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THE REACTION OF CYCLOHEXYLBENZENE OXIDATION IN THE PRESENCE OF SOLVENTS

E. A. Kurganova, A. S. Frolov, G. N. Koshel, V. S. Kabanova

Ekaterina A. Kurganova, Doctor of Chemical Sciences, Associate Professor. http://orcid.org/0000-0002-0087-1784
Alexandr S. Frolov, Candidate of Chemical Sciences, Associate Professor. https://orcid.org/0000-0002-0491-7452
Georgy N. Koshel, Doctor of Chemical Sciences, Professor. https://orcid.org/0000-0002-1020-4643
Viktoriya S. Kabanova, Student. https://orcid.org/0000-0001-6635-6315
Yaroslavl State Technical University, Yaroslavl, Russia, kurganovaea@ystu.ru

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Abstract. *The paper concerns the process of aerobic liquid-phase oxidation of cyclohexylbenzene to hydroperoxide in the presence of different solvents. It has been found that it is preferable to carry out the reaction in an acetonitrile medium. We investigate the effect of different process parameters on the oxidation of cyclohexylbenzene in this solvent. Based on the results of the research, conditions were chosen that make it possible to achieve a hydrocarbon conversion rate of 11% in 2.5 hours with a hydroperoxide formation selectivity of about 93%. The average oxidation rate of cyclohexylbenzene increases about 1.3 times in compare with the process carried out in the absence of solvent.*

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Introduction

Phenol and cyclohexanone are large-tonnage products of basic organic petrochemical synthesis. They are widely used in various branches of the chemical industry and related industries [1, 2]. For example, phenol is used in the production of plastics, alkylphenols, synthetic dyes, additives for fuels and oils, electrical insulation varnishes and plasticizers. It is also used in the production of pharmaceuticals, surfactants, antiseptics, toxic chemicals and perfumes [3-5].

Cyclohexanone is the basic monomer for the polyamide polymer industry, plastics, insulating materials, etc. It is also used as a solvent for resins, fats, oils, waxes, acetates and nitrates [6].

The main quantities of phenol and cyclohexanone both in Russia and abroad are produced by the cumene method and the liquid-phase catalytic oxidation of cyclohexane (CH) respectively. Despite the well-established technology and considerable operating experience, these processes have a number of drawbacks. The acetone formed in the cumene process has no market equivalent for phenol. The oxidation of cyclohexane leads to an extremely low (4-5%) hydrocarbon conversion with a ketone formation selectivity of no more than 80-85%. In order

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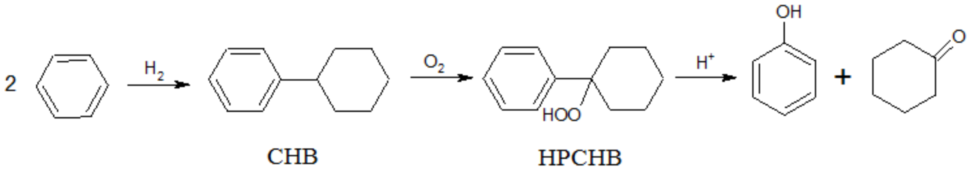
to eliminate the above drawbacks, the benzene-based co-production process for phenol and cyclohexanone is being developed which includes the following steps:

- hydrodimerization of benzene to form cyclohexylbenzene (CHB);
- selective liquid-phase oxidation of cyclohexylbenzene to *tert*-hydroperoxide (*tert*-HP-CHB);
- acid decomposition of *tert*-hydroperoxide of cyclohexylbenzene to phenol and cyclohexanone according to the following scheme:



This article presents the results of the liquid-phase aerobic oxidation of cyclohexylbenzene to hydroperoxide in different solvents.

Results and Discussion

Although catalytic oxidation of cyclohexylbenzene compared to initiate oxidation can increase the reaction rate by a factor of 1.2-1.4, nevertheless the selectivity of the process is significantly reduced and the practical implementation of this technique under industrial conditions is fraught with several difficulties [7].

