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CATALYSIS

Liquid-Phase Heterogeneous Oxidation of Hydroxypivalaldehyde with Oxygen in Alkaline Aqueous Solution in the Presence of Supported Palladium Catalyst

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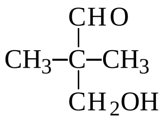
Abstract—The kinetics of a model reaction of hydroxypivalaldehyde oxidation with molecular oxygen in alkaline aqueous solution in the presence of 4% Pd/Al_2O_3 was studied with the aim of searching for promising heterogeneous catalysts for *D*-glucose oxidation.

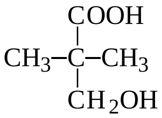
Previously [1–3] we have shown that *D*-glucose can be rapidly and selectively oxidized with molecular oxygen in the presence of sodium nitrite in strongly acidic aqueous solutions. *D*-Gluconic or *D*-glucaric acid is formed, depending on the conditions of catalytic oxidation. Although the oxidation in the presence of sodium nitrite is highly selective, a search for catalysts allowing this process to be performed on the industrial scale is a topical problem. Oxidation of organic compounds on supported heterogeneous catalysts is widely used in practice. The use of these catalysts appreciably increases the oxidation selectivity [4]. It is known [5] that *D*-glucose derivatives can be oxidized to *D*-glucuronic acid in weakly alkaline solutions in the presence of a heterogeneous catalyst, 1.8% Pd/C. However, this process is slow and complex, especially in the stage of isolation of the oxidation products. There are no reports on heterogeneous catalytic oxidation of *D*-glucose to *D*-gluconic and *D*-glucaric acids. Our previous results [1–3, 6] and published data [5, 7] show that the kinetics of catalytic oxidation of *D*-glucose with oxygen is complex. However, the features of chemical transformations of reaction centers in these reactions can be revealed using similar model substrates. To simulate *D*-glucose oxidation, we studied in this work the oxidation of hydroxypivalaldehyde (HPA), which, as *D*-glucose, contains terminal hydroxy and aldehyde groups:



$$CH_3-\overset{\displaystyle CHO}{\underset{\displaystyle CH_2OH}{C}}-CH_3$$

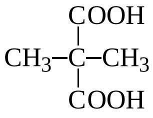
HPA

The presence of hydroxy and aldehyde groups in an HPA molecule suggests that its oxidation is similar to that of *D*-glucose. The absence of "internal" hydroxy groups (which are present in *D*-glucose) in HPA has no effect on the reactivity of the terminal groups being oxidized and does not complicate the kinetic study of the catalytic oxidation. The study of HPA oxidation was also stimulated by the fact that its oxidation products, hydroxypivalic acid (HPAc) and dimethylmalonic acid (DMMA)



$$CH_3-\overset{\displaystyle COOH}{\underset{\displaystyle CH_2OH}{C}}-CH_3$$

HPAc



$$CH_3-\overset{\displaystyle COOH}{\underset{\displaystyle COOH}{C}}-CH_3$$

DMMA

are precursors of plasticizers of a new generation. For HPA oxidation we used the conventional industrial heterogeneous supported catalyst, 4% Pd/Al_2O_3. No data on the kinetics of HPA oxidation with oxygen in the presence of heterogeneous palladium catalysts have been reported. However, palladium catalysts are successfully used in oxidation of various alcohols and aldehydes [8–10].

EXPERIMENTAL

Kinetic experiments on liquid-phase catalytic oxidation of HPA were performed in a temperature-controlled gasometric unit in a closed volume under conditions providing kinetic control of the reaction. The oxidation was performed in alkaline aqueous solutions in a glass reactor magnetically stirred at 3000 rpm. The volume of the liquid phase of the system being

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oxidized was 3 ml. The process was initiated by adding NaOH. The oxidation rate was monitored by the rates of oxygen uptake and accumulation of the oxidation products. The oxidation products were analyzed by GLC on a Tsvet-500 chromatograph equipped with a 5-m steel column, 2.2 mm i.d., packed with 5% OV-17 on Chromaton N-AW-DMCS. The column was heated to 60–150°C at a rate of 10 deg $\min^{-1}$; the vaporizer temperature was 200°C. Nitrogen was the carrier gas.

Since these are no published data on use of 4% Pd/Al_2O_3 supported catalysts in HPA oxidation with molecular oxygen, we optimized the oxidation conditions by the Box-Wilson procedure [11]. We found that the most important parameters affecting the HPA oxidation were the amount of catalyst, temperature, and NaOH concentration. The experimental results were fitted by the equation

$$Y = 13.590 + 0.848X_1 + 1.768X_2 + 2.025X_3, \quad (1)$$

where Y is the volume (ml) of oxygen taken up within 30 min; X_1 is the catalyst concentration (wt %), $X_1 = \omega_{cat} \times 100\%$, where $\omega_{cat} = m_1/m_2$ is the content of heterogeneous catalyst (wt %), m_1 is the weight of 4% Pd/Al_2O_3 (g), and m_2 is the weight of the system being oxidized (g); X_2 is the NaOH concentration (M); and X_3 is temperature (K).

