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PRINCIPLES OF AEROBIC OXIDATION OF ETHYLBENZENE TO HYDROPEROXIDE UNDER THE PRESENCE OF PHTHALIMIDE CATALYSTS

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Abstract. *The article describes a study of basic principles of aerobic liquid-phase oxidation of ethylbenzene to hydroperoxide. According to the research, the use of phthalimide catalysts (N-hydroxyphthalimide and its derivatives) can increase the oxidation rate of this hydrocarbon by 1.5-2 times compared with initiators of different nature. At the same time, high selectivity of target hydroperoxide formation is still present - about 90%. The authors recommend conditions for oxidation of ethylbenzene in the presence of phthalimide catalysts based on experimental data. The results obtained can be used to improve the technology for co-production of propylene oxide and styrene, valuable products of the main chemical and petrochemical synthesis.*

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Introduction

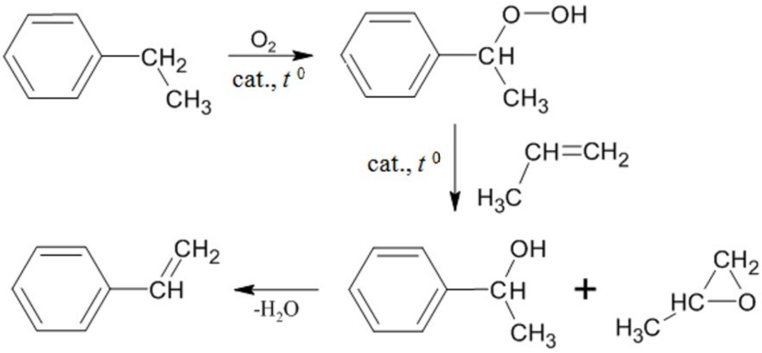
Propylene oxide is a valuable intermediate product for the basic organic synthesis of polymers. Thus, such major companies as LUKOIL and SIBUR Holding are interested in polymer production expansion [1]. Propylene oxide is mainly produced by chlorohydrin method or by epoxidation of propylene with organic peroxides or hydrogen peroxide [2]. Another interesting process for producing propylene oxide is known, too. They use cumene hydroperoxide to transfer oxygen. This process has been implemented by Sumitomo Chemical [3]. "Halcon" is a process for production of propylene oxide and styrene, based on use of ethylbenzene hydroperoxide (EB HP). It is implemented abroad. Domestic implementation is provided by OAO "Nizhnekamskneftekhim". The ethylbenzene (EB) oxidation process conducted at the plant produces

EB HP with a selectivity not exceeding 70-75% wt. The maximum concentration of EB HP that can be obtained is 7-10% wt. This mode of EB oxidation produces a large number of by-products and is associated with significant energy consumption (water, electricity, steam, etc.).

Nowadays, there is no effective catalyst which allows us to achieve high conversion of EB and selectivity of formation of EB HP (more than 90%). These would certainly reduce the production cost. In this regard, search of conditions of EB oxidation process (including use of effective catalysts), which would allow us to increase EB conversion, increase reaction rate, reduce reaction time at preservation of high indicators of its formation selectivity, is an actual task. This paper presents the results of studies aimed at intensifying the oxidation process of EB using *N*-hydroxyphthalimide (*N*-HPI) as a catalyst, which has proven to be an effective catalyst in oxidation reactions [4].

Main body

Many processes aimed at production of valuable oxygen-containing compounds are based on liquid-phase aerobic oxidation of aromatic hydrocarbons [5]. For example, oxidation of ethylbenzene to hydroperoxide, which is then used in propylene epoxidation reaction, is the basis of "Halcon"-process. Methylphenylcarbinol obtained in the latter reaction undergoes dehydrogenation, thus two valuable compounds - styrene and propylene oxide - are obtained in the process. Their production is one of the major areas of the chemical industry in Russia and abroad.



