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Reaction scheme: oxidation of *p*-dicyclohexylbenzene to mono- and dihydroperoxides

Figure 1: Reaction scheme: oxidation of *p*-dicyclohexylbenzene to mono- and dihydroperoxides

Fig. 1. Autooxidation of *p*-dicyclohexylbenzene in the presence of 6 mg/mol manganese resinate and 2 mg/mol soda at 110° (1, 2) and at 130° (3, 4). 1, 3—hydroperoxide concentration; 2, 4—oxidation depth according to absorbed oxygen

Figure 2: Fig. 1. Autooxidation of *p*-dicyclohexylbenzene in the presence of 6 mg/mol manganese resinate and 2 mg/mol soda at 110° (1, 2) and at 130° (3, 4). 1, 3—hydroperoxide concentration; 2, 4—oxidation depth according to absorbed oxygen

Abstract

Full Text

CHEMISTRY

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AUTOOXIDATION OF *p*-DICYCLOHEXYLBENZENE

(Presented by Academician A. V. Topchiev, June 29, 1962)

Recently, the liquid-phase autooxidation of dialkylbenzenes has been attracting ever increasing attention from researchers ([1]). We chose *p*-dicyclohexylbenzene (I) as the object of our investigations. This hydrocarbon is crystalline and can be obtained in a high degree of purity, which is very important in studying the kinetics of autooxidation of dialkylbenzenes and in clarifying the question of the influence of alkyl groups on the reactivity of the hydrocarbon.

It has been shown that (I) is very readily oxidized by oxygen in the presence of manganese resinate alone or with certain alkaline additives to mono- and dihydroperoxide. The reaction is consecutive and may be represented by the following scheme:

$$\text{(I)} \xrightarrow{O_2} \text{(II, OOH)} \xrightarrow{O_2} \text{(III, OOH, OOH)}$$

Fig. 1. Autooxidation of *p*-dicyclohexylbenzene in the presence of 6 mg/mol manganese resinate and 2 mg/mol soda at 110° (1, 2) and at 130° (3, 4). 1, 3—hydroperoxide concentration; 2, 4—oxidation depth according to absorbed oxygen.

The attack by oxygen is directed at the tertiary carbon atoms of the cyclohexane ring. The relative amounts of mono- and dihydroperoxides depend strongly on the depth of oxidation. Thus, at an oxidation depth of I of 40%, the weight ratio of II to III is 8 : 1. If the data obtained for I are compared with those for the previously studied cyclohexylbenzene ([2]), it may be concluded that introduction of a cyclohexyl group into the *p*-position of cyclohexylbenzene increases the rate of oxidation of I almost twofold in comparison with cyclohexylbenzene. As shown in Fig. 1, with an increase in temperature from 110 to 130°, the oxidation rate and the depth of conversion of I increase; however, the hydroperoxide content in the reaction mass drops sharply, since hydroperoxides II and III, like cyclohexylbenzene hydroperoxide, are thermally not very stable and decompose vigorously at temperatures above 150°. At 200°, the absorption of oxygen by *p*-dicyclohexylbenzene also proceeds vigorously, but the main oxidation product proves to be *p*-cyclohexylbenzoic acid.

Experimental Part

p-Dicyclohexylbenzene (I) was obtained by cycloalkylation of cyclohexylbenzene with cyclohexanol in the presence of concentrated sulfuric acid in molar ratios equal to 3 : 1 : 3, at a temperature of 20-25°

(best conditions) in a yield of 70% of the theoretical; after recrystallization from ethyl alcohol it had m.p. 101-102°.

Autoxidation of I was carried out with oxygen until the maximum concentration of hydroperoxide in the reaction mixture was formed, or until its complete disappearance, in the apparatus shown in Fig. 2, in the following manner.

Table 1

p-Dicyclohexylbenzene, mol | Manganese resinate, mg/mol | Alkaline additive, 2 g/mol | Temp., °C $±$1° | Rate of oxygen absorption, l/mol · h | Max. amount of hydroperoxide in the reaction mixture, % | Degree of oxidation of dicyclohexylbenzene, by oxygen | Degree of oxidation of dicyclohexylbenzene, by hydrocarbon |

|—:|—:|—|—:|—:|—:|—:|—:| | 0.1 | 6 | Na_2CO_3 | 110 | 1.44 | 56 | 62 | 66 | | 0.1 | 6 | Na_2CO_3 | 130 | 4.76 | 36 | 83 | 65 | | 0.1 | 6 | NaOH | 110 | 1.07 | 51 | 62 | 59 | | 0.2 | 6* | Na_2CO_3 | 110 | 2.01 | 40 | 40 | 37 | | 0.1 | 6 | $(NH_4)_2CO_3$ | 110 | 1.44 | 25 | 25 | 32 | | 0.1 | 6 | —| 110 | 1.50 | 45 | 63 | 60 | | 0.2 | 6 | —| 200 | 3.40 | —| 90 | 60 |

* In the experiment, 2% dicyclohexylbenzene hydroperoxide was added to the manganese resinate.

