# Kinetics and mechanism of hydrogen peroxide decomposition in the presence of the tetraaquapalladium(11) complex

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Kinetics of hydrogen peroxide decomposition in the presence of the tetraaquapalladium(II) complex in an aqueous solution at 40–70 °C was studied. The reaction rate is the first order with respect to the concentration of both  $Pd^{II}$  and  $H_2O_2$  and the negative first order with respect to perchloric acid. Using free radicals traps, the reaction mechanism was found to differ from the traditional free-radical mechanism known for d-metal aqua ions and proceeds without generation of hydroxyl radicals. The kinetic data obtained suggest a mechanism involving the formation of an intermediate palladium complex with oxygen.

Key words: hydrogen peroxide, tetraaquapalladium(II) complex, catalysis.

Activation of oxygen and hydrogen peroxide by d-metal ions and compounds is a subject of numerous publications.<sup>1-7</sup> Oxidation processes are complicated, their reactions can proceed *via* various routes, and they are of importance for biology and industrial catalysis. Palladium compounds are especially significant due to their high catalytic activity in such processes as the oxidation of unsaturated hydrocarbons,<sup>8,9</sup> the Baeyer–Villiger reaction,<sup>10</sup> and others. In the most part of works, the interaction of palladium compounds with molecular oxygen and hydrogen peroxide was studied in nonaqueous or aqueous-organic media.

We have previously<sup>11,12</sup> found the catalytic activity of the tetraaquapalladium(II) complex in the oxidation of alcohols with molecular oxygen to form hydrogen peroxide as one of the reaction products. The character of interaction of hydrogen peroxide with the tetraaquapalladium(II) complex is poorly studied. Hydrogen peroxide decomposition in an aqueous solution in the presence of palladium(II) in the chloride<sup>13</sup> and carboxide systems<sup>14</sup> is mainly known.

In this work, we studied the reaction of hydrogen peroxide with the tetraaquapalladium(11) complex.

#### **Experimental**

A 30% aqueous solution of  $H_2O_2$  (perhydrol) was used. Special requirements were imposed on purity of the starting solution of hydrogen peroxide and a reaction vessel. The tetraaquapalladium(11) complex was prepared according to an earlier published procedure.<sup>15</sup> The concentration of perchloric acid was determined by acid-base titration.

The kinetics of hydrogen peroxide decomposition in the presence of the tetraaquapalladium(II) complex in a perchloric acid medium was studied in a temperature range of 40–70 °C at the following reactant concentrations: tetraaquapalladium(II) complex,  $(1-10) \cdot 10^{-3}$  mol L<sup>-1</sup>; perchloric acid, 0.3–2.8 mol L<sup>-1</sup>; and hydrogen peroxide, 0.01–0.2 mol L<sup>-1</sup>.

The reaction was studied in a shaken temperature-controlled reactor by monitoring  $O_2$  evolution by the volumetric method. The solution volume was 10 mL in all experiments. The reaction solution was prepared by the addition of a calculated amount of a solution of hydrogen peroxide to a thermostatted solution of the tetraaquapalladium(II) complex. The initial and final concentrations of hydrogen peroxide were measured by iodometric titration. All samples were 10-fold diluted before analysis to decrease the influence of palladium on hydrogen peroxide determination by a procedure used earlier.

In experiments with a tetranitromethane additive, its saturated solution in water was used.

Hydrogen peroxide was decomposed in the presence of benzene under argon. The reaction solution was a heterophase system, which was vigorously stirred by shaking. To decrease a probability of the reaction between benzene and Pd<sup>II</sup> (oxidative coupling), whose contribution becomes substantial at temperatures >65 °C, H<sub>2</sub>O<sub>2</sub> decomposition was carried out at 55 °C. The conversion products of benzene were analyzed by GC-MS (HP 5890 GCD, column HP-5 Crosslinked 5% PH Siloxane 30 m).

The concentrations of palladium(II) were measured spectrophometrically by a known procedure.<sup>16</sup> The concentrations of benzaldehyde and acetophenone were determined by gravimetry (in the form of 2,4-dinitrophenylhydrazones).<sup>17</sup> Formaldehyde was determined spectrophotometrically in the presence of sodium chromotropate.<sup>18</sup>

Palladium black was obtained by the reduction of a solution of the tetraaquapalladium(II) complex with potassium borohydride. Palladium black for hydrogen peroxide decomposition

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was taken in amount corresponding to that of palladium in tetraaquapalladium(II).

