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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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CHEMISTRY

S. R. SERTIENKO and N. Ya. CHERNYAK

KINETICS AND MECHANISM OF THE LIQUID-PHASE OXIDATION OF DIBENZYL AND DICYCLOHEXYLETHANE

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The oxidation of hydrocarbons was carried out in a closed glass circulation apparatus with oxygen bubbling through the liquid product. The absorption of oxygen during the reaction was monitored from the pressure drop in the system, and at definite time intervals a measured amount of oxygen was added to the system up to the initial pressure. After completion of the experiment, the product from the reaction vessel was subjected to analysis for the content of the initial hydrocarbon in it (by adsorption separation on silica gel), as well as of peroxides, acids, esters, and alcohols by the method of potentiometric titration (^{1}), and of benzaldehyde by the polarographic method (^{2}).

Fig. 1. A –Kinetics of oxygen absorption during the oxidation of dibenzyl (solid curves) and dicyclohexylethane (dashed curves). **B** –Semilogarithmic anamorphosis of the oxygen-absorption curves during the oxidation of dibenzyl

The oxidation of dibenzyl was carried out at temperatures of 110, 130, 140, and 150° (Fig. 1). The S-shaped course of the curves and the fact that the semilogarithmic anamorphoses of their initial portions are straight lines indicate that the reaction proceeds by a chain mechanism with pronounced branching (^{3}). The activation energy for the onset of the oxidation process is 29 kcal/mol. The curves shown in Figs. 2 and 3 for the consumption of the initial substances and the accumulation of intermediate and final products of dibenzyl oxidation at 110 and 140° indicate

about a qualitative analogy in the course of the process at both temperatures.

[Figure 2 graph]

Fig. 2. Kinetics of consumption of the starting materials and accumulation of intermediate oxidation products of dibenzyl (solid curves) and dicyclohexylethane (dotted curves) at 110°.

In the initial stage of oxidation, practically only peroxides are detected among the reaction products; moreover, the curves for their formation practically coincide with the curves for oxygen uptake and dibenzyl consumption, which is direct evidence for the formation of dibenzyl monohydroperoxide. Other oxidation products are formed as a result of the decomposition of this hydroperoxide and subsequent oxidation of the resulting products, as shown by the following experiment. Oxidation of dibenzyl was carried out until the maximum amount of peroxides had formed (over 3 hours), after which the oxygen in the system was replaced by nitrogen, and heating was continued in a nitrogen atmosphere for 3 hours. Analysis of the reaction mixture obtained in this experiment showed the absence of peroxides, owing to their decomposition, and a corresponding increase in benzaldehyde and alcohol. The acid content remained at the same level as after 3 hours of oxidation, since there was no oxygen in the system necessary for the further oxidation of the benzaldehyde and alcohol formed during peroxide decomposition.

After the slowing of oxygen uptake, its further uptake proceeds at a constant, very low rate, an order of magnitude lower than the maximum. Addition to the reaction mixture at this stage of oxidation of a fresh portion of dibenzyl up to its initial amount, i.e., up to 10 g, did not increase the rate of oxygen uptake: over 110 hours oxygen was absorbed uniformly at a rate of ~10 ml/hour; 4.5 g of dibenzyl was consumed in this process. From these experiments it follows, first, that inhibition of oxidation is caused not by consumption of the initial dibenzyl, but by formation, in the course of the reaction, of substances that inhibit the oxidation reaction; and, second, that after the appearance of these substances among the oxidation products, the subsequent reaction proceeds by a mechanism different from that in the initial period of oxidation. The addition to the initial dibenzyl of small amounts of resinous substances formed in previous experiments on its oxidation caused strong inhibition of the oxidation reaction (Fig. 4).

[Figure 3 graph]

Fig. 3. Kinetics of consumption of the starting materials and accumulation of intermediate oxidation products of dibenzyl (solid curves) and dicyclohexylethane (dotted curves) at 140°.

In addition to experiments with additions of resin, a series of experiments was carried out with additions of various intermediate products of the oxidation reaction (Fig. 4). Additions of benzyl alcohol and benzaldehyde before the start of the reaction retard the oxidation of dibenzyl, whereas their addition to an ongoing oxidation process has no appreciable effect on the course of the reaction. Addition of hydroperoxide before the start of the reaction greatly accelerates it. This accelerating effect of the hydroperoxide addition is also manifested when