In this connection the oxidation of cyclohexylbenzene in the presence of solvents, which are known to have a significant influence on the oxidation rate of hydrocarbons and the selectivity of hydroperoxide formation, is of practical interest. We used tertiary cyclohexylbenzene hydroperoxide as the initiator.

The oxidation reaction of cyclohexylbenzene is preferably carried out in acetonitrile medium. In this solvent the average oxidation rate is increased by a factor of 1.3 compared to oxidation without solvent and the hydroperoxide formation selectivity remains high (Table 1).

Table 1. Influence of the nature of the solvent on the oxidation of cyclohexylbenzene. Temperature is 125 °C; initiator concentration (HP CHB) is 0.75% wt.; solvent concentration is 25% wt.

Solvent	Time, hours	Concentration in oxidate, % wt.			Conversion, %	Selectivity, %
		hydroperoxide	ketons	acids		
*-	4.0	13.0	0.67	0.03	11.5	94.1
-	4.0	14.9	1.35	0.02	13.7	91.0
-	2.5	8.1	0.19	0.10	7.2	95.6
Acetonitrile	2.6	9.0	0.64	0.02	10.9	92.5
Benzonitrile	2.6	6.6	0.64	-	8.2	90.5
Chlorobenzene	2.6	5.2	0.14	-	5.7	95.0
Benzene	2.6	5.1	0.79	-	6.7	86.1
tert-butylalcohol	2.6	6.4	1.22	0.08	8.8	81.3

* - the experiment was carried out in a glass reactor.

The comparison of solvent-free oxidation data for cyclohexylbenzene in glass and metal reactors shows (see Table 1) the material of the reactor wall also has almost no influence on the quantitative reaction values. Finally, this made it possible to study the liquid-phase oxidation reaction of cyclohexylbenzene under conditions as close to industrial as possible. To keep the acetonitrile in the liquid phase the oxidation of cyclohexylbenzene was carried out under pressure at an airflow rate of 15-18 l/h. The system pressure is maintained at 10 atm, as its variation in the range 10-30 atm had no effect on either conversion or process selectivity.

By Fig. 1, increasing of acetonitrile concentration the conversion of cyclohexylbenzene at the same reaction time does not increase in proportion to the solvent concentration. Up to an acetonitrile concentration of 5 mol/l, a straightforward relationship between hydrocarbon conversion and acetonitrile concentration is maintained, and then the rate reaches its limit. The oxidation selectivity decreases from 95 to 89%. The decrease of the reaction selectivity as a function of solvent concentration is greater at acetonitrile concentrations >7 mol/l.

Comparison of indices of cyclohexylbenzene oxidation process in acetonitrile medium and without solvent at the same cyclohexylbenzene conversion shows the13% hydrocarbon conversion reaction selectivity in acetonitrile medium (10.5 mol/l concentration) is lower than without solvent and at 11% conversion (acetonitrile concentration 5.5 mol/l) selectivity in both systems is equal. By the dependence of hydrocarbon conversion on acetonitrile concentration the acetonitrile concentration of 5.5 mol/l (25% wt.) is recommended for oxidation of cyclohexylbenzene.

The increase of the oxidation rate of cyclohexylbenzene in the presence of acetonitrile can be explained by the formation of a hydroperoxide complex with this solvent. The enthalpy of formation of the hydroperoxide-acetonitrile complex is higher (11.7 kJ/mol) than that of the hydroperoxide-cyclohexylbenzene complex (≈4.2 kJ/mol), therefore the O-O bond in the hydroperoxide-acetonitrile complex is weaker. It is the reason for the increased rate of decomposition of the hydroperoxide molecules to free radicals in acetonitrile medium. The increase of the oxidation rate can also be related to the influence of the solvent on the ratio of chain propagation rate constant and chain termination rate constant $k_2/\sqrt{k_6}$ [8].

