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## Intensification of Cyclohexanone Purification Stage from Impurities in Caprolactam Production Using Phase Transfer Catalysis

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**Abstract**—Impurities in the oxidate, which was produced in the oxidation of cyclohexane in an industrial environment, were analyzed and identified. It is found that the amount of esters and ethers is 30% of the impurities produced, among which a cyclohexyl ethers amount is more than 50%. The process of purifying the oxidate from the impurities by hydrolysis in the presence of phase transfer catalysts and without them was studied. It has been shown that the use of trioctylmethyl ammonium chloride (Aliquat-336) in the the stage of saponification of esters enabled a removal of 90–96% of esters with reducing of reaction time in a 1.5-fold, in contrast to non-catalytic process.

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It is known that the quality of finished caprolactam directly depends on the quality of cyclohexanone, which is intermediate in its production. Purification of cyclohexanone is paid much attention; complexity of the process consists in the presence of a wide range of impurities resulted and in their low content ( $10^{-3}$ – $10^{-4}$  mol L<sup>-1</sup>).

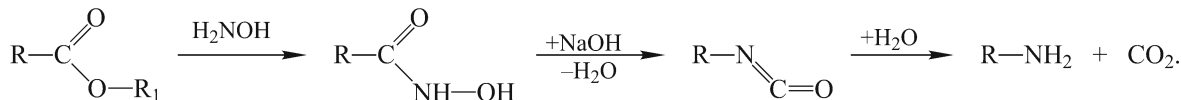
Esters, aldehydes, alcohols, carboxylic acids, and unsaturated peroxy compound are major impurities contained in the cyclohexanone [1, 2]. Getting of a small amount of these compounds to the finished cyclohexanone can significantly affect a quality indicator such as the permanganate index (content of easily oxidized impurities).

Esters (mainly, difficult-to-saponify esters of monocarboxylic acids) in an oximation stage at treating with hydroxylamine form hydroxamic acids, whose traces can reach a distillation stage, where in the interaction with the alkali they undergo Lossen rearrangement to form the amine [3]:

In industry there are several consecutive purification stages of oxidate: neutralization of acids, saponification (hydrolysis) of esters, and distillation. On saponification stage, which proceeds in the presence of 5–10% aqueous alkali solution, the amount of impurities is reduced as a result of hydrolysis of esters.

However, in accordance with an experience of existing manufactures the removal of ester impurities can be achieved only to 50–70% (with their concentration in oxidate entering the saponification stage of about 1–1.5 wt %).

Previously [4], it was found that an increase in the saponification temperature gives better removal of esters, but this leads to the formation of condensation products of cyclohexanone. It is shown that with increasing the temperature from 30 to 120°C the amount of the condensation products (resins) increases by 10 times.



Furthermore, at increasing the temperature the process should be carried out under pressure that requires a large capital outlay due to changes in equipment design of the process. Therefore, for enhancing the process it is necessary to find other ways.

It is known that the rate of hydrolysis of esters in a heterogeneous system, can be increased by using phase transfer catalysts (PTC) [5–9]. As a result of studies of the hydrolysis reactions of esters it was found that the process using PTC is suitable for sterically hindered esters, but in those cases where the ester has long carboxyl acid side chain, carboxylate can form associates with the cation of the catalyst, and the catalyst effect is reduced or completely disappears. Thus, efficiency and mechanism of the reaction under phase transfer catalysis should be considered only relative to a specific reaction systems.

The study purpose is identification of impurities in the oxidate entering the stage of saponification, investigation of the ester saponification process in the presence of PTC.

## EXPERIMENTAL

Analysis of oxidate (a product obtained by oxidation of cyclohexane on the catalyst, cobalt naphthenate, at a temperature 157–158°C, conversion 4.5–5%, selectivity in term of a total amount of cyclohexanol and cyclohexanone 55–57%) was performed by gas chromatography-mass spectrometry using a Shimadzu GCMS QP2010 Ultra device. Conditions for the analysis: capillary column DB-1ms of 30 m × 0.25 mm, injector temperature 250°C, column thermostating mode 60°C–(5 min)–10° min<sup>-1</sup>–260°C, carrier gas helium, a split ratio 1/100.