## **Results and Discussion**

The catalytic decomposition of hydrogen peroxide in the presence of the tetraaquapalladium(II) complex is described by the reaction

$$2 H_2 O_2 \xrightarrow{\text{Pd}^{\text{II}}} 2 H_2 O + O_2. \tag{1}$$

The kinetic curves of oxygen formation during hydrogen peroxide decomposition are presented in Fig. 1.

Hydrogen peroxide decomposes with a constant rate up to the 60% conversion of  $H_2O_2$  without formation of Pd black. At the conversion >60%, the Pd black begins to form, increasing the formation rate of  $O_2$  due to  $H_2O_2$ decomposition over the Pd black. A special experiment



**Fig. 1.** Kinetic curves of oxygen formation during hydrogen peroxide decomposition at  $[H_2O_2] \cdot 10^2 = 2.2$  (*1*), 4.4 (*2*), 8.8 (*3*), and 17.6 mol L<sup>-1</sup> (*4*);  $[Pd^{II}] = 5 \cdot 10^{-3} \text{ mol } L^{-1}$ ,  $[HCIO_4] = 0.7 \text{ mol } L^{-1}$ , T = 65 °C.



**Fig. 2.** Rate of oxygen formation *vs.* initial concentration of H<sub>2</sub>O<sub>2</sub>; [Pd<sup>II</sup>] =  $5 \cdot 10^{-3}$  mol L<sup>-1</sup>, [HClO<sub>4</sub>] = 0.7 mol L<sup>-1</sup>, T = 65 °C.

showed that the rate of  $H_2O_2$  decomposition in the presence of the Pd black under similar conditions  $([H_2O_2]_0 = 0.088 \text{ mol } L^{-1}, [HClO_4] = 0.7 \text{ mol } L^{-1}, T = 65 \text{ °C}, Pd$ black weight 6 mg) fourfold exceeds the rate of  $H_2O_2$ decomposition in the presence of the tetraaquapalladium(1) complex.

The plots of the rate of reaction (1) vs. concentrations of hydrogen peroxide and palladium( $\Pi$ ) are shown in Figs 2 and 3, respectively.

The linear change in the reaction rate with a change in the hydrogen peroxide and palladium(II) concentrations indicates the first reaction order with respect to these substances.

The decomposition rate of hydrogen peroxide decreases with an increase in the perchloric acid concentration (Fig. 4). The inhibition of the reaction by perchloric acid corresponds to the inverse first order.



Fig. 3. Rate of oxygen formation vs. initial concentration of Pd<sup>II</sup>;  $[H_2O_2]_0 = 8.8 \cdot 10^{-2} \text{ mol } \text{L}^{-1}$ ,  $[\text{HCIO}_4] = 0.7 \text{ mol } \text{L}^{-1}$ ,  $T = 65 \,^{\circ}\text{C}$ .



**Fig. 4.** Rate of oxygen formation *vs.* inverse concentration of perchloric acid;  $[Pd^{II}] = 5 \cdot 10^{-3} \text{ mol } L^{-1}$ ,  $[H_2O_2]_0 = 8.8 \cdot 10^{-2} \text{ mol } L^{-1}$ ,  $T = 65 \circ C$ .

Based on the obtained kinetic data, we can write the following kinetic equation for the rate of catalytic decomposition of  $H_2O_2$ :

$$-d[H_2O_2]/(2d\tau) = d[O_2]/d\tau = k[Pd^{II}][H_2O_2]/[HClO_4], \quad (2)$$

where  $k = (1.1 \pm 0.2) \cdot 10^{-2} \text{ s}^{-1}$  at 65 °C.

It is known<sup>2,19</sup> that the decomposition of hydrogen peroxide with d-metal aqua ions, in particular, the aquairon(III) complex, proceeds *via* the radical mechanism

$$\begin{array}{ccc} H_2O_2 + [Fe(H_2O)_6]^{3+} & \longleftarrow & [Fe(H_2O)_5(H_2O_2)]^{3+} & \longleftarrow \\ & \bigoplus & [Fe(H_2O)_5(HO_2)]^{2+} + H^+, \end{array} \tag{3}$$

$$Fe(HO_2)^{2+} \longrightarrow Fe^{2+} + HO_2^{\cdot}, \qquad (4)$$

$$HO_2^{\cdot} \iff H^+ + O_2^{\cdot -}, \tag{5}$$

$$HO_2 \cdot + Fe^{3+} \longrightarrow O_2 + Fe^{2+} + H^+, \tag{6}$$

$$O_2^{-} + Fe^{3+} \longrightarrow O_2 + Fe^{2+} + H^+,$$
 (7)

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + OH,$$
 (8)

$$Fe^{2+} + OH \longrightarrow Fe^{3+} + OH^-,$$
 (10)

$$OH^- + H^+ \iff H_2 O. \tag{11}$$

In this scheme, reactions involving the ferryl ion  $[FeO]^{2+}$ , whose role remains disputable, are omitted.

