STUDY OF CYCLOHEXYLBENZENE LIQUID-PHASE OXIDATION PRODUCTS COMPOSITION

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The paper examines the contents of products of liquid-phase oxidation of cyclohexylbenzene. The study proves the existence of tertiary and secondary hydroperoxide in the oxidation products of cyclohexylbenzene. The hydroperoxides were determined directly by NMR^{1}H-spectroscopy and indirectly by their products of reduction to ketones and alcohols. By comparing integral intensities of tertiary and secondary cyclohexylbenzene hydroperoxide proton signals, we can assume that the content of the latter is approximately 15-20% of the total hydroperoxide content present in the cyclohexylbenzene oxidation products. The general scheme of oxidative transformations of cyclohexylbenzene is compiled based on the experimental data obtained and the existing knowledge of the essence of liquid-phase oxidation of alkylsubstituted aromatic and cycloaliphatic hydrocarbons. The study shows a considerable decrease in selectivity of oxidation process when cyclohexylbenzene conversion increases up to 40-50%.

Introduction

Phenol and cyclohexanone are large-volume products of basic organic and petrochemical synthesis, demand for which increases every year due to increase in production of various polymeric materials. At present, the main consumers of phenol are the producers of plastics, synthetic fibers, epoxy resins, alkylphenols, synthetic dyes, additives for fuels and oils, electrical insulating varnishes, and plasticizers. Besides, phenol is used to produce medicine, surfactants, antiseptics, pesticides and perfume [1]. Cyclohexanone is widely used in production of adipic acid, caprolactam (as an intermediate). It is also used as a solvent for resins, fats, oils, waxes, acetates, and nitrates [2].

The main industrial methods of phenol and cyclohexanone production are respective processes of aerobic liquid-phase oxidation of cumene [3, 4] and cyclohexane [2]. Cyclohexane oxidation is simple and has only one stage. At the same time, despite the noted advantages, it has a number of significant drawbacks. For example, during cyclohexane oxidation

(temperature 120-160 °C, air pressure 1-2 MPa, with cobalt-containing catalysts) cyclohexane conversion does not exceed 3-5%, target product formation selectivity does not exceed 70-75%, and cyclohexanone/cyclohexanol ratio in the obtained oxidate is close to 1:1 [5]. The usual high costs of disposal of by-products, separation, and purification of cyclohexanone significantly reduce the profitability of this production.

An alternative to the separate methods of phenol and cyclohexanone production is their joint synthesis based on liquid-phase initiated oxidation of cyclohexylbenzene (CHB) to hydroperoxide (HP). There are numerous related studies all over the world, which shows that the development of a new method of obtaining phenol and cyclohexanone [6-10] is both important and promising.

The presence of tertiary and a large number of secondary C-H bonds in the CHB molecule suggests that it is possible to form two types of HP as well as a number of oxygen-containing compounds during the oxidation of CHB. There is limited information on the nature and composition of the products formed during oxidation of CHB. At the same time, they largely determine the further possibility of oxidative transformations of CHB in chemical engineering. Thus, it is important and relevant nowadays to study the composition of CHB liquid-phase oxidation products.

Study

Although the liquid-phase oxidation of CHB into HP proceeds with high selectivity (95-98%) of oxygen utilization, the acid decomposition of CHBHP contained in oxidation products results in phenol yield slightly lower (by 15-20%) than theoretically possible. Changes of oxidation mode of CHB to HP do not give a way to increase phenol yield at the final stage of the process. At the same time, the acid decomposition of synthetically produced *tert*-cyclohexylbenzene hydroperoxide (*tert*-CHBHP) brings specific phenol yield. The facts presented above indisputably testify to the presence of two types of HP, tertiary and secondary, in the oxidation products of CHB.

To verify this theory, we studied the nature of the primary oxidation products of CHB (I) as well as their products of reduction to ketones and alcohols.

Tertiary (II) and secondary (III) CHBHP content was determined directly in the products of CHB oxidation by NMR[1]H-spectroscopy. It was alternatively determined indirectly by products of their reduction to ketones and alcohols by IR-spectroscopy using a number of substances of known structure obtained by counter-synthesis.

It was found that the spectrum of NMR [1]H-products of the selective oxidation of CHB to HP differs from the spectrum of *tert*-CHBHP (II) obtained by oxidation of 1-phenylcyclohexanol (V) with hydrogen peroxide. The difference is the existence of a 3.75 ppm signal on the spectrum of CHB oxidation products, which is usual for the CHO proton of the secondary HP (*sec*-HP). By comparing integral intensities of tertiary and secondary CHBHP proton signals, we can assume that the content of the *sec*-CHBHP (III) is approximately 15-20% of the total HP in the CHB oxidation products.