Most components of oxidate entering hydrolysis stage were identified by the mass spectra available of the spectral database NIST (components nos. 1–20, 22, 25, 27, 31, 33) [10]. The remaining components were identified by the products of fragmentation of the molecular ions [11]. Sum of ethers and esters was 30% of the impurities produced, the amounts cyclohexyl among them was more than 50%. The total amount of impurities in the oxidate determined by gas-liquid chromatography was on average 1.5–2% (see the table). Two esters: dibutyl adipate (DBA) and dicyclohexyl adipate (DCHA) were taken as model objects of the most difficult-to-saponify esters. Aqueous sodium hydroxide (5% in the case of DBA and 10% in the case of DCHA) was used as hydrolyzing agent; trioctylmethyl ammonium chloride ([N(C<sub>8</sub>H<sub>17</sub>)CH<sub>3</sub>]Cl,

TOMAC, Aliquat-336), tetrabutylammonium bromide ([N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>]Br, TBAB), benzyltriethylammonium chloride ([N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>C<sub>7</sub>H<sub>7</sub>]Cl, TEBA).

## RESULTS AND DISCUSSION

It is known that the efficiency of the catalyst depends on its structure and reaction conditions. Thus, in neutral or weakly alkaline media high lipophilic catalysts of Aliquat-336 or Catamine AB are active, but in systems with strong alkali more hydrophilic catalyst such as TEBA are preferred [12]. In the study of 10% NaOH solution the efficiency of both high lipophilic (TOMAC and TBAB) and low lipophilic (TEBA) catalysts were compared.

The study of ester saponification process under PTC conditions was performed in a model system that was a mixture close to industrial conditions (approximately 40% of cyclohexane, 40% of cyclohexanol, 20% of cyclohexanone), in which modeling esters were added in an amount of 5 wt % (calculation in term of the organic substrate). The mixture was heated to a preset temperature (70°C) and stirred until complete dissolution of ether, then the catalyst and alkali solution (preheated to a desired temperature) were rapidly added, and finally sampling was conducted maintaining the ratio between the phases.

Samples were analyzed by the gas-liquid chromatography. A sample preparation was performed as follows: the sample was neutralized with hydrochloric acid until neutral reaction to remove the residual alkali and the water, then after anhydrous magnesium sulfate was added, kept for 30 min and filtered off. In the obtained sample the internal standard (dibutyladipate) was entered.

Chromatographic analysis was performed on a software and hardware complex Hromatek-Analitik based on a chromatograph Crystal-2000M with the following parameters: capillary column with grafted phase DB-1 of 101 m × 0.25 mm; column temperature 200°C–15° min<sup>-1</sup>–260°C; evaporator temperature 300°C, detector temperature 270°C; carrier gas helium; the split ratio 1/80; analysis time 30 min.

The general PTC scheme for the hydrolysis of esters using Starks model are shown in Scheme 1: the catalyst passes through the phase interface performing permanent transitions from phase to phase.

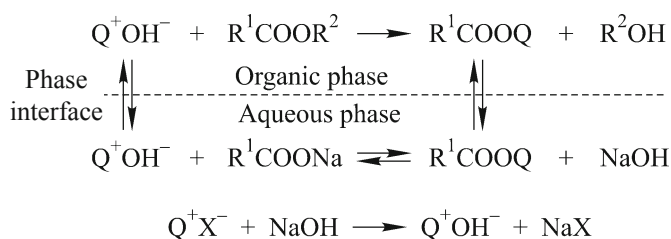
It is known that when extraction of OH<sup>-</sup> on the organic phased are required, it is better to use ammonium