Our experiments showed that  $H_2O_2$  decomposition in a strongly acidic medium (at pH 0) in the presence of the aquairon(111) ion is described by the following kinetic equation

$$-d[H_2O_2]/(2d\tau) = d[O_2]/d\tau = k[Fe^{III}][H_2O_2]/[HClO_4], (12)$$

where  $k = (3.9 \pm 0.4) \cdot 10^{-2} \text{ s}^{-1}$  at 65 °C.

Equation (12) agrees well with the known<sup>19</sup> equation of the rate of hydrogen peroxide decomposition with the  $Fe^{III}$  ions.

Comparing kinetic equations (2) and (12) suggests the reaction mechanism for the tetraaquapalladium(II) complex and aquairon(III) ion with rate-determining step (4) to be the same. This is indirectly indicated by an insignificant difference in activation energies. For example, Fe<sup>III</sup>-induced hydrogen peroxide decomposition is characterized<sup>1</sup> by an activation energy of 92.2 kJ mol<sup>-1</sup>. For the system with the tetraaquapalladium(II) complex, the Arrhenius dependence of hydrogen peroxide decomposition found by us in a temperature range of 40–70 °C

$$k = 2.6 \cdot 10^{10} \exp[-81700/(RT)]$$

corresponds to an activation energy of  $81.7 \pm 0.8 \text{ kJ mol}^{-1}$ .

The inhibition effect of protons on the rate of reaction (1) is due, most likely, to the step of acid-base equilibrium preceding the redox decomposition of hydrogen peroxide

$$H_2O_2 + [Pd(H_2O)_4]^{2+} \iff [Pd(H_2O)_3(HO_2)]^+ + H^+.$$
 (13)

Equilibrium (13) can be considered as the substitution of an  $H_2O$  molecule by  $H_2O_2$  in the inner sphere of the starting Pd<sup>II</sup> complex followed by the acid dissociation of the entering ligand.

For the perchloric acid concentration used in our experiments, the influence of acid dissociation of hydrogen peroxide  $(K_a = 10^{-12} \text{ mol L}^{-1} \text{ at } 25 \text{ °C})^2$  on the kinetics of reaction (1) is insignificant.

The introduction into the system of chloride ions, whose coordination produces chloride complexes<sup>20</sup> of the type  $[Pd(H_2O)_{4-n}Cl_n]^{2-n}$  due to the fast ligand substitution in the inner sphere of the tetraaquapalladium(II) complex, substantially inhibits hydrogen peroxide decomposition. In a high excess chloride ions ( $[Pd^{II}] : [Cl^{-1}] > 1 : 10$ ), this introduction completely terminates the reaction. This fact confirms that the redox decomposition of hydrogen peroxide should be preceded by its coordination with the Pd^{II} atom. As known, ligand substitution in the palladium(II) chloride complexes is much slower than that in the case of the labile tetraaquapalladium(II) complex.

The further intramolecular redox decomposition of the peroxide palladium complex (reaction (14)) finally produces molecular decomposition products of hydrogen peroxides: water and  $O_2$ .

$$[PdOOH]^{+} \overbrace{\qquad}^{[PdO_{2}] + H^{+}} 1$$
(14)  
Pd^{+} + HO\_{2}^{\cdot}

Reaction (14) is, most likely, the rate-determining step of hydrogen peroxide decomposition in the presence of the tetraaquapalladium(II) complex

$$w = k_{14}[PdOOH]^{+},$$
  

$$[PdOOH]^{+} = K_{13}[Pd^{2+}_{aq}][H_2O_2]/[H^{+}],$$
  

$$w = k_{14}K_{13}[Pd^{2+}_{aq}][H_2O_2]/[H^{+}].$$
(15)

Thus, the rate constant in Eq. (2) is the product  $k_{14}K_{13}$ .

