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> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

## **Base-Catalyzed Autocondensation of Cyclohexanone**

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Abstract—Autocondensation of cyclohexanone in air at 119–137°C, catalyzed with a solid alkali, was studied.

Cyclohexanone is an intermediate in industrial organic synthesis. Its characteristic feature is tendency to undergo autotransformations yielding a series of products [1]. In synthesis of caprolactam [2] and adipic acid [3], autocondensation is a side reaction, whereas in the first step of industrial synthesis of 2-phenylphenol (a bactericide) [4–6] or 2-cyclohexylcyclohexanol (a fragrance) [7], this is the principal process. To improve the existing processes involving cyclohexanone and develop new ones, it is appropriate to study the kinetic features of its autocondensation, primarily with the aim to obtain input data for simulation of flowsheets and process equipment.

The condensation is nonselective and yields a mixture of isomers; the resulting compounds with double bonds are not quite stable. Therefore, not all of the products of deep autocondensation of cyclohexanone have been identified. Compounds I-III have been studied in most detail [1, 8–10].



Formation of condensation products containing three and more rings was considered in [11–13]. The autocondensation is reversible, and, at elevated temperatures, compounds **II** and **III** are hydrolyzed back to cyclohexanone in the presence of water. The kinetic (in the range  $180-290^{\circ}$ C) and thermodynamic characteristics of this reaction, which is very important for processing by-products from caprolactam production [14], have been considered previously [15–17].

Data on liquid-phase autooxidation of cyclohexanone under various conditions are summarized in Table 1. It is seen that the major influence on the reaction rate is exerted by the temperature and catalyst. Virtually no data are available for the interval from 80 to 210°C in which the majority of industrial processes are performed. In this study, we examined the kinetics of cyclohexanone autocondensation in air at 119–137°C, catalyzed with a solid alkali.

## **EXPERIMENTAL**

The kinetics of liquid-phase aldol condensation of cyclohexanone was studied in a laboratory installation consisting of a round-bottomed three-necked glass flask fully immersed in a thermostat with silicone oil.

<i>T</i> , °C	Catalyst/solvent	Other conditions	Analytical method	References
25 30–70 80	Aqueous NaOH Alcoholic or aqueous-alcoholic KOH -/- -/CCl <sub>4</sub> -/CCl <sub>4</sub> + DPPH <sup>*</sup>	Analysis of aqueous and organic layers Preliminary purging with argon Under $N_2$ , in the dark, with removal of water	IR <sup>1</sup> H NMR GLC	[8] [9] [18]
119–137 210±0.5 (0.6 MPa)	KOH(cr.)/– Al, Fe oxides/decalin	In air, with removal of water Under $N_2$ , without removal of water	GLC GLC	This work [19]

Table 1. Kinetics of liquid-phase autocondensation of cyclohexanone

\* DPPH is 1,1-diphenyl-2-picrylhydrazyl (inhibitor of radical reactions).

Т,	τ, min	Cyclo- hexanone, wt %	Condensation products, wt %			
°Ċ			II + III	IV	V	
119	5	98.7	1.2	0.1	0.1	
	10	96.9	2.9	0.1	0.1	
	20	93.6	6.0	0.1	0.3	
	40	90.9	8.6	0.2	0.3	
	80	87.6	11.6	0.2	0.5	
	160	84.2	14.7	0.5	0.6	
125	5	98.1	1.8	0.1	0.1	
	10	96.0	3.8	0.1	0.1	
	20	92.1	7.5	0.2	0.2	
	42	88.4	11.0	0.3	0.3	
	84	85.0	14.5	0.5	0.5	
	160	81.4	17.3	0.6	0.7	
129	5	95.9	3.7	0.2	0.1	
	10	92.7	6.9	0.2	0.3	
	20	89.4	10.0	0.3	0.4	
	40	85.8	13.0	0.5	0.5	
	80	81.7	17.0	0.6	0.7	
	160	76.7	21.4	0.9	0.9	
133	5	95.0	4.0	0.2	0.1	
	10	92.0	6.9	0.2	0.2	
	20	88.5	11.3	0.3	0.3	
	40	84.4	14.4	0.4	0.2	
	80	79.0	18.2	0.6	0.5	
	160	72.3	25.3	1.4	1.0	
137	5	92.4	7.1	0.3	0.2	
	10	90.2	9.3	0.2	0.3	
	20	86.0	13.2	0.4	0.5	
	40	79.6	18.7	0.8	0.8	
	80	68.0	28.7	1.7	1.5	
	160	56.0	38.2	3.5	2.4	

