2668 Russian Chemical Bulletin, International Edition, Vol. 52, No. 12, pp. 2668—2674, December, 2003

Catalytic oxidation of aliphatic alcohols in the tetraaquapalladium(II) complex—iron(III)—dioxygen system

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The selective low-temperature (40—70 °C) catalytic oxidation of methanol, propan-1-ol, and propan-2-ol in the presence of the tetraaquapalladium(II) complex and iron(III) ions and/or molecular oxygen as cooxidants was studied. The corresponding carbonyl compound is the product of alcohol oxidation. The kinetic regularities of the reaction were established. In the reaction mechanism proposed, the key step is palladium(I) formation.

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

Selective organic synthesis involving transition metal complexes as catalysts plays an important role in modern chemistry.[1,2] One of such processes is the partial catalytic oxidation of organic compounds with molecular oxygen. In this respect, reactions of alcohol oxidation to carbonyl compounds in the presence of palladium compounds are of interest.[3,4]

The kinetics and mechanism of oxidation of aliphatic alcohols have previously[5—7] been studied using palladium(II) chloride as a catalyst. The stoichiometric oxidation of alcohols with palladium(II) was mainly studied. Dioxygen served as an oxidant of alcohols in the first works.[8,9] The $Pd_{561}Phen_{60}(OAc)_{180}$ giant palladium cluster was shown to catalyze the low-temperature oxidation of aliphatic alcohols with oxygen to form a whole series of products, *viz.*, esters, aldehydes, anhydrides of carboxylic acids, and acetals.[10]

It has been shown in studying[11—14] the oxidation of C_1—C_4 aliphatic and alkylaromatic alcohols with the tetraaquapalladium(II) complex that palladium(II) selectively oxidizes alcohols to the corresponding carbonyl compounds in the stoichiometric reaction.[14] The specific feature of this reaction is its autocatalytic character and sensitivity of the system to the composition of a gaseous atmosphere.[13,15] The rate of tetraaquapalladium(II) complex reduction is maximum in an inert gas (Ar) atmosphere, whereas it is minimum in an oxygen atmosphere. The latter was attributed by the authors to a possibility of the catalytic oxidation of alcohol with oxygen. However, the role of oxygen in this process was not studied systematically. The exceptions are the works devoted to the study of benzyl alcohol oxidation with molecular oxygen, although this reaction occurs in the presence of reduced colloidal palladium obtained *in situ* from the tetraaquapalladium(II) complex.[16,17]

In this work, we considered the oxidation of methanol, propan-1-ol, and propan-2-ol in an aqueous solution in the presence of the catalytic system consisting of the tetraaquapalladium(II) complex and iron(III) and/or dioxygen as cooxidants.

Experimental

Alcohols were reagent grade. The tetraaquapalladium(II) complex was synthesized according to a previously described procedure.[18] The concentration of perchloric acid in a solution was determined by acid-base titration. The source of Fe^{III} ions was a solution of $Fe_2(SO_4)_3 \cdot 9H_2O$ in perchloric acid.

Alcohols were oxidized at the following initial concentrations of the reactants (mol L^{-1}): Pd^{II}, $(1—5) \cdot 10^{-3}$; Fe^{III}, $(5—30) \cdot 10^{-3}$; $[HClO_4]$, 0.2—0.7; and [ROH], 4. The reaction in the presence of iron(III) was performed in an Ar atmosphere in a reactor equipped with a sampler.

The rate of alcohol oxidation in an O_2 atmosphere was determined by the rate of oxygen uptake in a shaken reactor at a constant temperature using a volumetric method. In all experiments, the volume of the reaction solution was 10 mL. The shaking frequency was selected in such a way that the reaction rate was frequency-independent. Dioxygen was diluted with argon to vary its partial pressure.