The hydrocarbon (1) was placed in the reactor flask, the system was tested for tightness, manganese resinate was introduced either alone or together with an alkaline additive, the reactor was placed in a thermostat, the temperature of which was maintained to an accuracy of $±$1-2° with the aid of a contact

Fig. 2. Apparatus for autoxidation: 1 —reactor flask, 2 —thermostat, 3 — sampling device, 4 —hollow stirrer, 5 —absorbers with calcium chloride and activated charcoal, 6 —graduated gasometers, 7 —manometer

Figure 3: Fig. 2. Apparatus for autoxidation: 1 —reactor flask, 2 —thermostat, 3 —sampling device, 4 —hollow stirrer, 5 —absorbers with calcium chloride and activated charcoal, 6 —graduated gasometers, 7 —manometer

thermometer, the stirrer (4) was switched on, and the time at which oxidation began, the pressure, and the volume of oxygen in the gasometer (6) were recorded. With the aid of the sampling device (3), every 2 h a sample was withdrawn, in which the hydroperoxide content was determined iodometrically.

Fig. 2. Apparatus for autoxidation: 1 —reactor flask, 2 —thermostat, 3 —sampling device, 4 —hollow stirrer, 5 —absorbers with calcium chloride and activated charcoal, 6 —graduated gasometers, 7 —manometer.

The volume of absorbed oxygen was measured every hour, and from the volume of oxygen reduced to normal conditions the percentage content of hydroperoxide in the reaction mixture was also calculated and compared with the data of iodometric analysis. Usually, in the first hours of oxidation, the amounts of hydroperoxide in the reaction mixture determined iodometrically and calculated from the absorbed oxygen coincided, but with time they began to diverge, which indicated the onset of decomposition of the hydroperoxide. In the first hours of oxidation the degree of oxidation calculated from oxygen and from hydrocarbon also coincides. With increasing degree of oxidation, and especially with increasing temperature, the difference between the degree of oxidation calculated from oxygen and that calculated from hydrocarbon becomes increasingly noticeable. All this serves as evidence that,

that the primary products of the interaction of the hydrocarbon with oxygen are hydroperoxides, which under certain conditions, upon decomposition, are converted into the most diverse products capable of further oxidation. The most characteristic experiments are summarized in Table 1.

Isolation of mono- and dihydroperoxides of *n*-dicyclohexylbenzene (I). 52 g of 40% hydroperoxide of *n*-dicyclohexylbenzene, obtained by oxidation of I, was dissolved in alcohol with heating; the mixture was filtered and cooled. The crystallized hydrocarbon I was filtered off and weighed. In this way 33 g of recovered I was obtained. From this amount the depth of oxidation with respect to the hydrocarbon was calculated. The remaining alcoholic solution of hydroperoxide, after separation of hydrocarbon I, was distilled in vacuo. The alcohol was distilled off, and the resulting hydroperoxide concentrate (86-89%) was dissolved in petroleum ether and cooled. The precipitated dihydroperoxide of *n*-dicyclohexylbenzene (III) (5 g) was recrystallized from petroleum ether. The resulting preparation of dihydroperoxide (III) (1.2 g) has m.p. 131-132°, 95-96% purity; it is a white powder, readily soluble in alcohol, ether, and acetic

acid, and reacts vigorously with concentrated sulfuric acid, being converted into hydroquinone.

From the filtrate after separation of dihydroperoxide (III) and evaporation of most of the petroleum ether, on standing, 12.3 g (102.5%) of monohydroperoxide of *n*-dicyclohexylbenzene (II) separated; on recrystallization from petroleum ether a preparation of 94-95% purity with m.p. 85-86° was obtained. Upon decomposition of this monohydroperoxide with concentrated H_2SO_4 in acetic acid by heating for 6 h at 50-60°, *n*-cyclohexylphenol was obtained in 75% yield, m.p. 127-128° [3], and cyclohexanone, characterized through its 2,4-dinitrophenylhydrazone [4].

From the oxidation products of *n*-dicyclohexylbenzene in the presence of manganese resinate at 200°, *n*-cyclohexylbenzoic acid was isolated in 20% yield, with m.p. 190-191°. Its methyl ester melts at 44-45°, which corresponds to the literature data [5].

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Note: Figure translations are in progress. See original paper for figures.