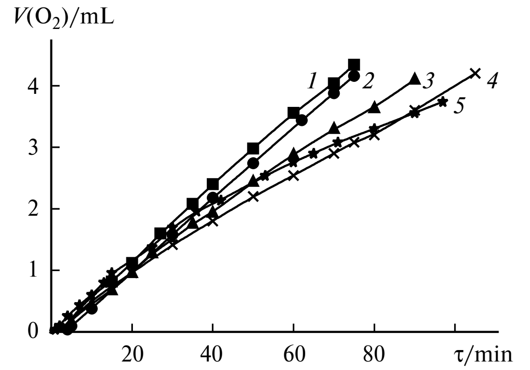

Fig. 3. Effect of the initial concentration of the Fe^{II} aqua ion on methanol oxidation: $[Fe^{II}]_0$ = 5 (*1*), 10 (*2*), 20 (*3*), 40 (*4*), and 60 mmol L^{-1} (*5*); $[Pd^{II}]_0$ = 5 mmol L^{-1}, [MeOH] = 4 mol L^{-1}, [PhCN] = 12 mmol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}, 65 °C.

Table 2. Material balance of methanol oxidation with dioxygen[a]

$[MeOH]_0$ /mol L^{-1}	$[Pd^{II}]_{aq,0}$	$[Fe^{II}]_{aq,0}$	t/min	$[Pd^{II}]_{aq}$[b]	$[Fe^{III}]_{aq}$[b]	$[CH_2O]$	$\Delta[O_2]$	$\Sigma w(O_2) \cdot 10^6$ /mol L^{-1} s^{-1}
	mmol L^{-1}			mmol L^{-1}				
1.5	5	20	100	5	7	21	11	1.8
2.5	5	20	90	5	7	16	11	2.9
4	5	20	90	5	6	32	18	3.6
7	5	20	65	4.8	2.1	36	19	6.4
10	5	20	50	4	1.5	37	19	9.1
4	5	5	75	4.7	1.4	35	18	3.6
4	5	10	75	4.8	2.8	36	19	3.6
4	5	20	90	4.8	6	33	18	3.6
4	5	20	55	5	6	16	10	3.6
4	5	20	25	5	6	7	5	3.6
4	5	20	15	5	5	3	3	3.6
4	5	30	100	4	10	28	18	3.8
4	5	40	90	4	13	27	18	3.8
4	5	60	90	4	16	26	17	4.2
4	5	100	70	3.6	48	16	19	9.7
4	2.5	20	130	2.1	6.2	27	15	2.2
4	8	20	55	6.2	5.7	35	19	5.6

[a] $[PhCN] = 12$ mmol L^{-1}, $[HClO_4] = 0.7$ mol L^{-1}, $p(O_2) = 0.1$ MPa, 65 °C.
[b] Concentration of the Pd^{II} and Fe^{III} aqua ions at the end of the reaction.

tribution of the reaction between Pd^{II} and Fe^{II} producing the catalytically active palladium species Pd_2^{2+} (see reactions (13)—(15)) that catalyze the oxidation of the alcohol and Fe^{II} with dioxygen.

The values of the rate of oxygen consumption ($\Sigma w(O_2)$) presented in Table 2 are equal to the sum of the oxidation rates of Fe^{II} and alcohol with dioxygen. The contribution of each reaction to the total rate of oxygen consumption depends on the initial conditions. The higher the methanol concentration, the higher the formation rate and the larger the amount of formaldehyde formed. If an insignificant amount of the palladium black formed is neglected, the material balance with respect to dioxygen obeys the following equation:

$$\Delta[O_2] = [F^{III}]/4 + [CH_2O]/2.$$

As follows from the data in Table 2 (see the dynamics of changing the Fe^{III} concentration), the steady-state concentration of Fe^{III} is established in the solution rather rapidly, during the first minutes of the reaction. Its value depends on the initial concentrations of Fe^{II} and alcohol and is independent of the initial Pd^{II} concentration. With an increase in the initial Fe^{II} concentration, the rate of Fe^{III} formation in reactions (10) and (13)—(15) increases, resulting in a proportional increase in the steady-state Fe^{III} concentration. In this case, the ratio of the Fe^{II} concentration in a solution of the oxidant to the steady-state Fe^{III} concentration remains constant, being ~2. When the initial alcohol concentration increases, the rate of formation of the Fe^{III} aqua ion and the steady-state Fe^{III} concentration decrease due to reaction (9). The fact of establishment of the steady-state Fe^{III} concentration indicates that the alcohol is oxidized with both the dioxygen and Fe^{III} aqua ion.