The process can develop in the subsequent steps *via* two routes: (1) according to the commonly accepted radical mechanism for d-metal aqua ions and (2) *via* the twoelectron transfer mechanism (molecular mechanism). In the case of radical mechanism, hydroxyl and hydroperoxide radicals are generated according to the following reactions:

$$Pd^{2+} + HO_2^{-} \longrightarrow Pd^+ + O_2 + H^+,$$
 (16)

$$\mathsf{Pd}^{+} + \mathsf{H}_2\mathsf{O}_2 \longrightarrow \mathsf{Pd}^{2+} + \mathsf{OH} + \mathsf{OH}^{-}, \tag{17}$$

$$\mathsf{Pd}^{+} + \mathsf{OH} \longrightarrow \mathsf{Pd}^{2+} + \mathsf{OH}^{-}, \tag{18}$$

$$OH^- + H^+ \iff H_2O.$$
 (20)

The interaction of hydrogen peroxide with Pd<sup>II</sup> acetate has previously<sup>14,21,22</sup> been shown to produce a superoxide palladium complex. It can be assumed that a similar compound is also formed under these conditions: complex 1 (superoxide oxygen is coordinated to the Pd<sup>I</sup> atom), which is further oxidized by the tetraaquapalladium(II) complex to form compound 2

$$[PdO_2] + Pd^{2+} \iff [Pd_2(O_2)]^{2+}.$$
 (21)  
1 2

Compound 2 can be considered as a complex of oxygen with a small palladium cluster. The interaction of complex 2 with the second  $H_2O_2$  molecule results in the final products and the regeneration of an oxidized palladium species

$$[Pd_2(O_2)]^{2+} + H_2O_2 \xrightarrow{+2 H^+} 2 Pd^{2+} + 2 H_2O + O_2.$$
(22)

Hydrogen peroxide in the palladium(1) complex decomposes more rapidly than in the presence of a Pd<sup>II</sup>-containing catalyst. Therefore, reaction (21) cannot be slower than reaction (14). Equations (21) and (22) describe the molecular decomposition of hydrogen peroxide.

The proposed mechanisms of hydrogen peroxide decomposition can be discriminated using traps of assumed intermediate species.

Tetranitromethane is  $known^{22}$  to be the trap for a hydroperoxide radical and superoxide radical anion related to the first acid-base equilibrium (reaction (5)). Our experiments showed that hydrogen peroxide decomposition in the presence of tetranitromethane is not accompanied by oxygen evolution until all the nitromethane is consumed. Then oxygen is evolved with the same rate as in the absence of tetranitromethane. Within the time of tetramethane reduction, the amount of decomposed  $H_2O_2$ was twofold smaller than the amount of H<sub>2</sub>O<sub>2</sub> reacted for the same time in the absence of tetranitromethane. The character of tetranitromethane effect cannot be explained unambiguously. First, it is impossible to distinguish kinetically whether tetranitromethane interacts with the free superoxide anion or with that bound in the palladium complex (in complex 1). Second, being a strong electron acceptor, a  $C(NO_2)_4$  molecule reacts efficiently with the low-valence metal species (in this case, Pd<sup>I</sup>). However, the influence of tetranitromethane on the kinetics of reaction (1) can be considered as a fact confirming that reaction (14) is a rate-determining step, because the oxidation of any above-mentioned species with tetranitromethane prevents reactions (16)—(19) or (21), (22), due to which the consumption rate of hydrogen peroxide decreases twofold.

It is important that, if tetranitromethane oxidizes the noncoordinated superoxide anion, then, according to the radical mechanism of hydrogen peroxide decomposition, the 'OH radical should exist inevitably during reaction (1). The use of inhibiting radical acceptors makes it possible to check the radical nature of the process under study. If the decomposition of hydrogen peroxide in the presence of the tetraaquapalladium(II) complex affords the 'OH radical, then the introduction of an aromatic compound should induce aromatic ring hydroxylation to form phenol and other products of deep oxidation,<sup>7,23</sup> for instance,



We found that hydrogen peroxide decomposition with Pd<sup>II</sup> in the presence of benzene does not change the color of the benzene layer. No phenol or diphenyl was found. Benzenesulfonic acid is also an efficient acceptor of an 'OH radical (reaction rate constant is  $1.5 \cdot 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>).<sup>24</sup> The introduction of *p*-toluenesulfonic acid (concentration 0.05 mol L<sup>-1</sup>) does not change the rate of hydrogen peroxide decomposition and the amount of oxygen formed in this reaction. Under similar conditions but in the presence of an aquairon(III) ion, no oxygen is evolved. This indicates different mechanisms of hydrogen peroxide decomposition induced by the aquairon(III) complex and tetraaquapalladium(II) complex.