The concentrations of palladium(II) and iron(III) were measured spectrophotometrically using procedures reported elsewhere.[19,20] The amount of formaldehyde formed was also determined spectrophotometrically in the presence of the sodium salt of chromotropic acid.[21] The concentrations of propanal and acetone were determined by the gravimetric method by measuring the amount of hydrazone formed upon the interaction with a solution of 2,4-dinitrophenylhydrazine.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2525—2530, December, 2003.

Results and Discussion

In an oxygen atmosphere, the carbonyl compound is formed in two parallel reactions

$$R^1R^2CHOH + Pd^{2+}_{aq} \longrightarrow R^1R^2CO + Pd^0 + 2\,H^+, \quad (1)$$

$$2\,R^1R^2CHOH + O_2 \xrightarrow{Pd^{2+}_{aq}} 2\,R^1R^2CO + 2\,H_2O. \quad (2)$$

The kinetic curves of oxygen uptake are presented in Fig. 1. The S-like shape of the curves indicates the autocatalytic character of the reaction.

Palladium black was precipitated in parallel with oxygen consumption. The total amount (volume) of consumed oxygen in the kinetic curves (see Fig. 1) corresponds to the complete transformation of palladium(II) into palladium black. As established previously,[14] the rate of stoichiometric oxidation of alcohols with the tetraaquapalladium(II) complex *via* reaction (1) increases in the series methanol < propan-2-ol < propan-1-ol. When considering that alcohol oxidation with oxygen is catalyzed by the palladium(I) compound formed in reaction (1) that precedes the formation of palladium black, one can expect that the slower the formation of palladium black, the longer the duration of the catalytic oxidation of an alcohol with oxygen in reaction (2). In fact, as can be seen in Fig. 1, the oxygen uptake is greater for the oxidation of propan-2-ol and methanol than that for propan-1-ol oxidation. The contribution of reaction (2) to the formation of the carbonyl compound becomes less significant with increasing temperature. The material balance with respect to formaldehyde, acetone, and propanal at the end of the process corresponds to the stoichiometry of reactions (1) and (2).

The presence of oxygen does not prevent the precipitation of platinum black. Most likely, only a small portion of colloidal Pd^0 or Pd^I interacts with oxygen, and the main fraction is transformed into palladium black. This is an expected result, because the system contains no substances capable of stabilizing low-valent palladium. Therefore, the efficiency of catalytic oxidation of alcohols with oxygen in reaction (2) is low under these conditions.

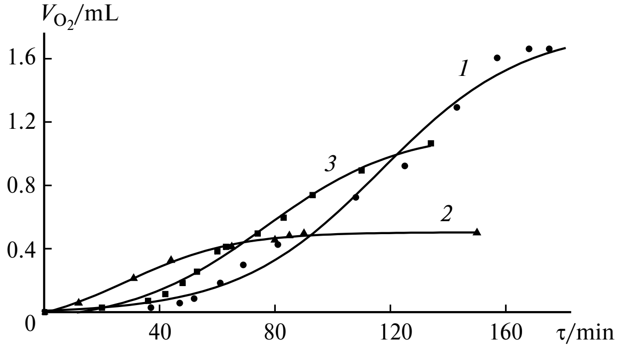


Fig. 1. Kinetic curves of oxygen consumption during the oxidation of methanol (*1*), propan-1-ol (*2*), and propan-2-ol (*3*) in the presence of the Pd^{II} tetraaqua complex; $T = 55$ °C; $[Pd^{2+}] = 5 \cdot 10^{-3}$ mol L^{-1}, $[HClO_4] = 0.65$ mol L^{-1}, and $[ROH] = 4$ mol L^{-1}.

As was previously established,[22] in the oxidation of tertiary alcohols with the tetraaquapalladium(II) complex, Pd^{II} catalyzes the reaction in the presence of the Fe^{III} ions. Assuming that the same rationale can be applied to the system studied in this work, we considered the reaction kinetics using methanol oxidation as an example.

