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SELECTIVE OXIDATION OF *L*-SORBOSE IN THE SYNTHESIS OF *L*-ASCORBIC ACID

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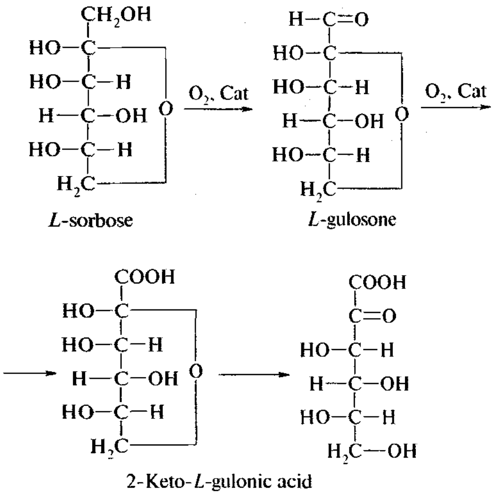
This work is focused on the selective oxidation of *L*-sorbose (I) with the formation of 2-keto-*L*-gulonic acid (II), the latter being a semiproduct in the commercial synthesis of vitamin C (ascorbic acid).

Ascorbic acid is an active participant of many redox processes and enters into the composition of some complex enzymes involved in the process of cell breathing [1]. Vitamin C participates in the carbohydrate and protein metabolism and in many other biochemical processes in the human organism. The problem of selectivity in the direct oxidation of *L*-sorbose is related to a polyfunctional structure of this molecule (hydroxy groups containing active hydrogen atoms) rendering it capable of forming a variety of side products.

The direct oxidation of *L*-sorbose to 2-keto-*L*-gulonic acid is based on the high reactivity of hydrogen atoms in position 1 caused by the carbonyl group activation [2]. The reaction scheme is as follows:



L-sorbose

L-gulosone

2-Keto-*L*-gulonic acid

An analysis of data published on the direct catalytic oxidation of *L*-sorbose to 2-keto-*L*-gulonic acid [3 – 6] showed that the monosaccharide oxidation by oxygen is usually conducted on platinum, palladium, or osmium catalysts, mostly those supported on activated charcoal. The process is performed at normal or elevated (50 – 70°C) temperatures and pressures in neutral or weakly alkaline media. The reaction does not proceed in acid solutions. Strongly alkaline media favor the formation of side products. An optimum pH range is 8 – 10. Alkalizing agents, usually representing the salts of weak organic or mineral acids, are added in several portions in the course of 2-keto-*L*-gulonic acid formation. Under optimum conditions, the process on an Pt/C catalyst (10% Pt) ensures a 50% yield of 2-keto-*L*-gulonic acid at a 70% conversion of *L*-sorbose.

In solving the problem of selectivity in the direct oxidation of *L*-sorbose, considerable effort is directed to the search for new selective modified catalytic systems based on platinum and palladium [7 – 10]. In recent years, this work is concentrated on the preparation and characterization of colloidal catalytic systems involving metal particles with nanometer dimensions (nanoparticles) dispersed in a polymer matrix providing their steric stabilization. The very large surface and small size of these particles account for the high activity of these systems [11]. Below we present some results of investigation of the catalytic properties of a new platinum-containing polymer system, based on super-crosslinked polystyrene (SPS) with Pt nanoparticles, and the kinetics of the selective oxidation of *L*-sorbose on this catalyst.

EXPERIMENTAL METHODS

The catalyst was prepared in the Nesmeyanov Institute of Organoelemental Compounds (Russian Academy of Sciences, Moscow) by impregnating an SPS matrix with an H_2PtCl_6 solution in THF followed by drying for 3 days in a vacuum of 150 kPa. The Pt content in the SPS – Pt catalysts varied within 3 – 6% [12]. Experiments on the oxidation of *L*-sorbose were performed in a specially designed setup [13], which allowed the process to be conducted in a periodic regime with variation of the following parameters: concentrations of sorbose and sodium bicarbonate, amount of catalyst, temperature, oxygen supply rate, and intensity of stirring.