About 70 thousand tons of propylene oxide and 170 thousand tons of styrene are produced annually in Nizhnekamsk using this technology [6]. At the same time on the Russian market there is an unsatisfied demand for propylene oxide, which is about 100 thousand tons and is filled by foreign supplies [7]. Technology of joint production of styrene and propylene oxide uses available and produced in a large scale ethylbenzene as a raw material. This technology provides simultaneous production of several target products and makes it possible to obtain styrene of higher quality compared with dehydrogenation process. Most of styrene is used for the production of polystyrene and copolymers (butadiene styrene, isoprene styrene, etc.), which are an important element of modern industry due to their wide applicability in various fields. Also styrene is used for producing rubbers, latexes, and resins [6, 8]. Magnetic composites derived from styrene are of great environmental importance as adsorbents for oil spills [9]. Propylene oxide is a raw material for production of many petrochemical products: polyurethanes, glycols, cosmetics, and medical preparations. Solid polyurethane foam derived from propylene oxide is widely used worldwide in various industries such as construction, transportation, shoes and furniture industry [6]. About 5% of propylene oxide is used to produce methylpropazole, a methyl ester of propylene glycol, which is used to make non-toxic coolants, refrigerants, and organic solvents. Also propylene oxide is used in relatively small amounts for production of non-ionic surface-active agents, isopropanolamines, allyl alcohol, propylene carbonate, and unsaturated polyester resins [10]. OAO "Nizhnekamskneftekhim" implements "Halcon" process using complex catalyst produced as a result of interaction of metallic molybdenum and ethylbenzene hydroperoxide in ethyl alcohol. However, experience in production operation has revealed disadvantages of the catalyst, namely low content of molybdenum in solution (0.4 to 0.7% wt.), significant consumption of ethylbenzene hydroperoxide to transfer molybdenum metal into solution, as well as instability of the catalyst [11].

Since the molybdenum catalyst has the above disadvantages, there were researches for search another catalytic systems and initiators of ethylbenzene oxidation process performed. In 2003 Melone et al. found that aerobic oxidation of ethylbenzene in acetic acid in the presence of catalytic complex I_2/*N*-HFI leads to a quantitative yield of methylphenylcarbinol [12]. Whereas, oxidation of EB in acetonitrile in the presence of *N*-HPI and acetaldehyde as initiator at 25 °C for 6 h leads to the formation of ethylbenzene hydroperoxide, acetophenone, and methylphenylcarbinol. Depending on conditions of the process conversion of EB is from 15 to 30% [13]. Additionally, there is the heterogeneous catalytic oxidation of EB to acetophenone in the presence of aluminosilicate-based nanocatalyst with cobalt and *N*-HPI adsorbed on its surface [14]. This catalyst achieves 80% conversion of EB within 10 hours, but the main reaction products are acetophenone and methylphenylcarbinol. In 2005, J.L. Fierro et al. studied the possibility of achieving high selectivity of EB HP formation (with EB conversion up to 10%) by oxidation of EB in the presence of barium compounds [15]. In 2009, using catalytic system *N*-HPI and trace amounts of sodium hydroxide, they managed to increase the conversion of EB to 15% with a selectivity of formation of EB HP of about 80% [16].

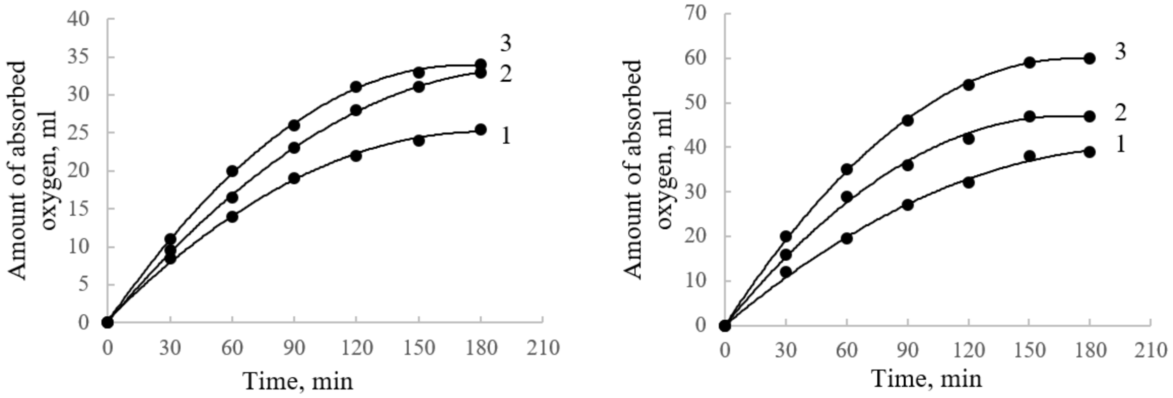
Therefore, it is possible to conclude that potential possibilities of intensification of processes of EB oxidation to its HP using catalysts (including phthalimide catalysts) are actual ones. The effective catalyst in the presence of which it would be possible to achieve high selectivity of formation of EB HP of EB and conversion of EB at high speed of its oxidation, acceptable for industrial realization, has not been found yet. This paper presents studies of the patterns of different parameters influence on the EB oxidation process: temperature, structure, concentration of the catalyst, duration of the reaction, etc.