Data on a possibility of molecular decomposition of hydrogen peroxide catalyzed by the tetraaquapalladium(II) complex were obtained by the study of reaction (1) in the presence of alcohols.

It is known<sup>25</sup> that 'OH radicals generated by hydrogen peroxide decomposition in the presence of transition metals initiate the chain-radical oxidation of alcohols with molecular oxygen.

In our experiments, when an alkylaromatic or aliphatic alcohol was added to the tetraaquapalladium(II) complex—hydrogen peroxide system, oxygen (Fig. 5) and the corresponding aldehyde (Table 1) formed simultaneously.

As can be seen from the data in Table 1, in the case of hydrogen peroxide decomposition with the aquairon(11) complex in the presence of the above-indicated alcohols, no oxygen evolved, and the formation of the corresponding carbonyl compound was not selective because of deep oxidation reactions, which are typical of radical processes.

Oxygen is absent from the decomposition products of hydrogen peroxide because of the fast reaction of molecular oxygen with hydroxyalkyl radicals RC<sup>•</sup>H(OH) formed from an alcohol molecule.

Based on the data in Table 1, the material balance of hydrogen peroxide consumption by the aquapalladium( $\Pi$ ) ion corresponds to the following equation:

$$\Delta[H_2O_2] = 2[O_2] + [R^1R^2CO].$$
(24)



**Fig. 5.** Kinetic curves of oxygen formation in reaction (1) under different conditions: *1*, no alcohol; *2*, in the presence of benzyl alcohol,  $[PhCH_2OH]_0 = 0.16 \text{ mol } L^{-1}$ ; and *3*, in the presence of *sec*-phenylethyl alcohol,  $[PhCH(OH)Me] = 0.07 \text{ mol } L^{-1}$ ;  $[Pd^{2+}_{aq}]_0 = 5 \cdot 10^{-3} \text{ mol } L^{-1}$ ,  $[H_2O_2]_0 = 8.8 \cdot 10^{-2} \text{ mol } L^{-1}$ ,  $[HCIO_4] = 0.7 \text{ mol } L^{-1}$ ,  $T = 65 \,^{\circ}\text{C}$ .

**Table 1.** Formation of carbonyl compounds and oxygen in thetetraaquapalladium(II)complex $-H_2O_2$ -alcohol system\*

Alcohol	Time /min	[O <sub>2</sub> ]	$\Delta[H_2O_2]$	[R <sup>1</sup> R <sup>2</sup> CO]
$(C/\text{mol } L^{-1})$		10 <sup>-3</sup> mol L <sup>-1</sup>		
No alcohol	120	26	52	_
Benzyl (0.08)	120	17	45	8
Benzyl (0.16)	120	8.2	28	12
sec-Phenylethyl (0.07)	120	19	46	5
Benzyl (0.16)**	15	0	61	44
sec-Phenylethyl (0.07)**	15	0	9.2	7.1
Methanol (1)**	30	0	70	10

\*  $[Pd^{2+}_{aq}]_0 = 5 \cdot 10^{-3} \text{ mol } L^{-1}$ ,  $[H_2O_2]_0 = 8.8 \cdot 10^{-2} \text{ mol } L^{-1}$ ,  $[HCIO_4] = 0.7 \text{ mol } L^{-1}$ ,  $T = 65 \circ C$ . \*\* No Pd<sup>II</sup> in the presence of Fe<sup>III</sup>,  $[Fe^{III}]_0 = 5 \cdot 10^{-3} \text{ mol } L^{-1}$ ,  $T = 65 \circ C$ .

It is most likely that conjugated alcohol oxidation during catalytic decomposition of hydrogen peroxide in the presence of the tetraaquapalladium(II) complex can proceed *via* a route different from the radical mechanism. When the initial alcohol concentration increases (see Table 1), the rate of benzaldehyde formation increases and, correspondingly, the rate of hydrogen peroxide decomposition decreases.