The change in the Fe^{II} concentration in the range 5—40 mmol L^{-1} induces no noticeable effect on the total rate of oxygen absorption, which is more sensitive to a change in the alcohol concentration and increases proportionally to the latter.

The linear dependence of the rate on the alcohol concentration indicates that the catalytically active palladium species are mainly formed in reaction (6), which is preceded by the rate-determining step of reduction of the Pd^{II} tetraaqua complex with the alcohol. The rate of reaction (6) depends on the initial concentrations of the alcohol and Pd^{II}. The dependence of the total rate of oxygen absorption on the initial concentration of the Pd^{II} tetraaqua complex is linear, indicating the first order with respect to the Pd^{II} concentration.

The dependence of the total rate of oxygen consumption on the partial oxygen pressure in the 0.02—0.1 MPa interval is characterized by the curve with saturation (Fig. 4).

It is known that the plots of this type are observed for the processes that proceed *via* the mechanism involving the formation of an intermediate catalytic complex in the equilibrium reaction between the initial reactant and catalyst. This complex is rather stable kinetically and is not transformed irreversibly into the reaction products. In this case, this is caused by reactions (7) and (8) in which complexes **I** and **II**, respectively, are formed.[14]

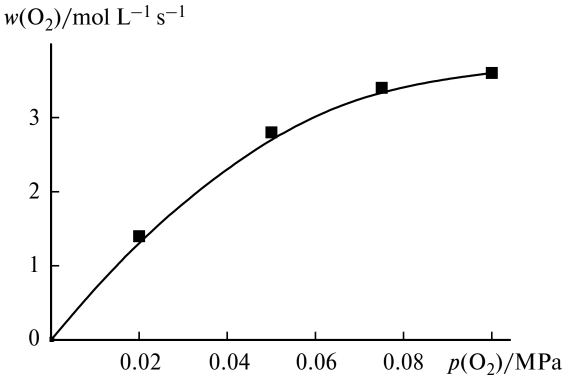

Fig. 4. Plot of the total rate of oxygen consumption ($\Sigma w(O_2)$) *vs.* oxygen pressure ($p(O_2)$) during methanol oxidation; $[Pd^{II}]_0$ = 5 mmol L^{-1}, $[Fe^{II}]_0$ = 20 mmol L^{-1}, [MeOH] = 4 mol L^{-1}, [PhCN] = 12 mmol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}, 65 °C.

The data on the dependence of the rate of oxygen consumption on the partial oxygen pressure during methanol oxidation at 65 °C are satisfactorily described by the Michaelis—Menthen equation

$$\Sigma w(O_2) = 6.6 \cdot 10^{-6} \cdot p(O_2)/[K + p(O_2)].$$

Based on the revealed kinetic regularities, we can present the equation of the rate of oxygen consumption in the interval of Fe^{II} concentrations from 5 to 40 mmol L^{-1} in the following form:

$$\Sigma w(O_2) = k[Pd^{II}][MeOH]p(O_2)/[K + p(O_2)],$$

where $k = 3.3 \cdot 10^{-4}$ L mol^{-1} s^{-1}, and K = 0.06 MPa at 65 °C.