Experimental part

Study of the effect of temperature and reaction time on the oxidation of ethylbenzene under the presence of catalyst and initiator

We studied the influence of temperature on the process of EB oxidation both under the presence of the standard initiator IPB HP and under the presence of *N*-HPI at the temperature range of 110-130 °C. As can be seen (Fig. 1, *a, b*) the character of kinetic curves of oxygen uptake in the oxidation of EB in the presence of *N*-HPI and IPB HP are similar.

We observed an increase in the EB HP content by a factor of about 2 in both cases when the temperature was increased from 110 to 130 °C (Table 1). For example, under the presence of IPB HP, the IPB HP content increased from 5.7 to 10.3% wt. and under the presence of *N*-HPI from 7.6 to 15.1%, while the selectivity of formation of EB HP remained approximately 90%.



a *b*

Fig. 1. Influence of temperature on the liquid-phase oxidation reaction of EB under the presence of: *a* - IPB HP, *b* - *N*-HPI. Temperature, °C: 1 - 110; 2 - 120; 3 - 130; IPB HP content is 2.5% wt.; *N*-HPI content is 3.0% wt.

Studies under the presence of IPB HP initiator have shown that the best results are achieved at a temperature of 130 ° C, the conversion of hydrocarbon in this case is 11.6% with a selectivity of hydroperoxide formation of 89.0%. The conversion of EB and the selectivity of its HP formation were 16.5% and 91.5%, respectively, in case of oxidation of EB with *N*-HPI. Thus, using *N*-HPI instead of IPB HP, an increase in the oxidation rate and conversion of EB by 1.5-2 times is observed, while maintaining a fairly high selectivity of the process.

Table 1. Influence of temperature and reaction time on the conversion of EB and the selectivity of its HP formation during oxidation. IPB HP content is 2.5% wt., *N*-HPI content is 3.0% wt.

Initiator/catalyst	Temperature, °C	Reaction time, h	The EB HP content in the oxidation products, % wt.	Selectivity of formation of EB HP, %	Conversion EB, %
IPB HP	110	3	5.7	88.0	6.5
	120		8.0	88.5	9.0
	130		10.3	89.0	11.6
N-HPI	110	3	7.6	89.3	8.6
	120		14.4	93.0	15.5
	130	1	10.0	93.3	10.7
		2	13.2	92.5	14.3
		3	15.1	91.5	16.5

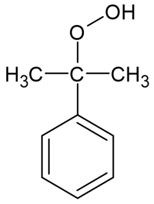
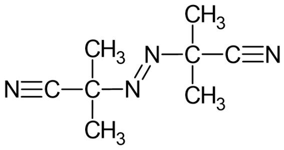
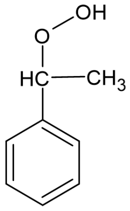
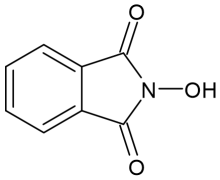
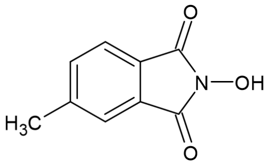
Based on the nature of the curves "amount of absorbed oxygen - time" (see Fig. 1), it can be seen the more active interaction of hydrocarbon with oxygen in the initial period of time, and, consequently, the rate of oxidation of EB over time changes, as evidenced by the results of studies. In this case, as can be seen from Table 1, the average rate of accumulation of EB HP decreases about 2 times from 10.0 to 5.0% wt. per hour. At the same time there is a slight decrease of selectivity of formation of EB HP from 93.3 to 91.5%.