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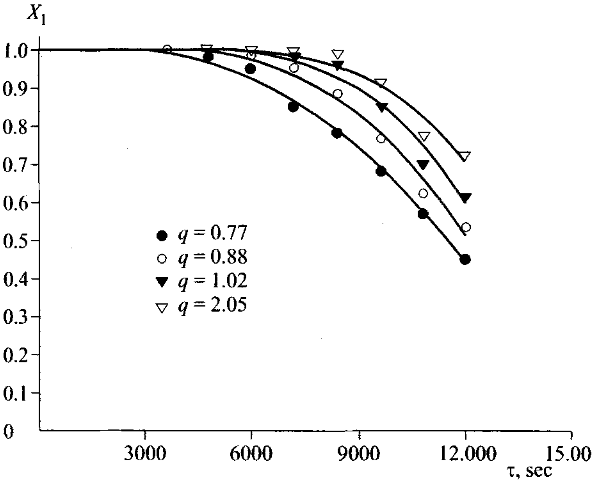

Fig. 1. Experimental plots of sorbose content X_1 versus reaction time τ for various values of catalyst loadings q.

The catalyst and the *L*-sorbose solution of preset concentration were placed into a temperature-controlled reaction cell equipped with stirrer and reflux cooler. The supply rate of the oxygen-containing gas was monitored with a rotameter. An equimolar amount of the alkalizing agent ($NaHCO_3$) could be added to the mixture in a single dose or by portions so as to maintain a certain pH level. Intensive stirring of the reaction mixture under a periodic reactor operation regime allowed the process to be conducted in the kinetic domain. The course of the process was monitored by periodically taking samples of the liquid phase for analysis. Upon termination of the experiment, the catalyst was separated by filtration. The filtrate was analyzed to determine the amounts of unreacted *L*-sorbose and the target product (2-keto-*L*-gulonic acid).

The residual monosaccharide was determined by gas chromatography (GC) on a Chrom-5 instrument equipped with a plasma-ionization detector and a glass column filled with 5% SE-30 on Chromaton N-AW. The GC analyses were performed in an isothermal regime. The amount of 2-keto-*L*-gulonic acid in the mixture was determined by the classical iodometric technique as described by Heyns [14].

RESULTS AND DISCUSSION

The kinetics of the selective oxidation of *L*-sorbose on the SPS – Pt catalytic system was studied under the conditions of variable catalyst loading $q = C_0/C_{cat}$, where C_0 is the initial sorbose concentration and C_{cat} is the catalyst content. The experimental process conditions were as follows: temperature, 70°C; oxygen-containing gas flow rate, 20×10^{-6} m^3/sec; single-dose alkalizing agent charging; stirring rate, 1000 rpm; $q = 0.77 - 2.05$ g/g. As seen from the plots of sorbose conversion versus reaction time (Fig. 1), the higher the catalyst loading q, the longer the reaction time.

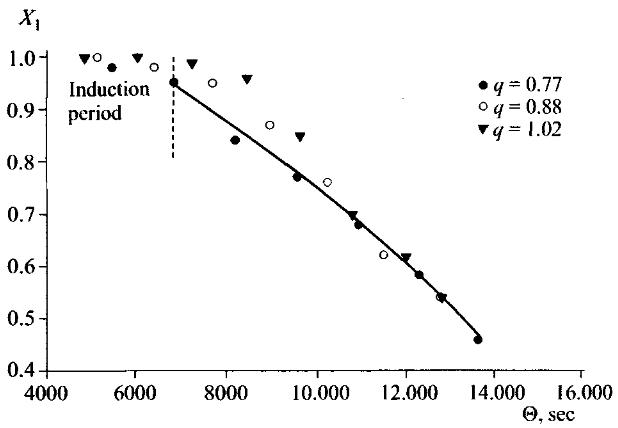

Fig. 2. Plot of the sorbose content X_1 versus reduced reaction time $\Theta = \tau/q^{0.5}$ (τ is the current time, q is the catalyst loading). Symbols show experimental data; the solid curve is calculated by Eq. (1).