At the initial Fe^{II} concentration of 0.1 mol L^{-1} the total rate of oxygen consumption is $9.7 \cdot 10^{-6}$ mol L^{-1} s^{-1} and close to the rate of oxidation of the Fe^{II} aqua ion with dioxygen in the presence of the Pd^{II} tetraaqua complex and benzonitrile ($8.2 \cdot 10^{-6}$ mol L^{-1} s^{-1}) at 65 °C.[8] The difference in the rates corresponds to the rate of oxygen consumption for alcohol oxidation. This change in the total rate of oxygen absorption with the change in the Fe^{II} concentration from 5—40 mmol L^{-1} to 0.1 mol L^{-1} can indicate a change in the step that causes the formation of the active palladium species. It can be assumed that the rate of oxygen consumption, in this case, will be determined by the kinetics of the reaction of Pd^{II} with Fe^{II} in which the key role also belongs to the cluster palladium species.

It follows from the data obtained by studying the temperature effect on the rate of oxygen absorption that the rate-determining step depends on the conditions of process.

The kinetic curves of oxygen consumption during methanol oxidation at different temperatures are shown in Fig. 5. The Arrhenius plot of the total rate of oxygen absorption on the inverse temperature (Fig. 6) indicates distinctly two temperature regions with different activation energies: 40—55 and 60—80 °C, where the activation energies are is 24.8±3 and 99.9±9 kJ mol^{-1}, respectively.

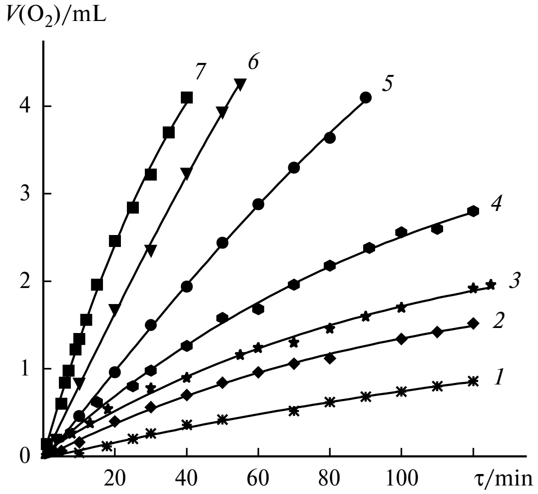

Fig. 5. Kinetic curves of oxygen consumption during methanol oxidation at temperatures 40 (*1*), 50 (*2*), 55 (*3*), 60 (*4*), 65 (*5*), 70 (*6*), and 80 °C (*7*); $[Pd^{II}]_0$ = 5 mmol L^{-1}, $[Fe^{II}]_0$ = 20 mmol L^{-1}, [MeOH] = 4 mol L^{-1}, [PhCN] = 12 mmol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}.

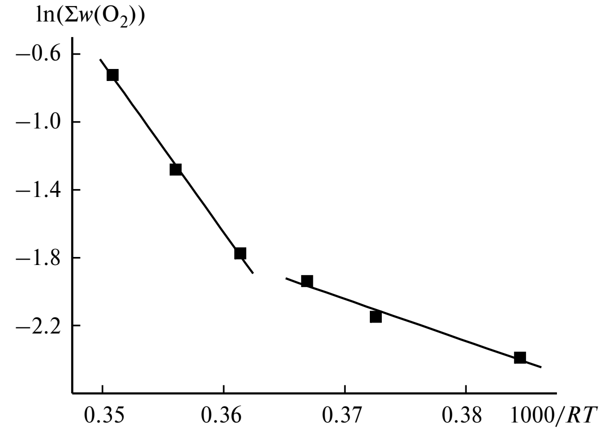

Fig. 6. Arrhenius plot of the rate of oxygen consumption in a methanol solution; $[Pd^{II}]_0$ = 5 mmol L^{-1}, $[Fe^{II}]_0$ = 20 mmol L^{-1} [MeOH] = 4 mol L^{-1}, [PhCN] = 12 mmol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}.

Similar character of the temperature dependence of the rate of oxygen absorption was found for the oxidation of other alcohols under study. The found values of the activation energy are given in Table 3.