## Impurities in oxidate entering the saponification stage

Impurities no.	Output time, min	Concentration, <sup>a</sup> %	Compound
1	2.54	0.76	<i>n</i> -Propylacetate
2	2.80	15.76	Methylcyclohexane
3	2.91	0.89	Ethylcyclopentane
4	3.09	8.94	1-Pentanol
5	3.19	0.50	Toluene
6	3.30	2.39	Cyclopentanol
7	3.95	6.09	Hexanal
8	4.77	2.51	1,2-Epoxy cyclohexane
9	5.05	1.69	Ethylbenzene
10	6.31	3.21	2-cyclohexen-1-one
12	7.49	1.56	Cyclohexyl formate
13	8.08	2.94	Hexanoic acid
14	9.18	2.61	1,5-Pentanediol
15	9.44	1.33	Cyclohexylacetate
16	9.62	3.90	1,2-Cyclohexanediol
17	10.5	13.08	1,3-Cyclohexanediol
18	11.42	0.44	Cyclohexyl propionate
19	12.53	0.49	Hexyl pentanoate, pentylhexanoate
20	13.09	1.12	Cyclohexylbutanoate
21	13.87	2.46	1,6-Hexanedal
22	14.73	4.29	Cyclohexyl pentanoate
23	14.96	0.39	Hexylcyclohexyl ester
24	15.23	5.56	Dicyclohexyl ether
25	15.52	0.99	Adipic acid pentyl ester
26	16.79	6.62	Glutaric acid hexyl ester
27	16.95	0.80	2-(Cyclohexenyl)cyclohexanol
28	17.26	1.59	Glutaric acid monocyclohexyl ester
29	17.8	0.74	Cyclopentanecarboxylic acid pentyl ester
30	18.35	2.76	Succinic acid dicyclohexyl ester
31	18.55	0.65	1'-Hydroxy[1,1'- bicyclohexyl]-one-2
32	18.63	0.56	1,2'-dihydroxy[1,1'-bicyclohexyl]
33	19.17	0.33	Bicyclohexyl-2,3'-dione
34	19.67	1.16	Cyclopentanecarboxylic acid cyclohexyl ester
35	20.35	0.90	Adipic acid butyl hexyl ester
		Σ 100	

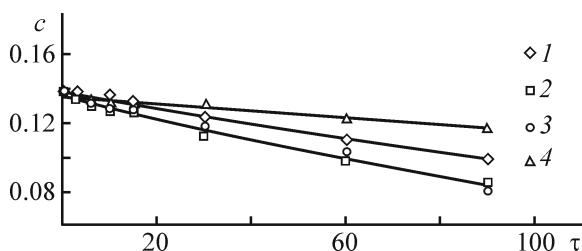
<sup>a</sup> Concentration are in the form of percentage of the total amount of the impurities equal to 1.5%.

## Scheme 1.



salt containing a lipophilic cation and anion, for which  $\Delta G_7^\circ$  (thermodynamic potential of ion transfer from the aqueous phase to the organic) is very high ( $\text{F}^-$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ).

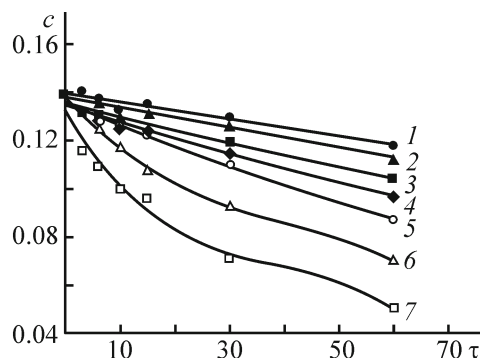
Figure 1 shows results of experiments with different catalysts. It is seen that the catalytic effect is due to the chemical nature of alkyl groups composed PTC and also associated with their length and structure, which



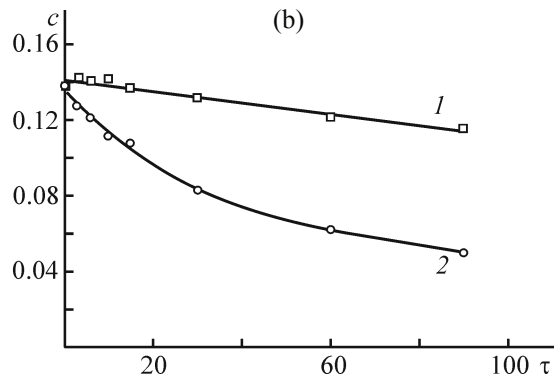
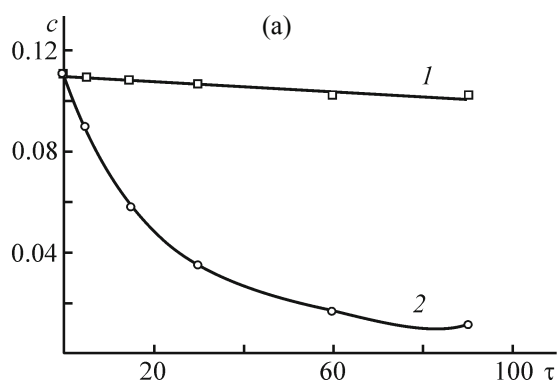
**Fig. 1.** Change DCHA concentration  $c$  (M) in time  $\tau$  (min) in hydrolysis in the presence of various PTC. Conditions:  $c(\text{DCHA}) = 5$ ,  $c(\text{NaOH}) = 10$ ,  $c(\text{PTC}) = 0.5$  wt %;  $70^\circ\text{C}$ . (1) TEBAC, (2) TBAB, (3) TOMAC, (4) without a catalyst.

