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Catalytic Condensation of Carbonyl Compounds during the Synthesis of Cyclohexanone in the Production of Caprolactam

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Abstract—Kinetic features of the condensation processes of carbonyl and unsaturated impurities in cyclohexanone have been studied using model mixtures in a heterophase system in the presence and absence of phase-transfer catalysts. It has been shown that linear aldehydes are condensed with cyclohexanone in the heterophase system in the presence and absence of phase-transfer catalysts under mild conditions (30–50°C). Noncarbonyl unsaturated compounds (e.g., 2-cyclohexene-1-ol) can be removed only at temperatures above 100°C in the presence of acidic catalysts (e.g., high-temperature sulfonated cation-exchange resins). Unsaturated cyclic ketones are characterized by both alkylation reactions over acid catalysts and aldol condensation reactions in the presence of an alkali, thereby suggesting the possibility of their elimination at different cyclohexanone purification steps. The theoretical models built can be used to develop an effective cyclohexanone purification technology that will substantially enhance the manufacturability of high-purity caprolactam and polyamide.

Keywords: cyclohexanone, caprolactam, condensation, phase-transfer catalysis

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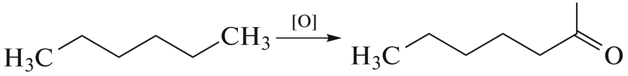
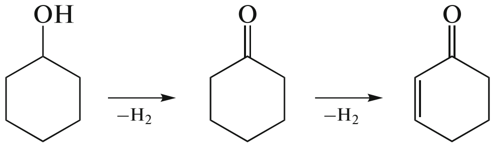
During the oxidation of cyclohexane to cyclohexanone in the production of caprolactam, a large number of oxygen-containing impurities are formed—more than 50 compounds (saponifiable and unsaponifiable) which possess various reactivities [1–4]. This complicates the selection of the optimum conditions for the synthesis and purification of the target products.

According to published data [5–7], aldehydes (e.g., butanal, pentanal, and hexanal) and unsaturated compounds (e.g., 2-cyclohexene-1-one) are the most detrimental unsaponifiable impurities that have negative influence on the quality of cyclohexanone and caprolactam. Linear aldehydes are formed as a result of the oxidation of *n*-butane, *n*-pentane, and *n*-hexane present in crude cyclohexane:



Unsaturated cyclic ketones are formed as a result of both oxidation of cyclohexane and dehydrogenation of cyclohexanol [8]:



In [9] we performed chromatographic–mass spectrometric analysis of industrial cyclohexanone synthesis products . The impurities were identified by existing mass spectra from spectral databases. As a result, it was shown that crude cyclohexanone contained about 6 wt % unsaponifiable impurities including 3.1% compounds containing the aldehyde group, 1.5% compounds containing the keto group, 1.1% hydrocarbons, and 0.1% unsaturated compounds. Some of them have both functional groups and unsaturated bonds in their molecule, e.g., 2-cyclohexene-1-one, 1-butoxy-2-cyclohexene, etc. When these compounds enter the next production stages (oximation, Beckmann rearrangement, and polymerization) together with cyclohexanone, they form impurities, due to which the mechanical strength of the polyamide fiber drops below the minimum requirements [10]. Thus, it was found [6] that 2-cyclohexene-1-one transforms into the corresponding unsaturated oxime and further to the unsaturated lactam (azocycloheptene-2-one) at the stage of Beckmann rearrangement. The latter sharply decreases the quality of caprolactam; thus, the permanganate number drops from 22500 to 2500 s already at the concentration of the impurity of 25 mg per 1 kg of caprolactam.

The aim of this work is to study the kinetic characteristics and to find the optimum conditions for the removal of unsaponifiable impurities for the purpose