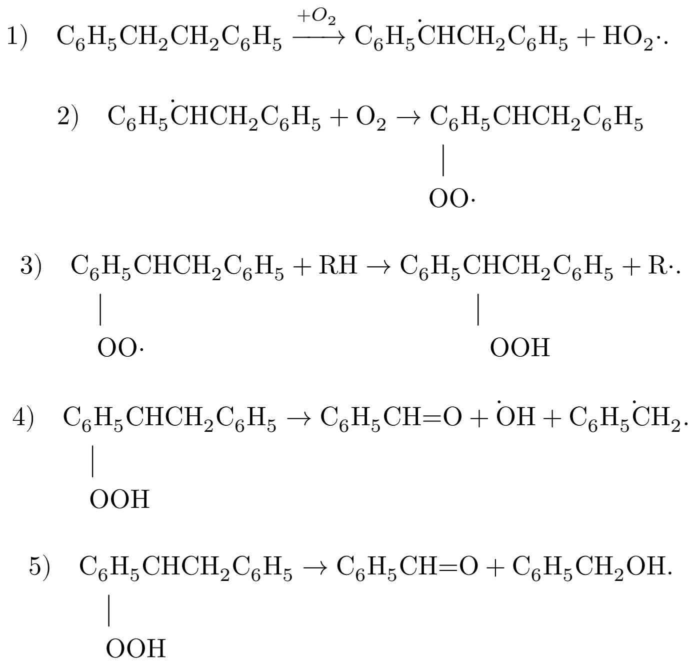
Fig. 4

Figure 2: Fig. 4

it is added at the stage of an already strongly inhibited oxidation reaction. The latter circumstance indicates that it is precisely the hydroperoxide that determines the autocatalytic character of the oxidation of dibenzyl in its first stage, and that the inhibitor formed in the course of the reaction acts on peroxide radicals in such a way that hydroperoxide cannot be formed. Consequently, after decomposition of the hydroperoxide already present by this time in the reaction products, the possibility of chain branching is lost, and therefore in the next stage the reaction proceeds by an unbranched path at a constant rate, substantially lower than the rate of the branched-chain reaction.

Fig. 4. Effect of additions of intermediate products on oxygen absorption during oxidation of dibenzyl at 140°: **1**—without addition, **2**—0.025 g of resin before the start of the reaction, **3**—0.09 g of resin before the start, **4**—1 g of resin before the start, **5**—10 mmol of C_6H_5CHO before the start, **6**—5.6 mmol of $C_6H_5CH_2OH$ before the start, **7**—6 mmol of C_6H_5CHO 3 hours after the start, **8**—5.6 mmol of $C_6H_5CH_2OH$ 3 hours after the start, **9**—3.5 mmol of hydroperoxide before the start and 1.3 mmol after the reaction had slowed down (the part of the curve marked ×).

On the basis of the experimental data presented, the following scheme of the radical-chain mechanism of dibenzyl oxidation may be proposed:



$$1)\quad C_6H_5CH_2CH_2C_6H_5 \xrightarrow{+O_2} C_6H_5\dot{C}HCH_2C_6H_5 + HO_2\cdot.$$

$$2)\quad C_6H_5\dot{C}HCH_2C_6H_5 + O_2 \rightarrow C_6H_5\underset{\underset{OO\cdot}{|}}{C}HCH_2C_6H_5$$

$$3)\quad C_6H_5\underset{\underset{OO\cdot}{|}}{C}HCH_2C_6H_5 + RH \rightarrow C_6H_5\underset{\underset{OOH}{|}}{C}HCH_2C_6H_5 + R\cdot.$$

$$4)\quad C_6H_5\underset{\underset{OOH}{|}}{C}HCH_2C_6H_5 \rightarrow C_6H_5CH{=}O + \dot{O}H + C_6H_5\dot{C}H_2.$$

$$5)\quad C_6H_5\underset{\underset{OOH}{|}}{C}HCH_2C_6H_5 \rightarrow C_6H_5CH{=}O + C_6H_5CH_2OH.$$

$$\mathrm{C_6H_5CH{=}O} \xrightarrow{+O_2}$$
$$\mathrm{C_6H_5COOH};\ \text{and inhibitor.}$$
$$\mathrm{C_6H_5CH_2OH} \xrightarrow{+O_2}$$

$$6)\ \mathrm{C_6H_5CHCH_2C_6H_5} + \text{inhibitor} \rightarrow \text{products} + \mathrm{R_1^{\bullet}O^{\bullet}}$$
$$\dot{\mathrm{O}}\mathrm{O^{\bullet}}$$

$$7)\ \mathrm{R_1O^{\bullet}} + \mathrm{C_6H_5CH_2CH_2C_6H_5} \rightarrow \mathrm{R_1OH} + \mathrm{C_6H_5\dot{C}HCH_2C_6H_5}.$$

$$8)\ \mathrm{2RO_2^{\bullet}} \rightarrow \text{termination.}$$

The oxidation of dicyclohexylethane was carried out at temperatures of 110, 120, 130, and 140°. The reaction is likewise self-accelerating, developing in the initial period according to an exponential law (see Fig. 1). The activation energy for the onset of oxidation is 30.7 kcal/mole. The rate of oxygen absorption after reaching a maximum gradually decreases. It can be increased somewhat by adding a fresh portion of the starting hydrocarbon to the reactor, but even in this case the rate is almost 9 times lower than the maximum. This indicates that the slowing of oxygen absorption is caused not so much by consumption of the starting hydrocarbon as by the appearance, among the reaction products, of substances that inhibit oxidation. However, addition to the starting hydrocarbon of 0.5 g of the oxidation products of dicyclohexylethane that are insoluble in it (and also in petroleum ether) had practically no effect on the kinetics of oxygen absorption; i.e., these oxidation products are not inhibitors of the reaction. In experiments in which 0.1 g of resin obtained in the oxidation of dibenzyl, and serving as an inhibitor of the oxidation of the latter, was added to the starting hydrocarbon, a 5-hour induction period appeared, after which oxidation proceeded at the usual rate. The dark coloration of dicyclohexylethane imparted to it by the added resin gradually disappeared, which is direct evidence of the gradual consumption of the added resin during the induction period.

The small amount of peroxide compounds, compared with that formed in the oxidation of dibenzyl, can apparently be explained by the lower thermal stability of dicyclohexylethane hydroperoxide as compared with dibenzyl hydroperoxide.

The higher oxidation rate of dicyclohexylethane as compared with dibenzyl, at the same activation energy for the onset of the process, can apparently also be explained by the fact that, in the oxidation of dicyclohexylethane, the reaction rate increases because of the lower stability of the hydroperoxide.

Institute of Petroleum
Academy of Sciences of the USSR

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