The catalytic selective oxidation of methanol occurs in an Ar atmosphere in the presence of the tetraaquapalladium(II) complex and iron(III) ions

$$MeOH + 2\,Fe^{3+}_{aq} \xrightarrow{Pd^{2+}_{aq}} HCHO + 2\,Fe^{2+}_{aq} + 2\,H^+. \quad (3)$$

Reaction (3) occurs with a constant rate being independent of the initial concentration of iron(III). This follows from the same slope of the straight lines describing the changes in the iron(III) concentration in time at different initial concentrations (Fig. 2).

Palladium black is not formed and the solution remains homogeneous during iron(III) reduction (until the moment designated by an arrow in Fig. 2).

Reaction (3) has the zero order with respect to iron(III) and the first order with respect to both palladium(II) (Fig. 3) and methanol (Fig. 4).

The dependence of the rate of reaction (3) on the perchloric acid concentration is linearized in the w—$[HClO_4]^{-1}$ coordinates (Fig. 5).

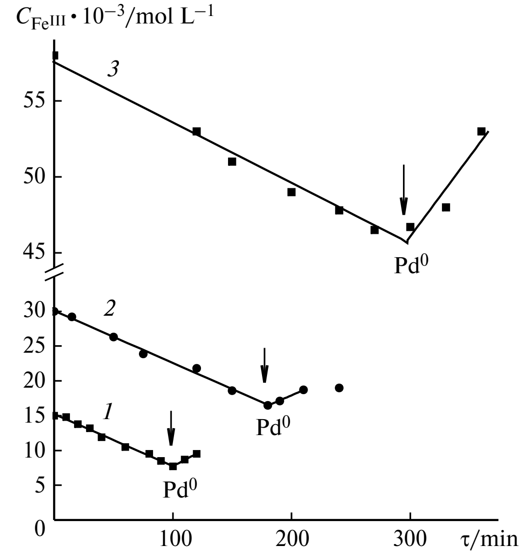


Fig. 2. Changes in the iron(III) concentration during methanol oxidation in the presence of the Pd^{II} tetraaqua complex. Initial concentration $[Fe^{3+}]_0$: 0.015 (*1*); 0.03 (*2*); 0.058 mol L^{-1} (*3*); $T = 55$ °C; $[Pd^{2+}]_0 = 0.005$ mol L^{-1}, $[MeOH] = 4$ mol L^{-1}, and $[HClO_4] = 0.7$ mol L^{-1}.

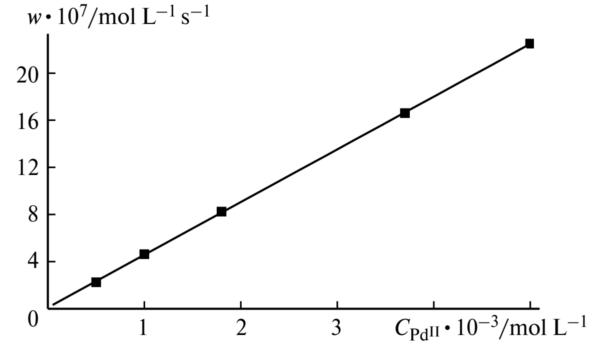


Fig. 3. The rate of reaction (3) *vs*. palladium concentration; $T = 55$ °C; [MeOH] = 4 mol L^{-1}, $[Fe^{3+}] = 0.03$ mol L^{-1}, and $[HClO_4] = 0.2$ mol L^{-1}.

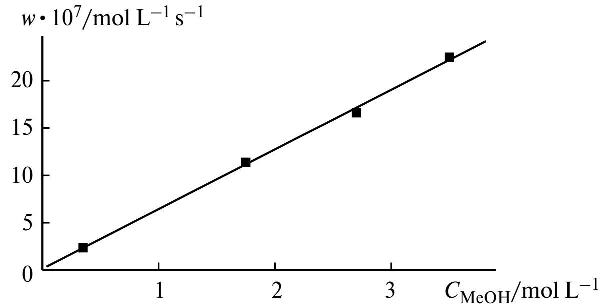


Fig. 4. The rate of reaction (3) *vs*. methanol concentration; $T = 55$ °C; $[Fe^{3+}] = 0.03$ mol L^{-1}, $[Pd^{2+}] = 5 \cdot 10^{-3}$ mol L^{-1}, and $[HClO_4] = 0.2$ mol L^{-1}.