Study on the effect of catalyst and/or initiator structure on the oxidation of ethylbenzene

We studied the effect of different catalysts and initiators on EB oxidation process at 120-130 °C, using IPB HP, AIBN and EB HP as initiators, *N*-HPI and 4-methyl-*N*-HPI as catalysts, and investigated joint action of *N*-HPI with EB HP and *N*-HPI with AIBN (Fig. 2).

Table 2 shows the oxidation of EB with the EB HP initiator proceeds at a slower rate compared to the use of IPB HP. Indeed, there is a slight increase in the selectivity of the formation of EB HP. The highest content of EB HP (15.1%) is formed by oxidation of EB at 130 °C in the presence of *N*-HPI. Combined action of *N*-HPI with EB HP allows us to obtain oxidate with 15.8% HP content, however at that decrease of selectivity of formation of HP from 91.5 to 89.0% is observed.

Table 2. Effect of different catalysts and initiators on the oxidation process of EB. Reaction time is 3 h; temperature is 130 °C

Initiator/catalyst	The EB HP content in the oxidation products, % wt.	Selectivity of formation of EB HP, %	Average rate of formation of EB HP, % wt./h
IPB HP 	10.3	89.0	3.4
AIBN 	10.0	90.0	3.3
EB HP 	8.7	90.1	2.9
N-HPI 	15.1	91.5	5.0
EB HP and *N*-HPI	15.8	89.0	5.2
AIBN and *N*-HPI	14.9	90.0	5.0
N-HPI*	14.4	93.0	4.8
4-methyl-*N*-HPI* 	14.2	92.0	4.7

* – temperature 120 °C

Study on the oxidation of ethylbenzene under the presence of 4-methyl-N-hydroxyphthalimide

We investigated the effect of the concentration of 4-methyl-*N*-HPI at 120 °C for 1.5 h. By Table 3, the increase of catalyst content from 1.7 to 3.3% wt. increases the oxidation rate of EB. 4-Methyl-*N*-HPI in comparison with initiator - isopropylbenzene showed higher catalytic activity in the process of liquid-phase oxidation of EB to HP.

Table 3. Effect of temperature and concentration of 4-methyl-*N*-HPI on the oxidation of EB. 4-Methyl-*N*-HPI catalyst content is 3.3% wt.; reaction time is 1.5 h

Temperature, °C	Catalyst content, % wt. of hydrocarbon feed	The EB HP content in the oxidation products, % wt.	Selectivity of formation of EB HP, %
110	3.3	9.1	91.0
120	1.7	11.3	90.0
	2.5	11.9	91.5
	3.3	13.6	92.3
130	3.3	15.2	89.8

We investigated liquid-phase oxidation of EB under the presence of 4-methyl-*N*-HPI. When studying the effect of temperature, the authors found that increasing it from 110 to 130 °C increases the content of EB HP from 9 to 15% wt. while keeping its formation selectivity of about 90% (Table 3, Fig. 3). We studied the effect of catalyst concentration at 120 °C because at 130 °C a decrease of selectivity is observed, an increase of catalyst concentration from 1.7 to 3.3% wt. leads to an increase of EB HP from 11 to 13%.

