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Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN and T. I. NARYSHKINA

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Abstract

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CATALYTIC DEHYDROGENATION OF CYCLOPENTENE

Only a few studies have been devoted to the investigation of transformations of cyclopentene under conditions of dehydrogenation catalysis. Thus, Plate ([1],[2]), passing cyclopentene at 450–500° over vanadium and chromium oxides deposited on alumina, observed partial dehydrogenation of cyclopentene to cyclopentadiene with simultaneous hydrogenation to cyclopentane.

Still earlier, Zelinsky and Arbuzov ([3]) showed that cyclopentene is quite stable under conditions of its contact with aluminum and chromium oxides at 450°. Greensfelder and Voge ([4]) found that, in the presence of a zirconium aluminosilicate catalyst at 500°, cyclopentene is converted mainly into aromatic hydrocarbons.

Vanass and Walters ([5]), studying the thermal decomposition of cyclopentene in a static system at 438–548° and a pressure of 38–244 mm, showed that under the conditions they selected the principal reaction is dehydrogenation; however, the degree of conversion of cyclopentene did not exceed 25%.

There are a number of works ([6]–[10]) in which it is shown that cyclopentadiene can be obtained directly by dehydrogenation of cyclopentane, but the yields of cyclopentadiene under these conditions did not exceed 3–11%.

We set ourselves the task of finding conditions under which the conversion of cyclopentene into cyclopentadiene would proceed most completely. It was found that at 600°, in the presence of an alumina–chromia–potassium catalyst described earlier by one of us ([11]), cyclopentadiene can be obtained in yields up to 58%. Since the dehydrogenation of cyclopentene to cyclopentadiene

$$\text{cyclopentene} \rightleftharpoons \text{cyclopentadiene} + \text{H}_2$$

proceeds with an increase in volume, and, consequently, lowering the pressure should shift the equilibrium from left to right, the reaction was carried out under reduced pressure (20 mm).

Cyclopentene was obtained by dehydration of cyclopentanol over anhydrous magnesium sulfate at 310–315° and had the following properties: b.p. 44.5°/758

mm; d_4^{20} 0.7714; n_D^{20} 1.4220; MR_D found 22.36; MR_D calculated for C_5H_8, F_1 22.62.

Dehydrogenation was carried out by the flow method in the presence of a catalyst consisting of oxides of aluminum, chromium, and potassium with a molar ratio of the components 42 : 7 : 1. In each experiment, 50 ml (38.6 g) of cyclopentene was taken and fed onto the catalyst at a rate of 1.0 h^{-1}.

The resulting catalyzates, after determination of their cyclopentadiene content by the Afanas' ev method ([12]), were subjected to careful fractionation—

on a column with an efficiency of 70 theoretical plates. The isolated fractions were analyzed by optical and chemical methods, while the composition of the gaseous products collected in traps cooled with liquid nitrogen was determined first on an Orsat–Lunge apparatus, and then in greater detail by a chromatographic method ([13]). The butadiene content in the gas was determined on Korotkov' s apparatus ([14]).

Table 1

Dehydrogenation of cyclopentene

Temperature, °C	Catalyst yield, g	Catalyst yield, %	Catalyst properties, n_D^{20}	Catalyst properties, d_4^{20}	Cyclopentadiene content in the catalyst, %	Yield of cyclopentadiene, %, calculated on the cyclopentene taken	Coke formation, %
500	31.9	82.4	1.4410	0.8015	55	45	8
500	32.4	83.6	1.4412	0.8019	53	44	7
550	31.1	80.5	1.4440	0.8039	69	56	8
550	29.8	76.9	1.4452	0.8047	70	54	8
600	29.5	76.1	1.4465	0.8085	76	58	10
600	28.7	74.1	1.4462	0.8095	74	55	11
650	26.3	68.5	1.4470	0.8090	77	53	13

The results of experiments on the dehydrogenation of cyclopentene are presented in Table 1. It can be seen from them that, as the temperature is raised from 500 to 650°, the cyclopentadiene content in the catalyst increases; however, the maximum yield of cyclopentadiene (58%, calculated on the cyclopentene taken) was obtained at 600°. The fractional composition and properties of the

Fig. 1. Distillation curve of the cyclopentene catalyst

Figure 1: Fig. 1. Distillation curve of the cyclopentene catalyst

combined catalyst are presented in Table 2, and the distillation curve in Fig. 1. For fractionation, 120 g of substance were taken. From consideration of the data in Table 2 it is seen that the cyclopentene catalyst consists mainly of cyclopentadiene (the adduct with maleic anhydride melted at 161° ([8])), a small amount of unchanged cyclopentene, and residue.

Fig. 1. Distillation curve of the cyclopentene catalyst

Table 2

Fractional composition and properties of the cyclopentadiene catalyst

Boiling temperature, °C (at 753 mm)	Fraction yield, g	Fraction yield, %	Fraction properties, n_D^{20}	Fraction properties, d_4^{20}	Optical-analysis data*
41–42	63.7	53.0	1.4420	0.7968	Cyclopentadiene with a small admixture of cyclopentene
42–43	20.5	17.1	1.4360	0.7867	Mixture of cyclopentadiene and cyclopentene in equal amounts
43–45	13.2	11.0	1.4260	0.7793	Cyclopentene (~75%) and cyclopentadiene (~25%)
Residue	19.4	16.0	1.5100	–	
Losses	–	2.9	–	–	

* The optical analysis was carried out by Yu. P. Egorov, to whom we express our gratitude.

Analysis of the carbonaceous deposits on the catalyst showed that in composition they are close to the polymer of cyclopentadiene $(C_5H_6)_x$ (found, %: C 90.81; H 9.19; calculated for C_5H_6, %: C 90.84; H 9.16).

In the collected gaseous products, hydrogen (25%), ethane (16%), ethylene (23%), propane (20%), propylene (13%), and butadiene (3%) were detected.

It is of interest to note that cyclopentane was not found among the liquid products, as was observed by Plate ([1,2]) in the dehydrogenation of cyclopentene under atmospheric-pressure conditions. Apparently, the hydrogen-redistribution reaction under reduced pressure takes place hardly at all. However, the ethane and propane detected in the gaseous products make it possible to assume that the latter were formed as a result of hydrogenation of fragments of the cyclopentene molecule.

Thus, carrying out the dehydrogenation reaction of cyclopentene under reduced pressure on an active dehydrogenating contact makes it possible to substantially reduce side processes and to direct the given reaction toward the production of cyclopentadiene in high yield—up to 58% based on the cyclopentene taken. Along with dehydrogenation, under the stated conditions only to an insignificant extent do coke formation and hydrocracking of cyclopentene occur, leading to the formation of gaseous products predominantly of the C_2 and C_3 composition.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.