We obtained further confirmation of the HP structure arising from the oxidation of CHB from the analysis of ketones and alcohols formed by the reduction of HPs by $FeSO_4$ [11] or hydrogen in the presence of Pd/Al_2O_3 [12] (Fig. 1).
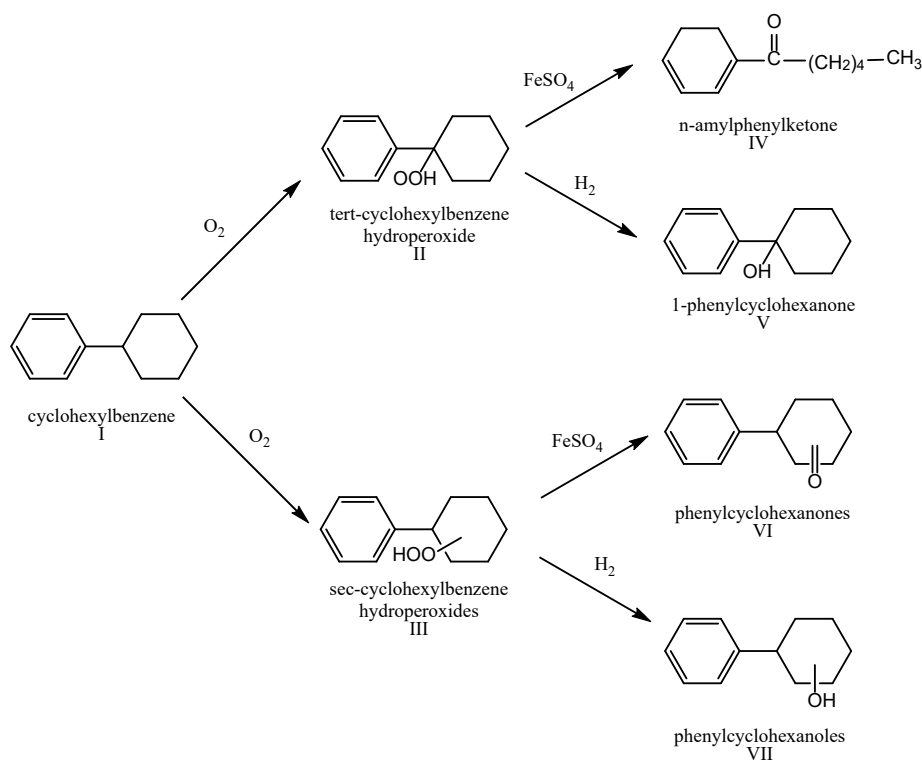

Fig. 1. Direction of reduction of cyclohexylbenzene hydroperoxides.

The analysis of IR-spectrum of products of liquid-phase oxidation of CHB (selectivity of HP formation – 100%, oxidation depth – 10%) showed that it contains only absorption bands of groups >C=O, which are common for n-amylphenylketone and 2-phenylcyclohexanone. The portion of the latter is 10-12% of the total ketone content.

The reduction of *tert*-CHBHP (II) by $FeSO_4$ is associated with the rupture of C-C-bond of a cyclohexane ring. It leads to forming amylphenylketone (V), which is isolated and identified. The reduction of *sec*-CHBHP (III) by $FeSO_4$ should lead to the formation of 2-phenylcyclohexanone (VI).

After analyzing IR-spectra of amylphenylketone (IV) and 2-phenylcyclohexanone (VI), we determined that the stretches of >C=O group of compounds (IV) and (VI) are 1683 and 1704 cm^{-1} respectively. It helps to determine the presence and ratio of these ketones both in artificial mixture and in the products of reduction of oxidized CHB. The content of amylphenylketone (V) and 2-phenylcyclohexanone (VI) in the CHB oxidation products treated with $FeSO_4$ is 5.2 and 1.2% respectively. It also indicates that 15-20% of the total HPs are secondary CHBHPs (III).

The reduction of HPs with alkali, triphenylphosphine, or hydrogen in the presence of a hydrogenation catalyst forms alcohols similar to the structure of the original HP. A convenient method to analyze such compounds is their interaction with nitric acid to form alkyl nitriles, which have maximum absorption of 320-400 nm. Analysis of the alcohols formed during

reduction of CHB oxidation products showed that the total alcohol content is 15% higher than that of 1-phenylcyclohexanol (V).

