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Abstract

Full Text

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TRANSFORMATIONS OF ISOPROPENYLCYCLOPROPANE IN THE PRESENCE OF KIESELGUHR

Previously we showed that the three-membered ring of alkylcyclopropanes, in the presence of a number of catalysts, opens comparatively readily at the bond lying next to the substituent, with the formation of open-chain olefins ([1,2]). The first attempt to study, under these conditions, the behavior of hydrocarbons of the cyclopropane series in which the ring is conjugated with a double bond was unsuccessful, since at the very beginning of the experiment the catalyst was completely poisoned by the reaction products ([3]).

In the present work, by carrying out short-duration experiments and analyzing the catalyzates by gas-liquid chromatography, we were able to study such transformations in somewhat greater detail using isopropenylcyclopropane as an example. It turned out that in the presence of kieselguhr, under the same conditions, an alkylcyclopropane and a "conjugated" hydrocarbon of the cyclopropane series behave quite differently. Thus, at 100°, isopropylcyclopropane underwent 30% isomerization to olefins, and the weight of the catalyzate obtained corresponded to the weight of the hydrocarbon taken into the reaction.

Fig. 1. Chromatogram of an artificial mixture:
1—trans-2-methylpentadiene-1,3; 2—isopropenylcyclopropane; 3—cis-2-methylpentadiene-1,3; 4—2-methylpentadiene-1,4.

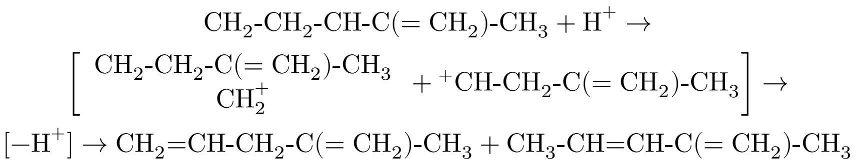
Under the same conditions (on a fresh catalyst), isopropenylcyclopropane in a 30-minute experiment gave only an insignificant amount of liquid catalyzate (8% of the weight of the initial hydrocarbon) and more than 90% polymer retained on the catalyst.

The polymeric product was readily separated from the catalyst by extraction with *n*-pentane and was a thick pale-yellow resin with a pleasant coniferous odor. It is intended to study the polymer in more detail later.

Analysis of the liquid catalyzates showed that they contain unreacted isopropenylcyclopropane, as well as all possible 2-methylpentadienes. The quantitative composition of the liquid reaction products is given in the experimental section; however, these data are of no special significance, since in the presence of kieselguhr double bonds in dienes can migrate.

As the polymer remaining on the catalyst was formed, the latter lost its activity, which could be observed in longer experiments. Thus, in a 200-minute experiment the weight ratio of liquid catalyzate to polymer (based on the catalyst weight) was no longer 8:92, as in the 30-minute experiment, but 53:47, and the total percentage conversion of isopropenylcyclopropane did not exceed 70%, instead of 93%.

The presence of 2-methylpentadienes in the catalyst can be explained by isomerization of the three-membered ring of isopropenylcyclopropane according to the following scheme:



$$\begin{gathered} \mathrm{CH_2\text{-}CH_2\text{-}CH\text{-}C(=CH_2)\text{-}CH_3} + \mathrm{H^+} \rightarrow \\ \left[\begin{matrix} \mathrm{CH_2\text{-}CH_2\text{-}C(=CH_2)\text{-}CH_3} \\ \mathrm{CH_2^+} \end{matrix} + {}^{+}\mathrm{CH\text{-}CH_2\text{-}C(=CH_2)\text{-}CH_3} \right] \rightarrow \\ [-\mathrm{H^+}] \rightarrow \mathrm{CH_2{=}CH\text{-}CH_2\text{-}C(=CH_2)\text{-}CH_3} + \mathrm{CH_3\text{-}CH{=}CH\text{-}C(=CH_2)\text{-}CH_3} \end{gathered} \tag{1}$$

The polymer—the principal product formed in the interaction of isopropenylcyclopropane with kieselguhr—may be formed either from methylpentadienes-1,3, i.e., as a secondary reaction product, or at an intermediate stage of the reaction, before stabilization of the carbonium ion, which itself may be the initial center of polymerization. It is not possible to make a definitive judgment about the reaction mechanism on the basis of the experimental data obtained in the present work; therefore we propose to continue these investigations. The very fact of intense polymerization occurring upon contact of a "conjugated" cyclopropane hydrocarbon with kieselguhr is, in our opinion, of considerable interest, since it indicates an increased reactivity of such systems.