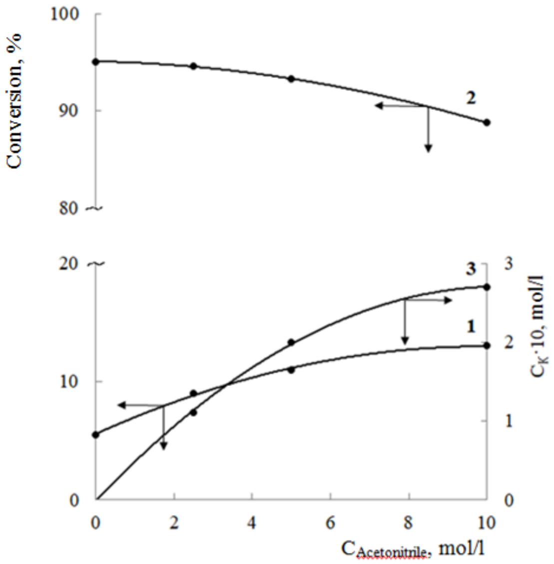


Fig. 1. Dependence of cyclohexylbenzene conversion (1), selectivity of its oxidation reaction (2) and concentration of the hydroperoxide-acetonitrile complex (3) on acetonitrile concentration. Temperature 125 °C, initiator concentration is 0.05 mol/l, reaction time is 2.5 h

The nature of the conversion dependence of cyclohexylbenzene on acetonitrile concentration can be determined by two factors. Firstly, the oxidation rate of the hydrocarbon depends on its concentration, so if cyclohexylbenzene is diluted with acetonitrile the reaction rate should decrease. At low concentrations of acetonitrile there will be a lower speed reduction due to dilution of the hydrocarbon. The formation of a hydroperoxide-solvent complex and the conversion of cyclohexylbenzene will be proportional to the solvent concentration. At acetonitrile concentrations greater than 5 mol/l the rate reduction will be very high. The conversion of cyclohexylbenzene will change less with further increases of solvent concentration. Secondly, as cyclohexylbenzene is diluted with acetonitrile, the fraction of hydroperoxide bound in the hydroperoxide-acetonitrile complex will increase, and at a certain concentration of acetonitrile all the hydroperoxide will be in the complex. If the oxidation rate depends on the concentration of the complex further increasing the concentration of acetonitrile will not increase the oxidation rate.

In order to find out which of these two factors is the determining one, the concentration of the hydroperoxide-acetonitrile complex (C_K) at different concentrations of acetonitrile (C_{AN}) was calculated:

$$C_K = KC_{HP}C_{AN},$$

in which C_K is the concentration of the complex; K is the equilibrium constant of complex formation (K(125 °C) = 0.09 l/mol); C_{HP} is the concentration of hydroperoxide; C_{AN} is the concentration of acetonitrile.

When the acetonitrile concentration is 10 mol/l there is not the hydroperoxide bound to the complex yet. The nature of the dependences of the complex concentration and cyclohexylbenzene conversion on the acetonitrile concentration are identical (see figure 1). In addition, if the concentration of the complex is calculated without considering the dilution of the hydrocarbon with acetonitrile, the same dependence will be linear one. These suggests the opinion of approaching the oxidation rate of cyclohexylbenzene to the limit value at acetonitrile concentration more than 5 mol/l is associated with a significant decrease of hydrocarbon concentration due to its dilution with solvent.

Increasing the concentration of the initiator (cyclohexylbenzene hydroperoxide) leads to higher hydrocarbon conversion and lower reaction selectivity so as in solvent free oxidation (Table 2). The most preferred initiator concentration is 0.047 mol/l.