Thus, the decrease of phenol (XV) yield at acid decomposition of CHB oxidation products is associated with the simultaneous formation of tertiary (II) and secondary (III) HP during CHB oxidation. The content of the latter is 15-20% of the total HP.

We also studied thermal decomposition of cycloalkylbenzene hydroperoxides in the 125-150 °C temperature range. The results showed that the most probable reason n-alkylphenylketones appear in the cycloalkylbenzenes oxidation products is the decomposition of *tert*-HP, which is accompanied by the breakage of $C_{tert.}$-$C_{sec.}$-bond in alicyclic ring with intermediate formation of 5-benzoylpental radical [13]. Further transformation of this ketoradical leads to n-amylphenylketone (IV).

Oxidation of *n*-amylphenylketone via α-ketohydroperoxide produces benzoic acid and valerian acid, which catalyze the decay of *tert*-CHBHP to cyclohexanone (XIV) and phenol (XV). Phenol is known to be one of the main factors slowing down the oxidation reaction, up to its cessation. Oxidative transformations of ketoradical lead to the production of δ-benzolvaleric acid (XIII). The latter can serve as an additional source for phenol, adipic, glutaric, and benzoic acids in the reaction products [14].

Thermal decomposition of *sec*-HP is accompanied by the formation of 2-phenylcycloalkanones. Oxidation of 2-phenylcyclohexanone and 2-phenylcyclohexanol, similarly to methylcyclohexanone and methylcyclohexanol, results in α-phenyladipic acid. Decarboxylation of α-phenyladipic acid can result in the formation of lower mono- and dicarboxylic acids [15]. Thus, we found (% wt.): benzoic (40-50), valerian (20-25), formic (8-12), acetic (7-10), and propionic (8-12) acids among volatile acidic products with water vapor after CHB oxidation. Among the non-volatile acids with water vapor, we found (% wt.): δ-benzoylvaleric (55-60), glutaric (25-30), oxalic (2-4), adipic (7-10), and α-phenyladipic (2-4) acids. The acids were analyzed by gas-liquid chromatography.

We present the scheme of oxidative transformations of cycloalkylbenzenes based on the obtained experimental data on the composition of cycloalkylbenzenes oxidation products, as well as the currently existing knowledge of liquid-phase oxidation of alkylsubstituted aromatic and cycloaliphatic hydrocarbons. This scheme uses cyclohexylbenzenes as an example in the study (Fig. 2).

All compounds in the scheme were found in the CHB oxidation products at high conversion of the latter (40-45%), which corresponds to a fairly low selectivity of the process. One of the studies [16] points out the complex nature of the oxidation products of phenylcyclohexane at great depths of its oxidation. Phenol, cycloalkanones, and phenylcycloalkanones are practically absent in the reaction products during selective oxidation of CHB.
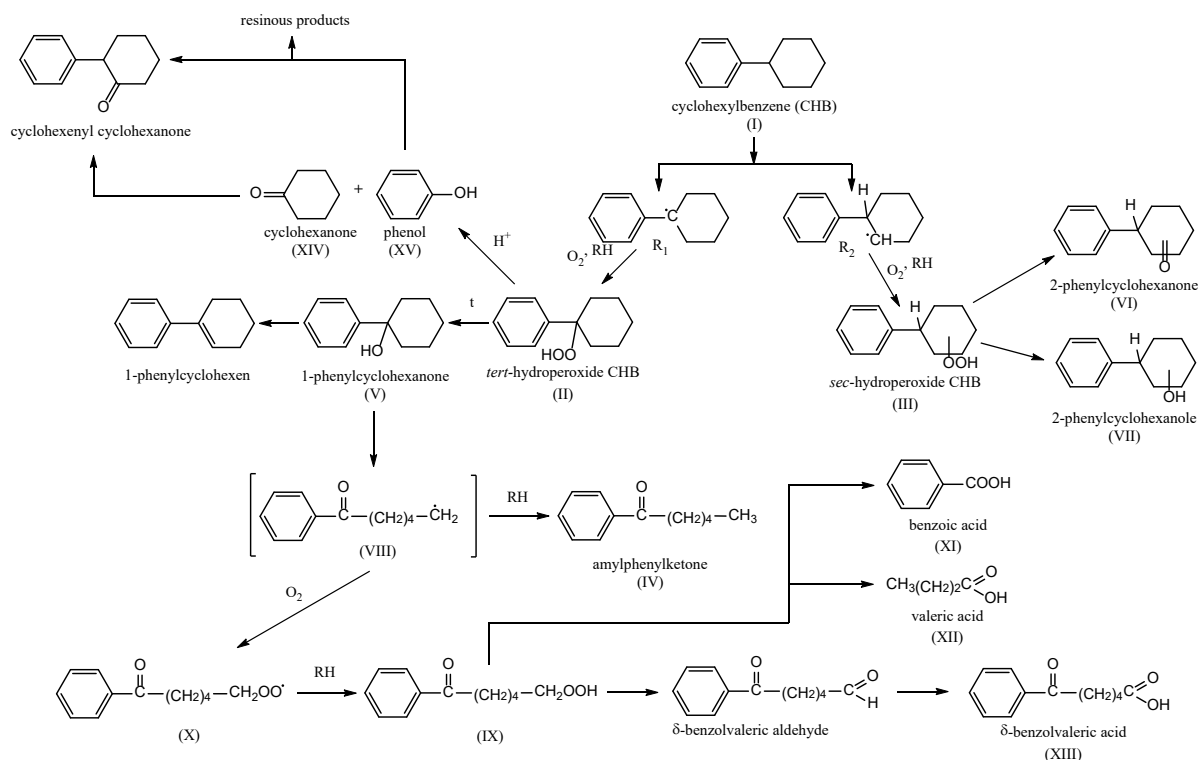
Fig. 2. Scheme of oxidative transformations of CHB