A kinetic study of the catalytic oxidation of HPA was performed under conditions optimized by experimental design. The concentrations of HPA and NaOH were varied from 0.2 to 1.2 and 0 to 1.2 M, respectively; $T = 293–323$ K; $P_{O_2} = 0.21–1$ atm; $\omega_{cat} = (0.1–1.8) \times 10^{-2}$ wt %. The total pressure in the system was maintained constant (1 atm).

As determined by both gas volumetric analysis and GLC, the HPA oxidation occurs in two consecutive steps. The first step is formation of hydroxypivalic acid by the reaction

$$2C(CH_3)_2(CH_2OH)(CHO) + O_2 \xrightarrow[NaOH]{4\%\ Pd/Al_2O_3} 2C(CH_3)_2(CH_2OH)(CHOH). \quad (I)$$

Hydroxypivalic acid is oxidized further to dimethylmalonic acid

$$C(CH_3)_2(COOH)(CH_2OH) + O_2 \xrightarrow[NaOH]{4\%\ Pd/Al_2O_3} C(CH_3)_2(COOH)_2 + H_2O. \quad (II)$$

This step obviously involves formation of dimethylmalonic acid monoaldehyde. However, this reaction is too fast for the aldehyde to be detected in the oxidation products.

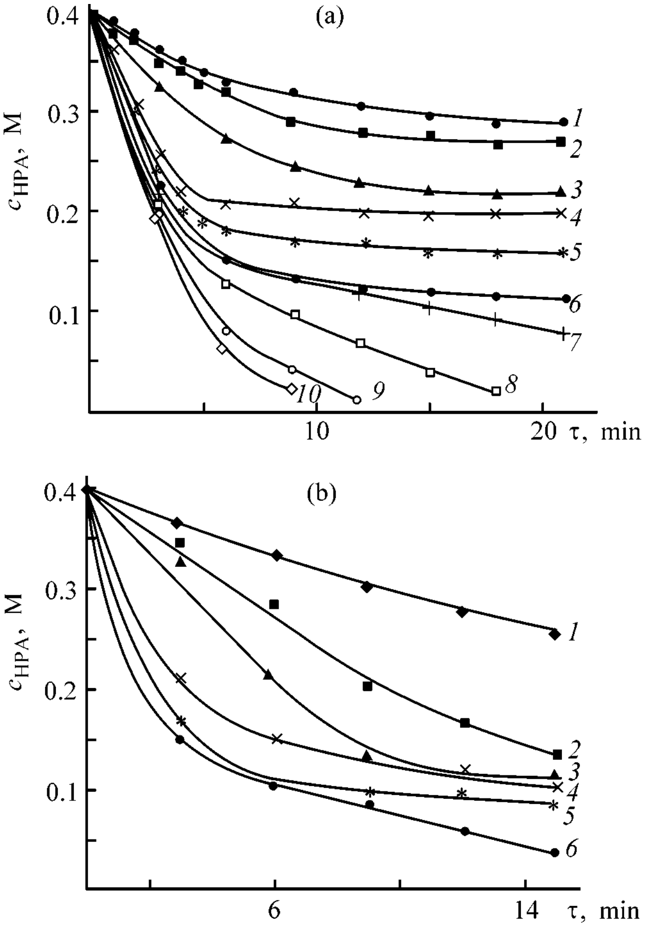

Fig. 1. Kinetic curves of HPA oxidation with oxygen: (a) at weight fraction of the catalyst $\omega_{cat} \times 10^2$: (*1*) 0.1, (*2*) 0.2, (*3*) 0.4, (*4*) 0.6, (*5*) 0.7, (*6*) 0.8, (*7*) 1.0, (*8*) 1.2, (*9*) 1.5, and (*10*) 1.8, $T = 313$ K; (b) (*1*) at 293, (*2*) 303, (*3*) 308, (*4*) 313, (*5*) 318, and (*6*) 323 K, $\omega_{cat} = 1 \times 10^{-2}$. Initial HPA and NaOH concentration 0.4 and 0.7 M, respectively, $p_{O_2} = 1$ atm.

In this work, we studied in detail the kinetics of the first step of HPA oxidation [reaction (I)]. All results of gas-volumetric measurements were recalculated in accordance with the stoichiometry of reaction (I) to the current HPA concentration c_{HPA} (M).

A mathematical treatment of the kinetic data showed that the reaction is first-order with respect to HPA in the whole range of HPA concentrations, i.e., at ω_{cat} = const

$$W = k_1 c_{HPA}, \quad (2)$$

$$k_1 = k_2 p_{O_2}, \quad (3)$$

where W is the rate of HPA oxidation (mol l^{-1} s^{-1}), and k_1 and k_2 are the rate constants of oxidation (s^{-1}).