Table 2. Effect of initiator concentration on the oxidation of cyclohexylbenzene in acetonitrile medium. Temperature is 125 °C, acetonitrile concentration is 5.5 mol/l, reaction time is 2.5 h

Initiator concentration, mol/l	Cyclohexylbenzene conversion, %	Selectivity, %
0.023	9.5	94.2
0.047	10.9	93.5
0.141	12.0	88.1

The study of temperature effect and duration of oxidation on the accumulation of reaction products (Fig. 2) allowed the selection of optimum conditions for the oxidation of phenylcyclohexane in acetonitrile medium, which provide a sufficiently high rate and selectivity of the reaction. Under these conditions (temperature 125 °C, initiator concentration 0.047 mol/l, acetonitrile 5.5 mol/l) a hydrocarbon conversion of 11% is achieved in 2.5 h with a hydroperoxide formation selectivity of 93%. The average oxidation rate of cyclohexylbenzene increases about 1.3 times in compare with the process carried out in the absence of solvent.

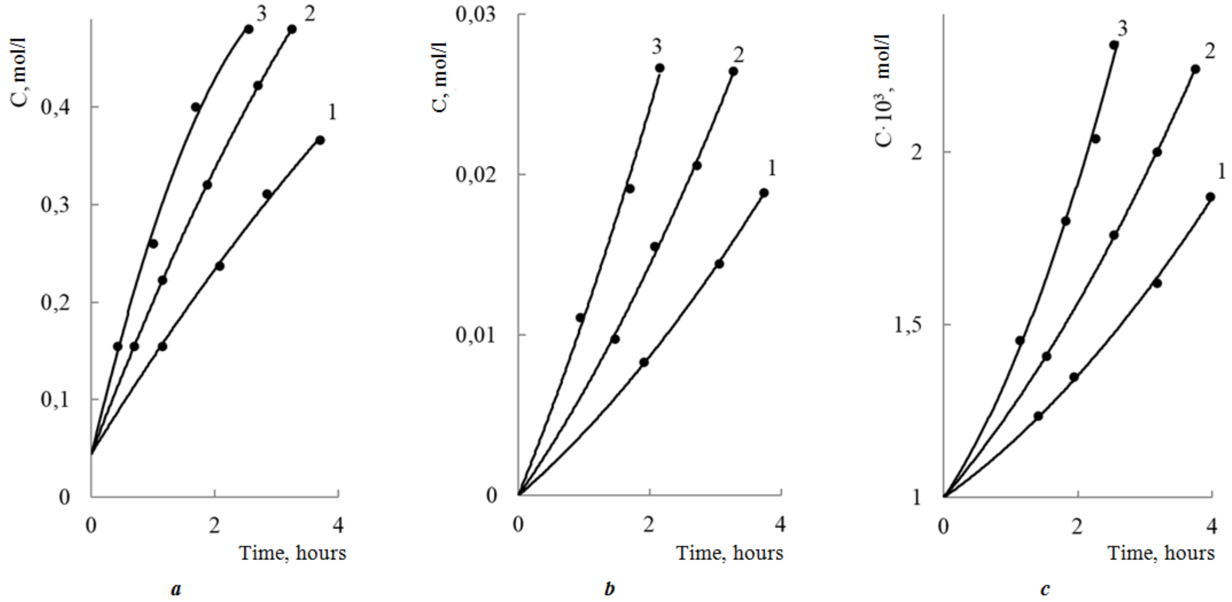


Fig. 2. Temperature effect and duration of oxidation of cyclohexylbenzene in acetonitrile medium on the accumulation of hydroperoxide (*a*), ketones (*b*) and acids (*c*). Temperature, °C: 1 - 120, 2 - 125, 3 - 130. Acetonitrile concentration is 5.5 mol/l

Table 3 shows the material balance of the oxidation of cyclohexylbenzene in acetonitrile medium.