Experiment

CHB (I) was obtained by alkylation of benzene with cyclohexanol in the presence of concentrated sulfuric acid. Mole ratio hydrocarbon : sulfuric acid : cyclohexanol was 3:1:3, temperature – 5-10 °C, reaction time – 1 h. The target product was extracted from alkylation products by vacuum distillation.

Liquid-phase oxidation of CHB was performed on a kinetic apparatus [17] at 120 °C in the presence of 1 wt. % CHBHP.

1-Phenylcyclohexanol (V) was obtained from phenylmagnesium bromide and cyclohexanone by the Grignard reaction [18, 19]. T_m = 61.5 °C (from petrolether). Found, %: C – 81.80; H – 9.14 $C_{12}H_{16}O$. Calculated, %: C – 81.79; H – 9.15.

Tertiary CHBHP (II) was obtained by oxidation of 1-phenylcyclohexanol with hydrogen peroxide (V) [20]. The reaction products were washed with water, 1% soda solution, again with water to a neutral medium and dried in vacuum.

2-Phenylcyclohexanone (VI) was obtained from 1-chlorocyclohexanone and phenylmagnesium bromide by the Grignard reaction [21]. T_m = 57 °C. Found, %: C – 82.98; H – 8.26 $C_{12}H_{14}O$. Calculated, %: C – 82.72; H – 8.10.

n-Amylphenylketone (IV) was obtained by reduction of tertiary CHBHP (II) with 1M iron sulfate solution. The product was washed with 4% NaOH solution, water, dried, and dispersed under vacuum. T_b = 101 °C (3 mmHg). Found, %: C – 81.65; H – 9.08 $C_{12}H_{16}O$. Calculated, %: C – 81.77; H – 9.15. CHB oxide was reduced with sulfuric iron in a similar manner.

CGB oxide was reduced to alcohols with hydrogen at room temperature in the presence of 2% Pd/C, 4% of weight of the reaction mixture in an apparatus similar to that used for the CHB oxidation.

Study methods NMR spectra ^{1}H were recorded on a NMReady-60PRO spectrometer (60MHz) relative to the internal reference, hexamethyldisiloxane. Mean square error of measurements ±0.02 ppm. IR spectroscopic analysis was performed on a Fourier IR RX-1. The spectra were recorded in the 4000-400 cm^{-1} range, as a micro-layer between KBr glasses or on one side of KBr.

Conclusion

As a result of the study, it was established that the liquid-phase oxidation of cycloalkylbenzenes features a high degree of selectivity in hydroperoxide formation – 95% and more. Tertiary and secondary C-H-bonds undergo oxidative transformations in the cycloalkylbenzenes molecule simultaneously, which results in the production of tertiary and secondary hydroperoxides, respectively. The secondary CH$_2$-bonds of cycloalkyl substituents in position 2 (β) with respect to the phenyl C-H-bond are mainly oxidized.

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