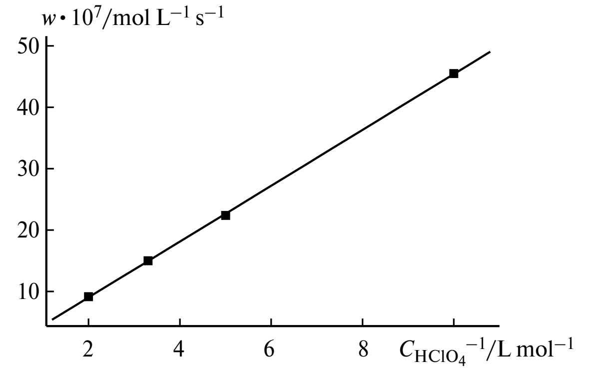


Fig. 5. The rate of reaction (3) *vs*. perchloric acid concentration; $T = 55$ °C; [MeOH] = 4 mol L^{-1}, $[Fe^{3+}] = 0.03$ mol L^{-1}, and $[Pd^{2+}] = 5 \cdot 10^{-3}$ mol L^{-1}.

Therefore, reaction (3) has the negative first order with respect to perchloric acid and is inhibited by this acid.

The zero order with respect to iron(III) indicates that the step involving Fe^{III}, namely, regeneration of palladium(II), follows the limiting step in the reaction scheme.

Thus, the kinetic equation of methanol oxidation in the tetraaquapalladium(II) complex—iron(III) system can be written as follows:

$$w = k[MeOH][Pd^{2+}{}_{aq}]/[HClO_4],$$

where $k = 2.6 \cdot 10^{-5}$ s^{-1} at $T = 55$ °C.

The oxidation of alcohols with the palladium(II) complexes in chloride and nonaqueous systems is assumed[23] to proceed *via* the "alkoxide" mechanism including the hydride transfer at the C_β atom in the internal sphere of a complex of palladium(II) with the alcohol molecule coordinated to the O atom. According to this mechanism, a secondary alcohol should be oxidized more rapidly than the corresponding isomeric primary alcohol. However, the inverse sequence is observed in the reaction involving the tetraaquapalladium(II) complex: a primary alcohol is oxidized more rapidly than a secondary alcohol. The possibility of a different mechanism of aliphatic alcohol oxidation is also indicated by the fact that iron(III) acts as a cooxidant with respect to palladium(II). The analysis of the thermodynamic data shows that iron(III) cannot oxidize palladium(0), because the standard redox potential of palladium ($E°_{Pd^{II}/Pd^0} = 0.98$ V) is higher than the corresponding potential of iron ($E°_{Fe^{III}/Fe^{II}} = 0.77$ V).

It can be considered that iron(III), in regenerating palladium(II), oxidizes palladium in the intermediate oxidation state, namely, Pd^I, instead of palladium(0) and a hydrogen-containing palladium derivative

$$Pd^{+}{}_{aq} + Fe^{3+}{}_{aq} \longrightarrow Pd^{2+}{}_{aq} + Fe^{2+}{}_{aq}. \qquad (4)$$

Reaction (4) is complementary and fast. In the absence of iron(III), palladium black is formed, most likely, in the reaction

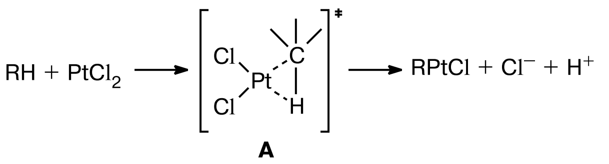
$$2\,Pd^{+}{}_{aq} \longrightarrow [Pd_2]^{2+} \rightleftharpoons Pd^0 + Pd^{2+}{}_{aq}, \qquad (5)$$

which is competitive to reaction (4). The formation and catalytic activity of the palladium(I) compounds were established in several processes involving the palladium(II) complexes.[24—26]