Table 3. Material balance of the liquid phase oxidation reaction of cyclohexylbenzene in acetonitrile medium. Temperature is 125 °C; reaction time is 2.5 h; conversion is 11.3%; selectivity is 93.2%

Components	Taken			Obtained		
	g	g-mol	% wt.	g	g-mol	% wt.
Cyclohexylbenzene hydroperoxide	5.0	0.026	1.0	48.5	0.252	9.5
Ketons	-	-	-	3.2	0.0181	0.63
Acids (calculation for benzoic acid)	-	-	-	0.12	0.0009	0.023
Cyclohexylbenzene	370.0	2.310	74.0	330.0	2.060	65.0
Acetonitrile	125.0	3.050	25.0	125.0	3.050	24.6
Losses	-	-	-	1.0	0.005	0.247
Total	500	5.386	100.0	507.8	5.386	100.0

Experimental part

Aerobic liquid-phase oxidation of cyclohexylbenzene was carried out under pressure (Fig. 3). Hydrocarbon, solvent, initiator were loaded into the reactor (1), which was attached to the head. There was a gas operating pressure in the system, monitored with a manometer, and the plant was checked for leaks. The contents of the reactor were then heated to reaction temperature using an electric furnace (2). The temperature in the reaction zone was monitored by anchromel-copel thermocouple wire in the hydrocarbon to be oxidised. Once the set temperature was reached, the agitator (3) was switched on, driven by the magnetic coil and core (4). The air flow rate was controlled by a rheometer (6) installed at the reactor air outlet. After the experiment, the reactor was quickly cooled down and disconnected from the system.

The study of the oxidation patterns of CHB under atmospheric pressure was carried out on a flow-closed type apparatus [9]. It characterized as a closed loop plant with the use of small quantities of hydrocarbon, the ability to measure absorbed oxygen and the ease of achieving a kinetic regime. Systems at atmospheric pressure used oxygen as the oxidizer, systems under pressure used common air.

The oxidation initiator, isopropylbenzene cyclohexylbenzene hydroperoxide, is obtained by oxidation of cyclohexylbenzene with more than 96% selectivity, washed with a 1% soda solution and concentrated to 94% wt.

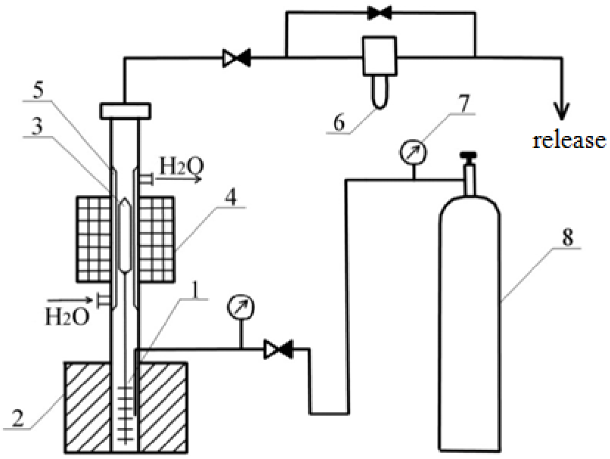


Fig. 3. Principle diagram of a pressurised hydrocarbon oxidation unit (PHOU): 1 - autoclave; 2 - electric furnace; 3 - magnetic stirrer; 4 - electromagnet; 5 - refrigerator; 6 - rheometer; 7 - reducer; 8 - compressed air cylinder; ►◄ - control valve

The solvents for the oxidation process of cyclohexylbenzene of the "p.a." and "pur" grades were additionally purified on a distillation column with an efficiency of 20 theoretical plates.

We determined the hydroperoxide in the oxidation products using the iodometric method [10].

Conclusions

The regularities of the reaction of liquid-phase aerobic oxidation of cyclo-hexylbenzene in the medium of acetonitrile have been studied. Conditions have been found that make it possible to obtain cyclohexylbenzene hydroperoxide with a selectivity of about 93% at an initial hydrocarbon conversion of 11%. Thus, during the oxidation of cyclohexylbenzene, hydroperoxide can be synthesized with a selectivity and rate acceptable for the technological design of the process. All this creates real prerequisites for considering the oxidation of cyclohexylbenzene as one of the stages in the synthesis of phenol based on it together with cyclohexanone.

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