The data in Table 3 show that at 40—55 °C the energy of the reaction is independent of the alcohol nature. In this case, the activation energy is close to that of oxidation of the Fe^{II} aqua ion in the presence of the Pd^{II} tetraaqua complex in the presence of the benzonitrile, which is equal to 31.7±3 kJ mol^{-1}.[7] In the temperature

Table 3. Activation energies for alcohol oxidation at 40—55 (I) and 60—80 °C (II)*

Alcohol	E_a/kJ mol^{-1}	
	I	II
Methanol	24.8±2.5	99.9±9
Propan-1-ol	24.8±2.5	53.4±5
Propan-2-ol	26.5±2.6	70.1±7
Butan-1-ol	25.4±2.5	48±4
Butan-2-ol	34±3	76±7

* $[Pd^{II}{}_{aq}]_0$ = 5 mmol L^{-1}, $[Fe^{II}{}_{aq}]_0$ = 20 mmol L^{-1}, [PhCN] = 12 mmol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}, $p(O_2)$ = 0.1 MPa.

range 60—80 °C the activation energy depends on the alcohol nature, changes according to the energy of alcohol oxidation with the Pd^{II} tetraaqua complex, and decreases on going from methanol to butan-1-ol.[1]

Thus, the palladium species exhibiting the catalytic activity in the oxidation of the alcohols and Fe^{II} aqua ion with dioxygen are formed *via* two routes. According to one route, the active intermediate palladium species are formed in the reaction between the alcohol and Pd^{II} tetraaqua complex, whereas the second route involves the reduction of the Pd^{II} tetraaqua complex with the Fe^{II} aqua ion. The contribution of each route depends on the temperature. At an elevated temperature the first route with the rate-determining step of the interaction of alcohol with Pd^{II} (reaction (6) is predominant). In the 40—55 °C temperature interval, the rate of the reaction is determined by another rate-determining step: the reaction between the Fe^{II} aqua ion and Pd^{II}.

The change in the rate-determining step during the temperature-dependent oxidation with dioxygen in the ROH—Pd$^{II}{}_{aq}$—Fe$^{II}{}_{aq}$—PhCN system is indicated by the kinetic isotope effect (KIE) found for methanol oxidation. At 50 °C the KIE is $k_{CH_3OH}/k_{CD_3OH} = 1$, and at 65 °C the KIE is 2. In the latter case, the KIE corresponds to the value found for methanol oxidation with the Fe^{III} aqua ion in the presence of the Pd^{II} tetraaqua complex in an inert atmosphere.[1]

Thus, the proposed reactions (2)—(15) of the complicated multi-route oxidation of alcohols with dioxygen in the presence of the aromatic compound in the catalytic system of the Pd^{II}—Fe^{III}—Fe^{II} aqua ions describe satisfactorily the oxidation process and agree with the observed kinetic regularities. As a whole, the system behaves itself as an interrelated harmonically working machine in which each component supplements and enhances the properties of another component. The Pd^{II} tetraaqua complex occupies the central position and acts as a catalyst precursor that generates the catalytically active palladium species stabilized by the benzene ring of the aromatic compound. Favorable conditions for the activation of a dioxygen molecule and the formation of a rather stable complex similar to the d-metal peroxide complexes[15] are thus created. Thus, the "strongly bound" dioxygen and activated dioxygen selectively oxidize the alcohol to the carbonyl compound. The Fe^{II} aqua ion favors the formation of the catalytically active cluster species, which exert a positive effect on the increase in the rate of alcohol oxidation with dioxygen. At the same time, the Fe^{III} aqua ion that formed control the redox process of alcohol conversion to the carbonyl compounds, restricting complete reduction of the Pd^{II} tetraaqua complex to Pd^0 and palladium black formation.

Table 4. Oxidation of the aliphatic alcohols with dioxygen in the presence of the Pd^{II}—Fe^{II}—Fe^{III} aqua ions*

Alcohol	$[R^1R^2CHOH]_0$	$[R^1R^2CHO]$	Yield (%)
	mmol L^{-1}		
Methanol	4	0.3	7
Ethanol	1.5	0.4	25
Propan-1-ol	0.5	0.3	60
Propan-2-ol	4	0.5	13
Butan-1-ol	0.5	0.3	66
Butan-2-ol	2	0.5	25

* $[Pd^{II}]_0$ = 5 mmol L^{-1}, $[Fe^{II}]_0$ = 20 mmol L^{-1}, $[Fe^{III}]_0$ = 5 mmol L^{-1}, [PhCN] = 12 mmol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}, 65 °C, $p(O_2)$ = 0.1 MPa.