It is important that the catalytic reaction of alcohol oxidation does not occur when $Fe^{3+}{}_{aq}$ ions are replaced by $Cu^{2+}{}_{aq}$ ions. Palladium black is precipitated from the very beginning of the reaction. The standard redox potential of the copper(II) aqua complex is $E°_{Cu^{II}/Cu^0} = 0.34$ V, and for the one-electron transition $E°_{Cu^{II}/Cu^I} = 0.16$ V. Therefore, the regeneration of palladium(II) by the oxidation of palladium(0) seems improbable in the presence of $Cu^{2+}{}_{aq}$ ions as well. Thus, the oxidation of Pd^0 to Pd^{II} with iron(III) or copper(II) in a perchloric acid medium is impossible. However, the fact that palladium black is not formed in the Pd^{II}—Fe^{III} system suggests that palladium in the intermediate oxidation state is oxidized with the cooxidant instead of Pd^0, and the redox potential of palladium in the intermediate oxidation state is 0.4—0.7 V.

It is established[27—29] that the oxidation of saturated hydrocarbons with platinum(II) and palladium(II) salts is preceded by the step of C—H bond activation *via* the electrophilic substitution mechanism to form both charged and radical species (Scheme 1).

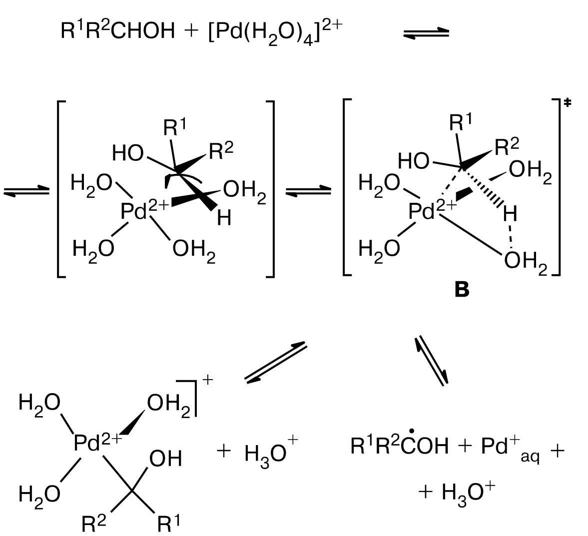
Scheme 1



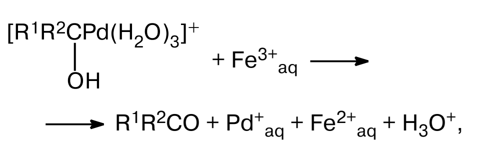
When a coordinated water molecule is present in the internal sphere of platinum, the proton transfer to the water molecule becomes especially favorable. Steric factors play a substantial role in the formation of transition state **A**. Therefore, the primary C—H bond is more easily activated than the secondary bond.

As for the oxidation of saturated hydrocarbons, the C—H bond of the alcohol molecule can be activated in the oxidation of aliphatic alcohols with a strong electrophilic oxidant, *e.g.*, tetraaquapalladium(II) complex (Scheme 2).

Scheme 2



Two possible routes of transformation of transition state **B** are shown in Scheme 2: the organopalladium compound bearing the Pd—C bond is formed in one of these routes, whereas the one-electron transfer *via* another route results in the formation of a hydroxyalkyl radical and palladium(I). Regardless of the method of decomposition of intermediate **B**, the further oxidation of both the organopalladium complex and hydroxyalkyl radical with the tetraaquapalladium(II) complex or iron(III) ions affords the carbonyl compound. When $[\mathrm{Pd^{2+}}_{aq}]_0 < [\mathrm{Fe^{3+}}_{aq}]_0$, this occurs in the reaction