determine compatibility with an organic substrate, the surface active properties, which provide the transfer of hydroxyl anions. All studied quaternary ammonium salts showed in a varying degree the catalytic effect. The greatest increase in the reaction rate was observed for catalysts TBAB and TOMAC; TEBAC exhibited less activity in the hydrolysis reaction, due likely to its less lipophilicity.

The effect of the PTC amount on the hydrolysis process was studied on an example of the catalyst TOMAC (Fig. 2). It was found that in the studied concentrations TOMAC belongs to a class of phase transfer catalysts, which do not block the interface. With increasing the PTC concentration more than 1.5% significant darkening of the reaction mixture occurs that may be associated with resinification. Further studies were conducted using the catalyst in the amount of 0.5 wt %.

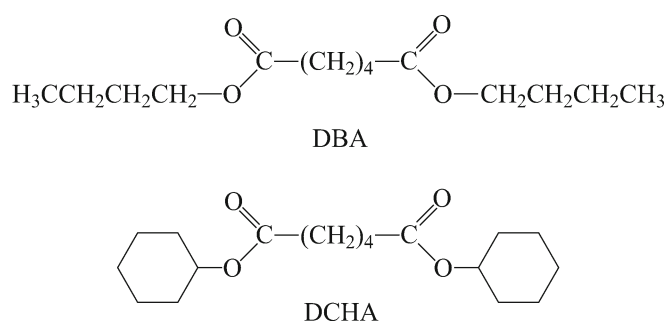


**Fig. 2.** DCHA change in concentration  $c$  (M) at time  $\tau$  (min) in hydrolysis in the presence of various amounts of PTC. Conditions:  $c(\text{DCHA}) = 5$ ,  $c(\text{NaOH}) = 10$  wt %;  $70^\circ\text{C}$ .  $c(\text{PTC})$ , wt %: (1) 0.2, (2) 0.3, (3) 0.5, (4) 0.6, (5) 0.8, (6) 1.2, (7) 1.4.



**Fig. 3.** Change of concentration of ester  $c$  (M) during the time  $\tau$  (min) in hydrolysis without PTC (1) and in the presence of volumes (2) at  $70^\circ\text{C}$ . Ester: (a) DBA, (b) DCHA. Conditions: (a)  $c(\text{DBA}) = 5$ ,  $c(\text{NaOH}) = 5$ ,  $c(\text{PTC}) = 1.5$  wt %; (b)  $c(\text{DCHA}) = 5$ ,  $c(\text{NaOH}) = 10$ ,  $c(\text{PTC}) = 1.5$  wt %.

Saponification of DBA and DCHA was conducted in the presence of TOMAC. The results of the experiments are shown in Fig. 3. As can be seen, the use of PTC significantly accelerates the hydrolysis process: in the case of DBA, the rate increases by 25 times (for 1.5 h the conversion was 90% compared to 8% in the case of non-catalytic process); and in the case of DCHA the rate increases by 5 times (the conversion up to 70% achieved for 1.5 h compared to 18 % of non-catalytic process). The lower rate in the case of DCHA can be explained by steric hindrances associated with the presence of two bulk substituents at the carboxyl group:



### CONCLUSIONS

Thus, in the concentrations of the catalysts, trioctylmethyl ammonium chloride (0.2–1.4 wt %) conducting saponification of the sterically hindered ester under phase-transfer catalysis enables reducing the contact time with increasing the conversion of the difficult-to-saponify esters 3–4 times (up to 90–96%), without changing the hardware design.

### ACKNOWLEDGMENTS

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