Based on the proposed mechanism, we determined the conditions for the highly selective synthesis of carbonyl compounds by the oxidation of alcohols involving the catalytic system of the Pd^{II}—Fe^{II}—Fe^{III}—O_2 aqua ions. The yields of the carbonyl compounds in alcohol oxidation with dioxygen in this catalytic system for 24 h at the selectivity of the process close to 100% are given in Table 4.

The reaction by-products are the products of oxidation and acid hydrolysis of benzonitrile, in particular, benzoic acid, which has earlier been discussed.[8] Benzonitrile is oxidized at the aromatic ring to form phenol derivatives, (in particular, hydroxybenzonitrile isomers), which are readily coordinated with the Pd^{II} tetraaqua complex. Due to ligand substitution, the initial labile Pd^{II} tetraaqua ion is transformed into the kinetically low-activity Pd^{II} complex and the catalytic process of alcohol oxidation ceases.

References

1. V. V. Potekhin, S. N. Solov´eva, and V. M. Potekhin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 2420 [*Russ. Chem. Bull.*, *Int. Ed.*, 2003, **52**, 2668].
2. V. V. Potekhin, V. A. Matsura, S. N. Solov´eva, and V. M. Potekhin, *Kinet. Katal.*, 2004, **45**, 407 [*Kinet. Catal.*, 2004, **45**, 381 (Engl. Transl.)].

3. G. Allegra, L. Porri, and A. Immirzi, *J. Am. Chem. Soc.*, 1965, **87**, 1394.
4. G. Allegra, G. Tettamant, A. Immirzi, L. Porri, and G. Vitulli, *J. Am. Chem. Soc.*, 1970, **92**, 289.
5. T. Murahashi and H. Kurosawa, *Coord. Chem. Rev.*, 2002, **231**, 207.
6. V. V. Potekhin, S. N. Solov´eva, and V. M. Potekhin, *Zh. Obshch. Khim.*, 2004, **74**, 866 [*Russ. J. Gen. Chem.*, 2004, **74** (Engl. Transl.)].
7. V. V. Potekhin, S. N. Solov´eva, and V. M. Potekhin, *Zh. Obshch. Khim.*, 2004, **74**, 709 [*Russ. J. Gen. Chem.*, 2004, **74** (Engl. Transl.)].
8. V. V. Potekhin, S. N. Solov´eva, and V. M. Potekhin, *Zh. Obshch. Khim.*, 2006, **76**, 895 [*Russ. J. Gen. Chem.*, 2006, **76** (Engl. Transl.)].
9. L. Elding, *Helv. Chim. Acta*, 1984, **67**, 1453.
10. S. I. Ginzburg, *Analiticheskaya khimiya platinovykh metallov* [*Analytical Chemistry of Platinum Metals*], Nauka, Moscow, 1972, 614 pp. (in Russian).
11. Z. Marczenko, *Kolorymetryczne Oznaczanie Pierwiastkow*, Wydawnictwa Naukowo-Techniczne, Warszawa, 1968, 500 (in Polish).
12. S. K. Ogorodnikov, *Formal´degid* [*Formaldehyde*], Khimiya, Leningrad, 1984, 280 pp. (in Russian).
13. V. V. Potekhin, *Zh. Obshch. Khim.*, 2006, **76**, 1477 [*Russ. J. Gen. Chem.*, 2006, **76** (Engl. Transl.)].
14. V. V. Potekhin, *Zh. Obshch. Khim.*, 2006, **76**, 1469 [*Russ. J. Gen. Chem.*, 2006, **76** (Engl. Transl.)].
15. I. I. Moiseev, *J. Mol. Cat. A: Chem.*, 1997, **127**, 1.

Received June 19, 2006;
in revised form November 20, 2006