Table 1. Processes and process conditions in the heterophase system

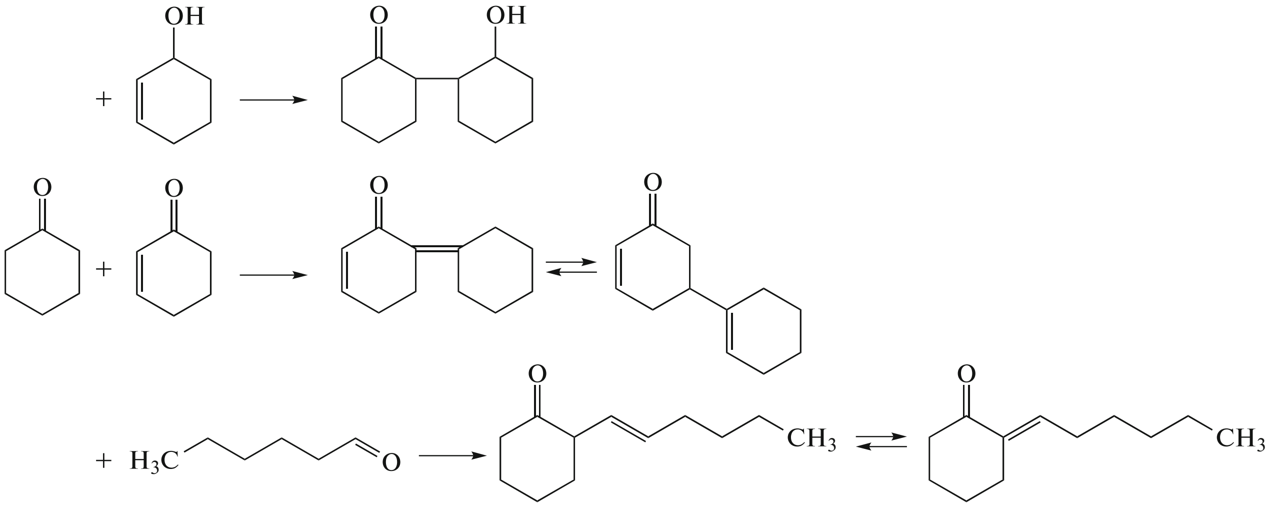
Process	Initial concentrations C_0, mol/L	T, °C
Reaction of 2-cyclohexene-1-ol (c-enol) with cyclohexanone in the presence of and without PTC (TOMAC)	C_0(c-enol) = 0.48 mol/L; C_0(NaOH) = 2.5 mol/L; C_0(PTC) = 0.01 mol/L;	70–80
Condensation of 2-cyclohexene-1-one (c-enone) with cyclohexanone in the presence or absence of PTC (TOMAC)	C_0(c-enone) = 0.50 mol/L; C_0(NaOH) = 1.75 mol/L; C_0(PTC) = 0.012 mol/L;	50–70
Condensation of hexanal (h-al) with cyclohexanone in the presence or absence of PTC (TOMAC)	C_0(h-al) = 0.47 mol/L; C_0(NaOH) = 1.75 mol/L; C_0(PTC) = 0.012 mol/L;	30–60

of improving the quality of commercial-grade cyclohexanone and caprolactam.

EXPERIMENTAL

The objects of the kinetic study were 2-cyclohexene-1-ol as a model of unsaturated impurities, hexanal representing aldehyde structures, and 2-cyclohexene-1-one modeling unsaturated/carbonyl impurities.

Three systems of the condensation reaction of cyclohexanone with unsaturated and aldehyde compounds in a heterophase system in the presence of alkaline, acidic, and phase-transfer catalysts (PTCs) were studied. Trioctylmethylammonium chloride (TOMAC) was used as the PTC:



I

II

III

Table 1 presents the conditions selected for studying in the heterophase system.

The quantitative determination was performed by means of GLC analysis on a Chromatec–Analitik software–hardware complex on the basis of a Kristall-2000M chromatograph using the internal standard method. For quantifying, a calibration coefficient was determined for each of the compounds relative to a standard. The standards used were pentanol-1 (for 2-cyclohexene-1-ol) and hexanol-1 (for 2-cyclohexene-1-one and hexanal).

The components were identified by the relative retention times of authentic pure substances or individual components synthesized for the purpose and thoroughly purified.

The catalytic studies were performed using model mixtures composed of the industrial “oxidate” (cyclohexane oxidation product after the stage of neutralization and removal of the main amount of unreacted cyclohexane, having the following composition: 38.8 wt % cyclohexane, 35.5 wt % cyclohexanone, 24.0 wt % cyclohexanol, and 1.7 wt % organic impurities) and the test substances 2-cyclohexene-1-ol, 2-cyclohexene-1-one, and hexanal. The volume ratio between the aqueous and organic phases was 1 : 1. A reactor equipped with a stirrer was charged with cyclohexanone, a model impurity under study, and a phase-transfer catalyst, and the mixture was heated to a set temperature and stirred until the complete dissolution of the impurity and the catalyst. Then, an alkali solution preliminary heated to the required temperature was rapidly introduced upon vigorous stirring. Reagent-grade potassium hydroxide, analytical grade sodium hydroxide, trioctylmethylammonium chloride (TOMAC) (assay >97.0 wt %), and sulfonated cation exchange resin Amberlyst 70 (Dow Chemical) were used as a catalyst.