Upon processing of the primary experimental data, we determined the time $\tau_{0.3}$ required for a 30% conversion of *L*-sorbose as a function of the catalyst loading. This dependence can be described by the formula

$$\tau_{0.3} \sim q^n \ (n = 0.5).$$

According to the results of GC analyses of the final catalytical reaction mixture, the process was highly selective and the amount of side products was extremely small. Based on these data, we may describe the process by a simple scheme

$$\mathrm{I} \xrightarrow{k_1} \mathrm{II},$$

where I is *L*-sorbose and II is 2-keto-*L*-gulonic acid.

In order to describe the whole body of experimental data obtained for various C_6 and C_{cat} values by a common family of curves, we introduce an independent variable (reduced time) $\Theta = \tau/q^n$, where τ is the time, q is the catalyst loading, and $n = 0.5$. Figure 2 shows the experimental data plotted in the coordinates of X_1 versus Θ, where X_1 is the current relative content of *L*-sorbose.

We have constructed a mathematical model for the process of *L*- sorbose oxidation on the SPS – Pt catalyst using an explicit integral method [15]. Of the numerous possible mathematical models provided by this approach, we have selected the following one that adequately describes the experimental data:

$$W = -kX_1^{-0.5}. \qquad (1)$$

Figure 2 shows that the experimental points well fit to the curve representing Eq. (1).

The initial portion of the plot in Fig. 2 corresponds to an induction period. The presence of this stage apparently corresponds to a nonstationary state of the catalyst surface and reflects additional processes leading to the formation of active centers. This phenomenon is well known in catalytical processes [16].

In order to gain additional information on the laws of *L*-sorbose oxidation on the SPS – Pt catalytic system, we have studied the effect of temperature on this process. The experiments were performed with an aqueous solution of *L*-sorbose with a concentration of 0.119 mole/liter oxidized using a system with $q = 0.88$ g/g. The temperature was varied from 60 to 80°C. Analysis of the experimental data showed that the rate of *L*- sorbose oxidation increased with the temperature. However, conducting the process at temperatures above 70°C led to a decrease in selectivity. This may be related either to the formation of 2-keto-*L*-gulonic acid peroxidation products as a result of increasing process rate or to the thermal decomposition of *L*-sorbose (known to be a rather unstable compound).

Using the results of experiments performed at various temperatures and the calculations according to model (1), we have constructed the Arrhenius plot of $\ln k$ versus $1/T$ and determined the apparent activation energy $E_{app} = 36$ kJ/mole, which is greater than the value for the Pt/SiO_2 system (28 kJ/mole) [13]. However, the reduced oxidation rate for the SPS – Pt catalyst (determined as mole[II]/(g Pt × mole[I])) was 1.2×10^{-3}, which is twice that of the Pt/SiO_2 system (0.6×10^{-3}) [13]. Apparently, the polymer catalyst provides for a greater number of active centers involved in the oxidation reaction.

In order to determine the optimum process conditions, we varied the following parameters: (i) catalyst content ($C_{cat} = 20 - 75$ g/liter); (ii) initial sorbose concentration ($C_0 = 0.22 - 0.44$ mole/liter); (iii) alkalizing component concentration ($NaHCO_3$, $C_{alk} = 0.22 - 0.44$ M); process temperature ($T = 60 - 80$°C); oxygen supply rate ($V_0 = (6 - 14) \times 10^{-6}$ m^3/sec); stirring rate ($S = 200 - 1000$ rpm).

Maximum selectivity of the oxidation reaction (98%) was observed for $C_{cat} = 63$ g/liter, $C_0 = 0.36$ mole/liter, $C_{alk} = 0.36$ mole/liter, $T = 70$°C, $V_0 = 14 \times 10^{-6}$ m^3/sec, and stirring grate $S = 1000$ rpm for the periodic process with continuous supply of the alkalizing agent.

Thus, the catalyst based on super-crosslinked polystyrene containing Pt nanoparticles (SPS – Pt) exhibits a high catalytic activity and ensures maximum selectivity in the direct oxidation of *L*-sorbose. An analysis of the kinetics of *L*-sorbose oxidation allowed us to select a mathematical model satisfactorily describing the experimental data.

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