 Table 2. Kinetic study of base-catalyzed autocondensation

 of cyclohexanone

The flask was equipped with a reflux condenser with a Dean–Stark trap, a high-speed glass stirrer with a glass hydroseal, and a control thermometer. The temperature in the flask was maintained with an accuracy of  $\pm 0.2^{\circ}$ C.



**Fig. 1.** Variation of the concentrations c of (1) cyclohexanone and of its condensation products (2) II + III and (3) IV with time  $\tau$  at 137°C.

Five experiments were performed at 119, 125, 129, 133, and 137°C. The flask was charged with 240 ml of purified cyclohexanone (main substance content >99.5%), which was preliminarily kept at the experimental temperature for 40 min. Granulated KOH (chemically pure grade), 2.4 g, was added with vigorous stirring. The time of mixing of the alkali with cyclohexanone was considered to be the start of the process. Samples of the reaction mixture (2-3 ml) were taken with a glass syringe 5, 10, 20, 40, 80, and 160 min after the start of the reaction. The samples were transferred into glass test tubes containing 1-tetradecene (pure grade, distilled). The reaction in a withdrawn sample was stopped by rapid cooling. Preliminary experiments showed that change in the reactant concentrations after rapid cooling to -20°C was negligible.

The amount of water collected in the Dean–Stark trap was insignificant. The maximum amount was about 5 ml at the highest experimental temperature (137°C). Therefore, despite the fact that the distillate was an azeotropic mixture of water and cyclohexanone, changes in the amount of cyclohexanone in the flask were negligible.

Samples were analyzed by gas–liquid chromatography (GLC) on a Tsvet-800 device (flame ionization detector; 2000 × 3-mm steel column packed with Chromaton N-Super + 3% OV-1; column temperature schedule: 140°C, 25 min; heating to 190°C at a rate of 25 deg min<sup>-1</sup>; 190°C, 35 min; vaporizer and detector temperatures 200°C; carrier gas nitrogen).

According to our results and those of Kim et al. [11], GLC makes it possible to determine the ratios of condensation products differing in the number of cyclohexane rings, but not the ratios of particular isomers, because the products undergo isomerization in the chromatographic column in the course of the analysis. Thus, we determined the total amount of products with two ( $\mathbf{II} + \mathbf{III}$ , retention time 10 min), three (IV, 35 min), and more (V, 52 min) cyclohexane rings. This assignment was based on the retention times of authentic samples of II [16], III [20], cis-2,6di(1-cyclohexen-1-yl)cyclohexanone (a representative of compounds IV) [13], 2,6-dicyclohexylidencyclohexanone [21], and dodecatriphenylene (a representative of compounds V) [22]. Compound I is thermally unstable [10] and decomposes in the course of the kinetic experiment.

The concentrations of cyclohexanone and its condensation products (Table 2) were calculated from the chromatograms using 1-tetradecene (retention time 5 min) as internal reference [23].



Fig. 2. Variation of the concentrations c of (a) cyclohexanone and (b) II + III with time  $\tau$  of autocondensation at (1) 119, (2) 125, (3) 129, (4) 133, and (5) 137°C.

The kinetic curves of consumption of cyclohexanone and accumulation of condensation products are shown in Figs. 1 and 2. The reaction order evaluated from these curves is abnormally high for all the temperatures except 137°C. We failed to interpret the kinetic curves in terms of formal kinetics and to suggest the condensation mechanism; apparently, several reactions occur simultaneously.

## CONCLUSIONS

(1) A procedure was developed for GLC analysis of products of cyclohexanone autocondensation, which differ in the number of cyclohexanone rings.

(2) The temperature dependences of the concentrations of the starting cyclohexanone and reaction products in autocondensation in air were obtained. The reaction is accompanied by formation of "heavy" condensation products in the entire temperature range studied (119–137°C); at 137°C, their amount reaches 4.5% in 2 h.

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