Samples were taken at certain time intervals simultaneously from the organic and aqueous phases in equal amounts for the purpose of avoiding a change in the ratio between the reagents. The concentration of the impurity in the samples was analyzed by GLC.

Preliminarily, a set experiments on the determination of the influence of the stirrer rotational speed on the reaction rate was conducted. All the subsequent experiments were performed at a stirring speed of ~3500 rpm, which corresponds to the kinetic region of the process.

2-Cyclohexene-1-ol was synthesized in this study from cyclohexene in two steps according to the procedure [11, 12]; the main substance content in the final product was more than 85 wt % (according to GLC data); T_b = 164–165°C. 2-Cyclohexene-1-one and hexanal were purchased from Sigma-Aldrich and had the purity of no less than 98.0 wt % according to GLC data.

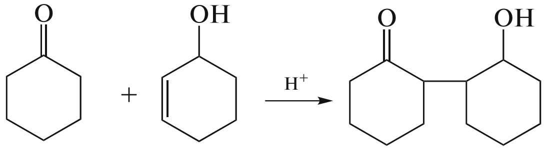
The kinetics of condensation reactions in the heterophase system was studied in the temperature range of 30–70°C (which is close to the conditions of the saponification step in the industry) by the initial rates using the isolation method [13].

The condensation reactions of 2-cyclohexene-1-ol with cyclohexanone in a homogeneous system in the presence of the KOH catalyst and in a heterophase system with the Amberlyst 70 catalyst were studied at 120°C, thus simulating the conditions of the industrial step of distillation in the temperature range of 90–130°C.

RESULTS AND DISCUSSION

Reaction of Cyclohexanone with 2-Cyclohexene-1-ol

The condensation reaction of cyclohexanone with 2-cyclohexene-1-ol was conducted in a two-phase system with an aqueous NaOH solution in the presence or absence of the PTC (TOMAC):



The results of the experiments are presented in Fig. 1. As is seen, this condensation reaction does not occur during saponification, and the presence of PTC has no effect on the process. Making the conditions harsher and changing the alkali (NaOH for KOH) also did not affect the rate of the condensation reaction.

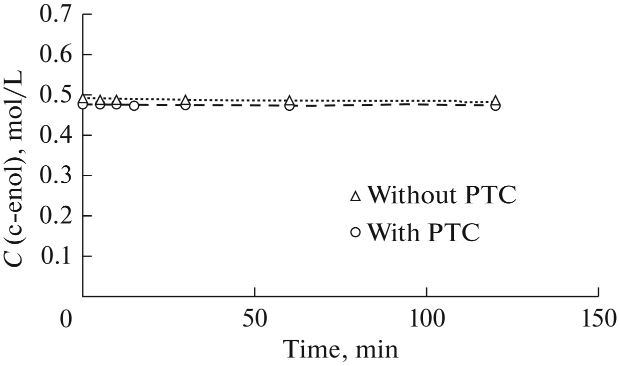


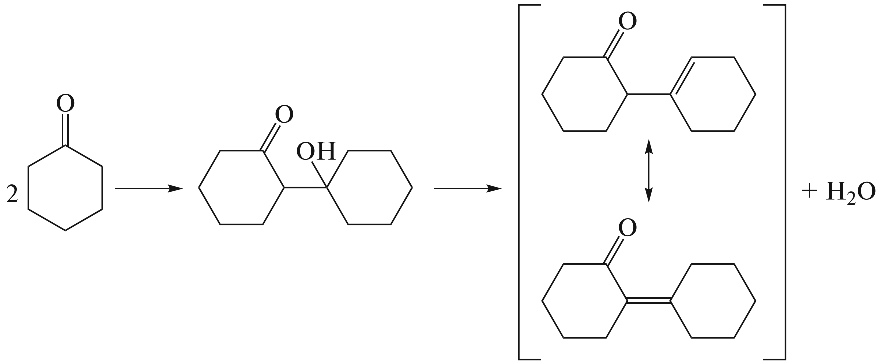
Fig. 1. Change in the 2-cyclohexene-1-ol concentration with time in the condensation process without a phase-transfer catalyst and in the presence of TOMAC. Conditions: C(c-enol) = 0.48 mol/L, C_0(NaOH) = 2.5 mol/L, C_0(PTC) = 0.012 mol/L, and T = 70°C.