$$\underset{\mathrm{OH}}{[\mathrm{R^1R^2CPd(H_2O)_3}]^+} + \mathrm{Fe^{3+}}_{aq} \longrightarrow$$
$$\longrightarrow \mathrm{R^1R^2CO + Pd^{+}}_{aq} + \mathrm{Fe^{2+}}_{aq} + \mathrm{H_3O^+}, \quad (6)$$

$$\mathrm{R^1R^2\dot{C}OH + Fe^{3+}}_{aq} \longrightarrow$$
$$\longrightarrow \mathrm{R^1R^2CO + Fe^{2+}}_{aq} + \mathrm{H_3O^+}. \quad (7)$$

The oxidation of palladium(I) occurs in reaction (4) and, as a result, the catalytic cycle of alcohol oxidation with the tetraaquapalladium(II) complex in the presence of the iron(III) aqua complex is closed.

In transition state **B** formed due to the activation of the C—H bond of a secondary alcohol, the H atom is less "acidic" than the substituted H atom of a primary alcohol due to the positive inductive effect. Therefore, binding the leaving proton to water during propan-1-ol oxidation occurs more easily than for the reaction with propan-2-ol. Steric hindrances appear when transition state **B** is formed in the reaction involving a secondary alcohol. As a result, secondary alcohols are oxidized more slowly than the respective isomeric primary alcohols. According to the mechanism proposed, the rate of alcohol oxidation should decrease with an increase in the acid concentration, which agrees with the results of the kinetic study.

We established that the kinetic isotope effect (KIE), which is $k_{\mathrm{MeOH}}/k_{\mathrm{CD_3OD}} = 1.8$ at 65 °C, is observed in the oxidation of methanol with the tetraaquapalladium(II) complex in the presence of iron(III). This indicates that hydrogen is involved in the limiting step, which is the activation of the C—H bond of the alcohol molecule. The comparatively low KIE value is explained by the fact that the dissociation energy of the C—H bond in the transition state decreases due to the polarizing effect of the solvent molecule, in the given case, water molecule.

Thus, the activation of the C—H bond with palladium(II) and binding the leaving proton with water occur in parallel, thus favoring the electrophilic substitution mechanism. The activation energies of the catalytic oxidation of methanol, propan-1-ol, and propan-2-ol with the tetraaquapalladium(II) complex in the 40—70 °C temperature interval are equal to 106.8, 85.2, and 93.8 kJ mol^{-1}.

Alcohol oxidation with the iron(III) aqua complex in the presence of the tetraaquapalladium(II) complex is ceased when the conversion of iron(III) reaches 30—50%. Thereafter palladium black is formed. As can be seen from the data in Fig. 2, the Fe$^{\mathrm{III}}$ concentration begins to increase after the "minumum point" marked by arrow with the simultaneous precipitation of palladium black. This is caused by the interaction of the accumulated iron(II) ions and tetraaquapalladium(II) complex

$$\mathrm{Pd^{2+}}_{aq} + 2\,\mathrm{Fe^{2+}}_{aq} \longrightarrow \mathrm{Pd^0} + 2\,\mathrm{Fe^{3+}}_{aq}. \quad (8)$$

The introduction of an oxidant capable of fast oxidation of iron(II) into the reaction system makes it possible to prevent reaction (8). Molecular oxygen can be one of these oxidants.