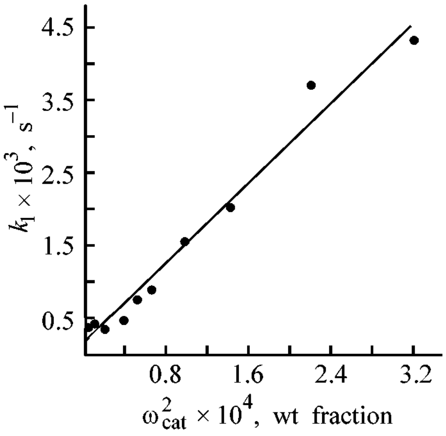

Fig. 2. Rate constant k_1 vs. the initial content of the catalyst, ω_{cat}. T = 313 K and p_{O_2} = 1 atm.

Figures 1a and 1b show how the rate of catalytic oxidation of HPA with oxygen depends on the catalyst content and temperature, respectively. We found that, under the above conditions, HPA oxidation starts at NaOH concentration of 0.3 M and higher. The results of a treatment of the kinetic data on HPA oxidation with oxygen in the presence of 4% Pd/Al_2O_3 are presented in the table.

These data show that at $c_{NaOH} \geq 0.3$ M and p_{O_2} = 1 atm.

$$\frac{\partial k_1}{\partial c_{NaOH}} = 0; \quad \frac{\partial k_1}{\partial \omega_{cat}}, \ \frac{\partial k_1}{\partial T} > 0. \tag{4}$$

Oxidation of HPA with oxygen in the presence of 4% Pd/Al_2O_3 at p_{O_2} = 1 atm

c_{HPA}	c_{NaOH}	$\omega_{cat} \times 10^2$	T, K	$k_1 \times 10^3$, s^{-1}
M				
0.2–0.7	0.7	1	313	1.55
0.4	0.3–1.2	1	313	1.55
0.4	0.7	0.1	313	0.313
0.4	0.7	0.2	313	0.333
0.4	0.7	0.4	313	0.351
0.4	0.7	0.6	313	0.521
0.4	0.7	0.7	313	0.769
0.4	0.7	0.8	313	0.909
0.4	0.7	1.2	313	2.00
0.4	0.7	1.5	313	3.67
0.4	0.7	1.8	313	4.33
0.4	0.7	1	293	0.521
0.4	0.7	1	303	1.39
0.4	0.7	1	308	1.50
0.4	0.7	1	318	1.67
0.4	0.7	1	323	2.22

The dependence of the oxidation rate on the catalyst content is shown in Fig. 2. The results presented in Fig. 2 and the table can be described by the equation

$$k = a + b\omega^2_{cat}, \tag{5}$$

where a and b are constants equal to 0.17×10^{-3} and 1.35×10^{-3} s^{-1}, respectively.

As seen from Eq. (5), the reaction is second-order with respect to the content of 4% Pd/Al_2O_3 supported heterogeneous catalysts.

A mathematical treatment of the temperature dependence of the rate constant of catalytic oxidation at $\omega_{cat} = 1 \times 10^2$, c_{NaOH} = 0.7 M, and p_{O_2} = 1 atm gave the following Arrhenius equation:

$$k_1 = 1.2 \times 10^8 \exp(-66\,510/RT), \tag{6}$$

with activation energy of the process equal to 66 510 J mol^{-1}.

On the basis of the above relationships, the kinetic equation for W (mol l^{-1} s^{-1}) of HPA oxidation to hydroxypivalic acid in the presence of 4% Pd/Al_2O_3 in alkaline aqueous solution ($c_{NaOH} \geq 0.3$ M) can be described by the equation

$$W = kc_{HPA}p_{O_2}\omega^2_{cat}. \tag{7}$$

It is known [12] that liquid-phase oxidation of hydrocarbons with molecular oxygen in the presence of heterogeneous supported catalysts may involve the step of oxygen activation by the reaction

$$S...S + O_2 \longrightarrow [S–S...O_2^{\delta-}], \tag{III}$$

where S is a catalyst.

Since water is a polar electron-donor solvent, it favors charge transfer to an electron-acceptor oxygen molecule when both are sorbed on the catalyst surface [13]:

$$H_2O\overset{\delta^+}{—}S\overset{\delta^-}{—}O_2.$$

As a result, molecular oxygen is intensively activated, with generation of radicals by a heterogeneous reaction, which do not escape into the liquid phase. As a results, nonchain intraspheric or purely heterogeneous selective catalytic oxidation occurs. Clearly, the mechanism of HPA oxidation with molecular oxygen in the presence of 4% Pd/Al_2O_3 is similar, which is confirmed by the experimental dependence (7). The features of HPA oxidation with oxygen in the presence of 4% Pd/Al_2O_3 suggest that the kinetics of *D*-glucose oxidation under similar conditions will be similar. The process will also occur in two steps. In the first step, formation of *D*-gluconic acid is possible, which will be further oxidized to *D*-glucaric acid.

CONCLUSIONS

(1) A kinetic study of liquid-phase oxidation of hydroxypivalaldehyde with molecular oxygen in the presence of a heterogeneous catalyst, 4% Pd/Al_2O_3, showed that the oxidation occurs in two steps. Hydroxypivalic acid formed in the first step is oxidized to dimethylmalonic acid in the second step.

(2) A kinetic equation of hydroxypivalaldehyde oxidation to hydroxypivalic acid was derived. The activation energy of this process was determined.

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