A similar result was obtained in the case of the condensation reaction of 2-cyclohexene-1-ol with cyclohexanone under homogeneous conditions in the presence of KOH at 120°C. Thus, it can be concluded that the condensation of 2-cyclohexene-1-ol with cyclohexanone in the presence of an alkali occurs neither during saponification under mild conditions (about 70°C) nor at the step of distillation under more severe conditions (90–130°C); that is, the impurity cannot be removed.

An experiment in metal ampoules (in airtight cylindrical reactors made of stainless steel with a volume of 5 mL) was performed at 120°C in the presence of potassium hydroxide and the acid catalyst Amberlyst 70 for 2 h. The reactor was successively charged with cyclohexanone, 2-cyclohexene-1-ol, and the catalyst. Then the reactor was sealed and placed in an air-bath oven. After expiration of the reaction time, the reactor was cooled down and unsealed, and the resulting products of the condensation reaction were analyzed by GLC.

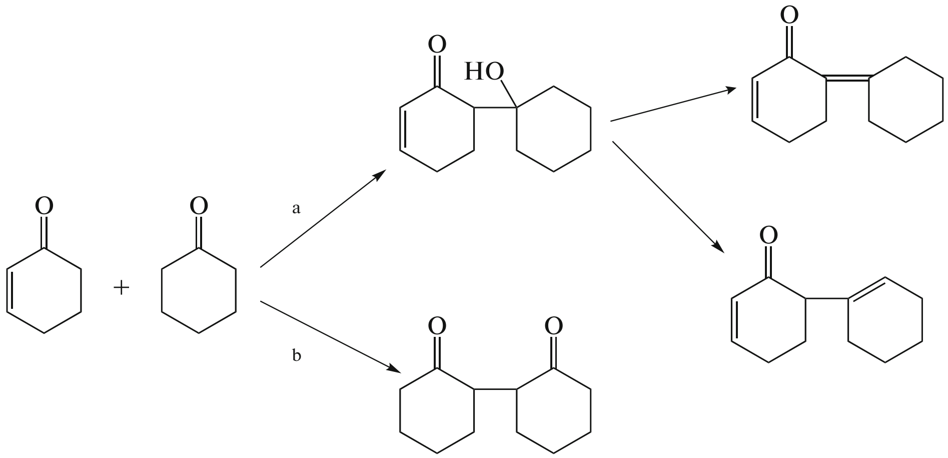
It was found that in the presence of acidic catalysts (high-temperature macroporous sulfonated cation-exchange resins), the condensation proceeded intensively, namely, the conversion of the reactant 2-cyclohexene-1-ol was 87% and the apparent rate constant for the condensation of 2-cyclohexene-1-ol with cyclohexanone was $k^0 = 0.044$ min^{-1} at 120°C (Fig. 2).

At the same time, it was found that the side self-condensation reaction of cyclohexanone intensely proceeded under these conditions to yield dimers in an amount of up to 30 wt % over 120 min of the reaction:



Reaction of Cyclohexanone with 2-Cyclohexene-1-one

The 2-cyclohexene-1-one molecule has an active carbonyl group, so that two types of reaction with cyclohexanone can be assumed, (a) the aldol condensation or (b) the alkylation:



To confirm this assumption, experiments on the condensation of 2-cyclohexene-1-one with cyclohexanone were performed in a two-phase system with an NaOH aqueous solution in the presence or absence of the PTC.