The interaction of iron(II) with oxygen in a perchloric acid medium is known[30] to occur very slowly. However,

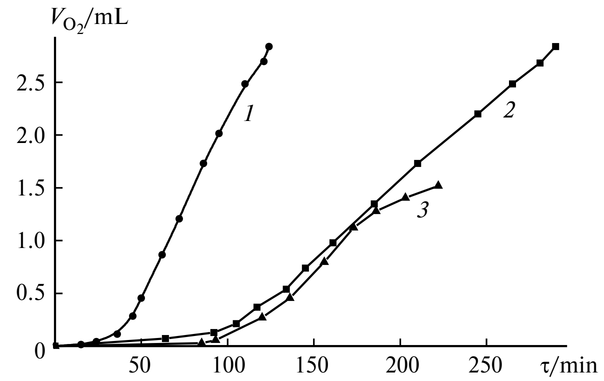


Fig. 6. Kinetic curves of the oxidation of propan-1-ol (*1*), propan-2-ol (*2*), and methanol (*3*) in the presence of Fe^{III} and dioxygen; T = 55 °C; $[Fe^{3+}]$ = 0.03 mol L^{-1}, $[HClO_4]$ = 0.65 mol L^{-1}, $[Pd^{2+}] = 5 \cdot 10^{-3}$ mol L^{-1}, and [ROH] = 4 mol L^{-1}.

in the presence of the tetraaquapalladium(II) complex, as we have already established in the independent experiment, iron(II) ions are oxidized with oxygen with a noticeable rate even at room temperature

$$4\,Fe^{2+}_{aq} + O_2 + 4\,H^+ \xrightarrow{[Pd]} 4\,Fe^{3+}_{aq} + 2\,H_2O. \qquad (9)$$

When the system simultaneously contains iron(III) ions and oxygen, the duration of catalytic alcohol oxidation increases (*cf.* Figs. 1 and 6).

Two regions can be distinguished in the kinetic curves presented in Fig. 6: the initial unstationary region characterized by slow oxygen uptake and the stationary region. In the initial region, alcohol is oxidized in reaction (3) in which iron(III) is consumed. This period is ceased after reaching a 30—50% conversion of iron(III) and appearance of a small amount of palladium(0) in a solution (at most 10% of its initial amount). A noticeable oxygen consumption starts from this moment, and the character of changes of the iron(III) concentration becomes dependent of the alcohol nature.

Evidently, the unstationary region corresponds to the accumulation of the catalyst (palladium complex) up to the quasi-stationary concentration. In our opinion, this catalyst is Pd^I.

As was mentioned above, the oxidation rates of methanol, propan-1-ol, and propan-2-ol are proportional to the initial concentrations of Pd^{II} and alcohol and inversely proportional to the perchloric acid concentration. The dependence of the reaction rate on the oxygen pressure in an interval of 0.025—0.1 MPa is characterized by the curve with saturation.

The duration of the unstationary stage increases with an increase in the initial concentration of iron(III), which indicates the competition between iron(III) and oxygen for the interaction with the catalyst. The higher the initial concentration of iron(III), the longer the time of achievement of the quasi-stationary concentration of palladium(I), which catalyzes alcohol oxidation with oxygen.

As was already mentioned, palladium black is precipitated quantitatively in the oxidation of alcohol with the tetraaquapalladium(II) complex in an oxygen atmosphere. However, if the system simultaneously contains iron(III), the amount of palladium black formed decreases and up to 40% of palladium remain in a solution. The quantitative data on the composition of the solution during the reaction of alcohol oxidation in the Pd^{II}—Fe^{III}—O_2 system at different temperatures are presented in Table 1.

The comparison of Figs. 1 and 6 shows that a larger amount of oxygen is consumed in the presence of Fe^{III}.

Table 1. Temperature effect on the composition of the solution for alcohol oxidation in the Pd^{II}—Fe^{III}—O_2 system*