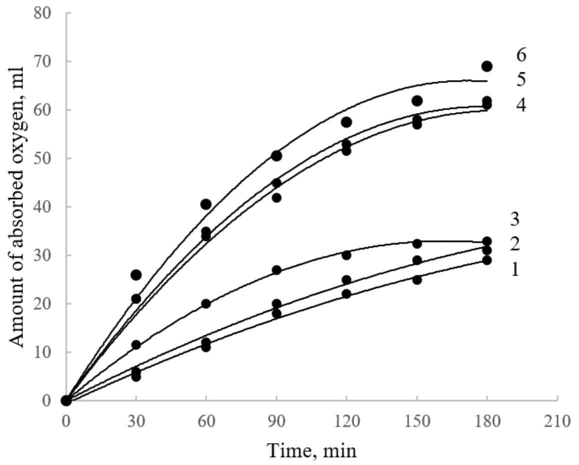


Fig. 2. Dependence of the oxidation rate of EB on the structure of the catalyst and /or initiator(s). Temperature is 130 °C; content: initiators (IPB HP, EB HP, AIBN) 2.5% wt., catalyst (*N*-HPI) 3.0% wt. Initiator/catalyst: 1 - EB HP; 2 - AIBN; 3 - IPB HP; 4 - *N*-HPI + AIBN; 5 - *N*-HPI; 6 - *N*-HPI + EB HP.

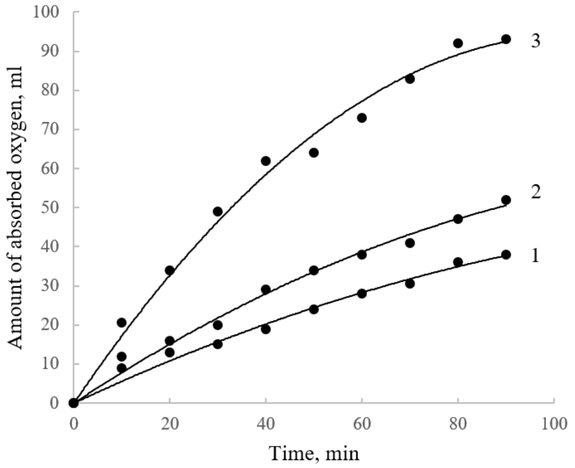


Fig. 3. Influence of temperature on the liquid-phase oxidation reaction of EB under the presence of 4-methyl-*N*-HPI. 4-methyl-*N*-HPI content is 3.3% wt.; temperature, °C: 1 - 110; 2 - 120; 3 - 130

Table 4 shows the material balance of EB oxidation under the most appropriate conditions.

Table 4. Material balance of the liquid phase oxidation of EB. Temperature is 130 °C; *N*-HPI catalyst content is 3.0% wt.; reaction time is 3 h

Components	Molecular weight, g/mol	input		output	
		g	mol	g	mol
EB	106	43.35	0.409	36.20	0.341
Oxygen	32	0.09	0.003	-	-
N-HPI	163	1.30	0.008	1.30	0.008
EB HP	124	-	-	6.76	0.055
Losses	-	-	-	0.50	0.016
Total	-	44.74	0.420	44.74	0.420

Conclusions

We studied principles of ethylbenzene oxidation under the presence of isopropylbenzene initiator and phthalimide catalysts as well as influence of different parameters: temperature, reaction time, concentration of catalyst/initiator. Thus, based on the studies conducted, it is possible to recommend the following reaction conditions of EB oxidation: phthalimide catalyst content of 3% wt. of hydrocarbon taken for oxidation, temperature is 130 °C, reaction time is 3 h. The content of formed EB HP is 15.1% wt., the selectivity of formation of EB HP is 91.5 %, which is almost 2 times higher than the parameters of the oxidation process of EB at the Nizhnekamsk chemical plant. The authors realized, that the presence of *N*-HPI in the process of liquid-phase oxidation of ethylbenzene allows us to increase the speed of hydrocarbon oxidation at maintenance of high (over 90%) selectivity of hydroperoxide formation approximately by 1.5-2.0 times. Consequently, application of 4-methyl-*N*-HPI in the ethylbenzene oxidation reaction provides the achievement the same qualitative indices of selectivity, hydrocarbon conversion, as in the case of application of *N*-HPI, with reduction of reaction time by 2 times. We conducted a balance experiment and compiled a material balance, which is important for the industrial implementation of this process. It allows us to monitor the material flows of raw materials, semi-products, plan the costs of reagents, and form an idea of the cost of the final product and the amount of waste.

Hence, the use of phthalimide catalysts increases the efficiency of ethylbenzene hydroperoxide production. It can be used to improve the technology of propylene oxide and styrene production - valuable products of basic chemical and petrochemical synthesis.

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