The results of the experiments are presented in Fig. 3. As can be seen, the condensation reaction of 2-cyclohexene-1-one with cyclohexanone is accelerated in the presence of the phase-transfer catalyst;

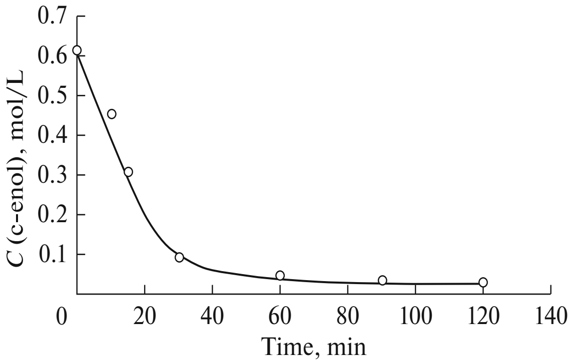


Fig. 2. Change in the 2-cyclohexene-1-ol concentration with time in the process of condensation with cyclohexanone over the Amberlyst 70 catalyst. Conditions: C(c-enol) = 0.6 mol/L, C_0(cat) = 10 wt %, and $T = 120°C$.

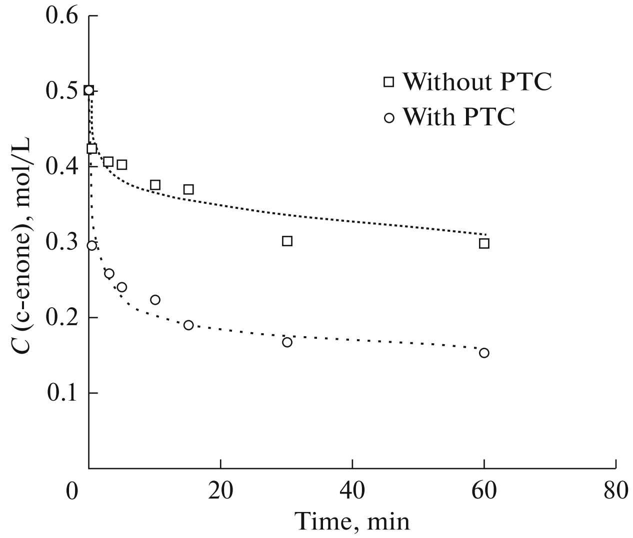


Fig. 3. Change in the 2-cyclohexene-1-one concentration with time in the condensation process without a phase-transfer catalyst and in the presence of TOMAC. Conditions: C(c-enone) = 0.50 mol/L, C_0(NaOH) = 1.75 mol/L, C_0(PTC) = 0.012 mol/L, and $T = 50$°C.

thus, the rate increases almost twofold and the conversion over 1 h is about 70% versus 40% in the case of the process without PTC.

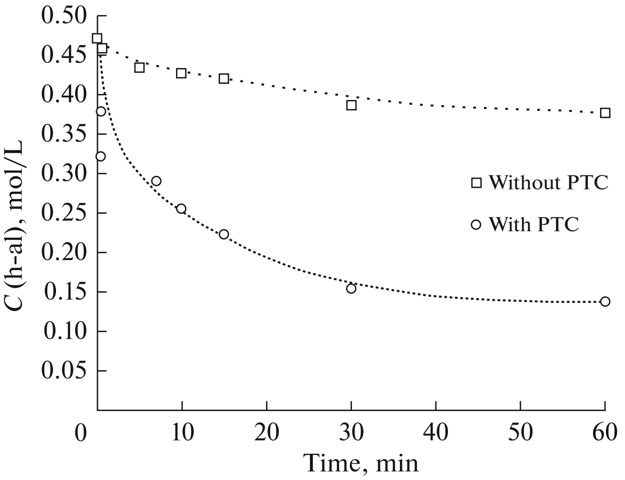
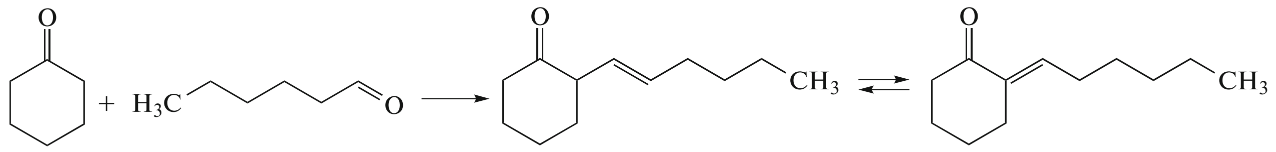


Fig. 4. Change in the concentration of hexanal with time in the process of its condensation with cyclohexanone in the presence and absence of a phase-transfer catalyst. Conditions: C_0(NaOH) = 1.75 mol/L, C_0(h-al) = 0.47 mol/L, C_0(PTC) = 0.012 mol/L, and $T = 30$°C.