Alcohol	T/°C	Reaction time /min	$[Fe^{3+}] \cdot 10^3$/mol L^{-1}		Amount of reacted substance/mol L^{-1}		Product,** $[R^1R^2CO] \cdot 10^2$ /mol L^{-1}
			after unstationary region	at the end of reaction	$[Pd^{2+}] \cdot 10^3$	$[O_2] \cdot 10^3$	
Methanol	50	330	18.8	23.6	2.7	6.5	1.7
	55	225	19.5	25.0	4.3	5.0	1.7
	60	145	19.4	27.5	2.9	6.3	2.0
	65	110	16.2	27.0	2.9	4.8	2.0
Propan-1-ol	50	260	9.2	14.2	3.1	12.7	3.6
	55	125	11.3	14.0	3.3	12.7	3.6
	60	90	6.5	11.5	3.5	15.2	4.3
	65	50	8.8	9.7	3.2	12.2	3.8
Propan-2-ol	50	310	18.3	20.0	0.7	3.8	1.3
	55	290	15.7	19.2	0.5	12.8	3.1
	60	185	18.0	19.7	3.4	12.7	3.4
	65	180	21.9	22.6	5.0	11.9	3.2

* $[Fe^{3+}]_0 = 30 \cdot 10^{-3}$ mol L^{-1}, $[Pd^{2+}]_0 = 5 \cdot 10^{-3}$ mol L^{-1}, $[HClO_4]$ = 0.7 mol L^{-1}, [ROH] = 4 mol L^{-1}.

** Formaldehyde, propanal, and acetone are the oxidation products of methanol, propan-1-ol, and propan-2-ol, respectively.

Table 2. Rates of alcohol oxidation* in the Pd^{II}—Fe^{III}—O_2 system**

Alcohol	w_1	w_2	w_3
	10^{-6} mol L^{-1} s^{-1}		
Methanol	0.6	1.7	0.9
Propan-1-ol	2.2	4.5	2.1
Propan-2-ol	1.3	2.8	1.1

* Designations: w_1 is the rate of carbonyl compound formation in the unstationary region, w_2 is the same in the stationary region, and w_3 is the rate of dioxygen consumption in the stationary region.

** T = 55 °C, $[Pd^{2+}] = 5 \cdot 10^{-3}$ mol L^{-1}, [ROH] = 4 mol L^{-1}, $[HClO_4]$ = 0.65 mol L^{-1}, and $[Fe^{3+}] = 30 \cdot 10^{-3}$ mol L^{-1}.

For example, ~0.5 mL of oxygen are absorbed for 85 min during propan-1-ol oxidation with oxygen in the absence of Fe^{III} (Fig. 1), and the complete reduction of palladium(II) is achieved. In a solution containing iron(III) ions, the volume of oxygen consumed for the same time is 1.9 mL (see Fig. 6). This increase in the amount of reacted oxygen is caused, perhaps, by the involvement of oxygen in two parallel reactions: interaction of iron(II) in reaction (9) and alcohol oxidation in reaction (2).

When oxygen reacts only with iron(II) in reaction (9), the iron(III) concentration remains constant, and the rate of its consumption should equal a half of the maximum rate of carbonyl compound formation in reaction (3). The maximum rates of carbonyl compound formation under different reaction conditions are presented in Table 2. It is seen that the rate of carbonyl compound formation and the rate of oxygen consumption in the stationary region (see Fig. 6) are higher than the rate of carbonyl compound formation in reaction (3). When considering that the formation of the carbonyl compound in the stationary region occurs *via* two reactions, namely, reactions (2) and (3), we can estimate the contribution of oxygen to the oxidation of iron(II)

$$\Pi_{O_2} = \frac{w_3 - (w_2 - w_1)/2}{w_3} 100\%.$$

On the average, the contribution of oxygen to iron(II) oxidation is 40%. Therefore, oxygen is mainly consumed to the catalytic oxidation of alcohol instead of iron(II) ions oxidation.

In the $Pd^{2+}{}_{aq}$—$Fe^{3+}{}_{aq}$—O_2 catalytic system, reaction (8) resulting in the fast formation of palladium black is suppressed. It is most likely that the combined effect of iron(III) and oxygen favors the stabilization of a "small" palladium cluster in which palladium is formally in the intermediate oxidation state and which is the catalyst of alcohol oxidation with oxygen in the presence of the tetraaquapalladium(II) complex.

This work was financially supported by the Nordic Energy Research Foundation (NEFP).

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Received February 17, 2003;
in revised form June 10, 2003