We have previously<sup>26</sup> found that benzyl alcohol is not oxidized by the tetraaquapalladium(11) complex without hydrogen peroxide but in the presence of oxygen. This means that an intermediate product of catalytic decomposition of hydrogen peroxide promotes alcohol oxidation, and the oxidation of alcohol and decomposition of  $H_2O_2$  involve the same catalytically active species. The molecular reaction route should be facilitated by coordination of a substrate (alcohol) molecule with an active palladium complex containing oxygen. This complex is, most likely, oxygen palladium complex **2**.

$$[Pd_2O_2]^{2+} + R^1R^2CHOH \xrightarrow{2 H^+} R^1R^2CO + 2 H_2O + 2 Pd^{2+}$$
(25)

Reactions (22) and (25) occur in parallel.

In the tetraaquapalladium(II) complex—hydrogen peroxide—aliphatic alcohol  $C_1$ — $C_3$  system, the rate of oxygen evolution somewhat increased with an increase in the reaction depth. This is caused by the catalytic decomposition of hydrogen peroxide involving both Pd<sup>II</sup> and Pd<sup>0</sup> (the latter is formed by the stoichiometric reaction between the tetraaquapalladium(II) complex and alcohol). Therefore, we studied the kinetic plots presented above by the method of initial rates to the H<sub>2</sub>O<sub>2</sub> conversion <60%.

Perhaps, in this system, the role of hydrogen peroxide is the regeneration of the oxidized palladium species according to the reaction

$$Pd^{0} + H_{2}O_{2} + 2 H^{+} \longrightarrow Pd^{2+} + 2 H_{2}O.$$
 (26)

In this case, the formation rate of a carbonyl compound is equal to the oxidation rate of alcohol with the tetraaquapalladium(II) complex; in the case of methanol (0.5 mol L<sup>-1</sup>), it is  $1.6 \cdot 10^{-7}$  mol L<sup>-1</sup> s<sup>-1</sup> at 65 °C.

Our experiments showed that the rate of carbonyl compound formation is independent of the initial concentration of hydrogen peroxide and is proportional to the concentrations of alcohol and Pd<sup>II</sup>. Since the reaction rate is independent of the hydrogen peroxide concentration, one can assume the formation of a catalytically active palladium complex with oxygen, which is characterized by a limiting concentration in a given interval of changing the hydrogen peroxide concentration. The concentration of the complex depends on the initial concentration of the tetraaquapalladium(II) complex. Since the rate of carbonyl compound formation is independent of the hydrogen peroxide concentration, one can compare the rates of alcohol oxidation with oxygen and with hydrogen peroxide at the same concentrations of Pd<sup>II</sup> and alcohol (Table 2). We have previously<sup>12</sup> found that alcohol oxidation with oxygen in the presence of palladium also contains a region in which the reaction rate is independent of the oxygen pressure (>0.07 MPa).

A comparison of the rates suggests that alcohol oxidation with both oxygen and hydrogen peroxide in the presence of the tetraaquapalladium(II) complex is catalyzed by an intermediate palladium complex of the same nature.

Based on the data obtained, the catalytic decomposition of hydrogen peroxide conjugated with alcohol oxidation can be presented by Scheme 1. 
 Table 2. Oxidation rate of alcohol with oxygen and hydrogen peroxide\*

Alcohol (C/mol L <sup>-1</sup> )	$w \cdot 10^7 / \text{mol } \text{L}^{-1} \text{ s}^{-1}$		
	I**	II***	
Methanol (0.5)	9.0	8.9	
Propan-1-ol (0.2)	9.6	10.0	
Propan-2-ol (0.5)	8.4	9.6	

\*  $[Pd^{2+}_{aq}] = 0.005 \text{ mol } L^{-1}$ ,  $[HClO_4] = 0.7 \text{ mol } L^{-1}$ ,  $T = 65 \,^{\circ}\text{C}$ . \*\* Formation of a carbonyl compound in the oxidation of alcohols with oxygen in the tetraaquapalladium(II) complex—oxygen—alcohol system at  $P_{O2} = 0.1$  MPa (according to published data<sup>12</sup>).

\*\*\* Rate of carbonyl compound formation in alcohol oxidation with hydrogen peroxide ( $[H_2O_2] = 8.8 \cdot 10^{-2} \text{ mol } L^{-1}$ ).

## Scheme 1



In the case of molecular oxygen, the formation of an oxygen palladium complex requires the presence of a lowvalence palladium complex different from palladium black. The formation of this complex involves a reducing agent (Red), which does not react with oxygen under the process conditions. This role can be played by an organic substrate or a transition metal aqua ion (preferentially, a one-electron reducing agent).

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