Condensation of Aldehydes with Cyclohexanone

The condensation of cyclohexanone with hexanal was performed in a heterophase system with NaOH in the presence or absence of the TOMAC catalyst:



It was shown (Fig. 4) that the use of the PTC also accelerated the condensation process by more than twofold; the conversion over 1 h was 70% versus 30% in the case of the process in the absence of PTC.

The kinetic studies were performed under the pseudo-first-order conditions with respect to cyclohexanone and the alkali (the reactant and the catalyst were taken in eightfold and fourfold excesses, respectively, relative to hexanal). The reaction order with respect to the aldehyde was set to unity according to published data [14]. The results are presented in Figs. 5 and 6.

The apparent rate constants of the pseudo-first-order reaction at various temperatures were estimated for the heterophase process of hexanal condensation with cyclohexanone (Table 2).

Thus, the obtained results lead to the following conclusions: linear aldehydes (hexanal) readily interact with cyclohexanone under the alkali catalysis conditions in the temperature range of 30–60°C, and the rate increases almost twofold in the presence of PTC.

Due to the presence of the active carbonyl group, unsaturated cyclic ketones (2-cyclohexyl-1-one)

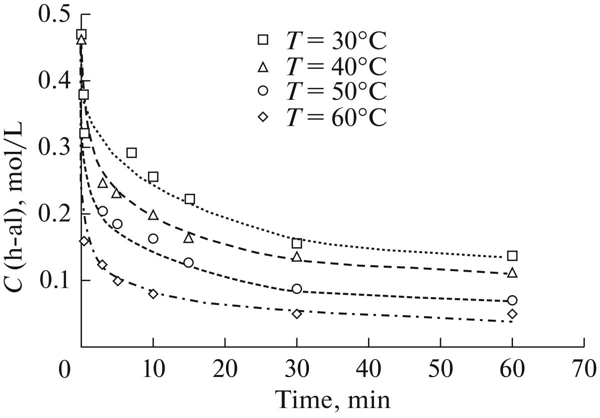


Fig. 5. Change in the concentration of hexanal with time at different temperatures for the condensation process in the presence of TOMAC. Conditions: C_0(NaOH) = 1.75 mol/L, C_0(h-al) = 0.47 mol/L, C_0(PTC) = 0.012 mol/L, and $T = 30$–60°C.

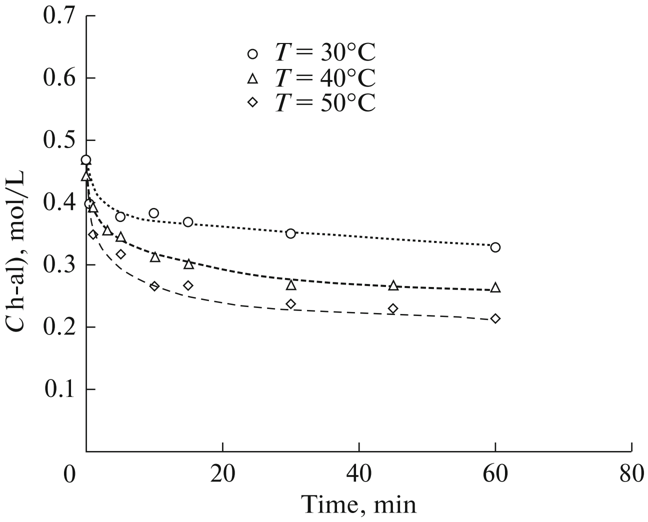


Fig. 6. Change in the concentration of hexanal with time at different temperatures for the process of heterophase condensation with cyclohexanone. Conditions: C_0(NaOH) = 1.75 mol/L, C_0(h-al) = 0.47 mol/L, and T = 30–50°C.

Table 2. Values for the apparent rate constant of the condensation reaction of hexanal with cyclohexanone

No.	T, °C	k^0_{app}, min^{-1}	
		with PTC	without PTC
1	30	0.125	0.077
2	40	0.208	0.133
3	50	0.286	0.135
4	60	0.435	–

interact with cyclohexanone via alkylation and aldol condensation reactions at 50–70°C. The rate of these reactions can be increased twofold by phase-transfer catalysis.

Unsaturated cyclic alcohols (2-cyclohexyl-1-ol) react with cyclohexanone only under the conditions of acid catalysis at temperatures above 100°C.

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