Fig. 2. Chromatogram of 2-methylpentadiene-1,3.
1—trans-2-methylpentadiene-1,3; 2—cis-2-methylpentadiene-1,3

Fig. 3. Chromatogram of the catalyst obtained in the catalysis of isopropenylcyclopropane at 100°.
1—trans-2-methylpentadiene-1,3; 2—isopropenylcyclopropane; 3—cis-2-methylpentadiene-1,3; 4—2-methylpentadiene-1,4

Experimental Part

1. Synthesis and properties of the hydrocarbons

Isopropenylcyclopropane was obtained by dehydration of dimethylcyclopropylcarbinol according to the previously described method (4). Isopropylcyclopropane was obtained by hydro-

of isopropenylcyclopropane in an autoclave over a copper–chromium catalyst at 100–130°. 2-Methylpentadiene-1,4 and a mixture of stereoisomeric 2-methylpentadienes-1,3 (standards required for analysis of the catalyzates) were obtained by fractionation on a column of products from the pyrolysis of tert-amyl alcohol acetate, synthesized from methallyl chloride and acetaldehyde.

The constants of the hydrocarbons obtained, as well as literature data on the constants, are given in Table 1.

Table 1

Hydrocarbon	b.p., °C (760 mm)	n_D^{20}	d_4^{20}
Isopropenylcyclopropane	70.3	1.4255	0.7513
Isopropenylcyclopropane	70.33*	1.42550*	0.75153*
Isopropylcyclopropane	58.2	1.3863	0.6981
Isopropylcyclopropane	58.37*	1.38639*	0.69829*
2-Methylpentadiene-1,4	56.3	1.4057	0.6928
2-Methylpentadiene-1,4	56**	1.405**	0.694**
cis-, trans-2-Methylpentadiene-1,3	75.5	1.4462	0.7207
cis-, trans-2-Methylpentadiene-1,3	76**	1.446**	0.719**

- According to (5). ** According to (6).

2. Experimental procedure.

The catalytic experiments were carried out according to the procedure described earlier (1). As catalyst, "Kisatibi" kieselguhr was used in an amount of 10 ml, preliminarily heated at 120° in a stream of nitrogen until moisture had been completely removed. For each experiment a fresh portion of catalyst was used; the space velocity of passing the hydrocarbon over the catalyst was in all cases equal to 0.2 hr^{-1}.

In chromatography the liquid phase was a saturated solution of silver nitrate in glycerol (7, 8), and the support was diatomaceous brick with particle size 0.25–0.5 mm. A thermal-conductivity detector was installed in the apparatus. The analysis was carried out at 40° and a carrier-gas (nitrogen) flow rate at the inlet of 30 ml/min. Table 2 and Fig. 1 give the results of chromatographic determination of the composition of an artificial mixture prepared

Table 2

Hydrocarbons	Prepared, wt. %	Determined from the chromatogram, wt. %
2-Methylpentadiene-1,3 trans, cis-	36.2	32.64.2
2-Methylpentadiene-1,4	20.3	21.2

Hydrocarbons	Prepared, wt. %	Determined from the chromatogram, wt. %
Isopropenylcyclopropane	43.5	42.1

Table 3

Hydrocarbon	Duration of experiment, min	Weight of hydrocarbon passed, g	Weight of catalyzate, g	Catalyst charge, g	Conversion, %
Isopropylcyclopropane	60	1.70	1.70	–	30*
Isopropenylcyclopropane	30	0.75	0.07	0.69	93
Isopropenylcyclopropane	200	6.50	3.10	3.10	70.0

- The determination of olefins in this experiment was carried out with the aid of bromine numbers.

from the hydrocarbons obtained by us. The chromatogram of the mixture of 2-methylpentadienes-1,3 is shown in Fig. 2. It shows that the mixture contains 89.3% trans isomer and 10.7% cis isomer.

3. Catalytic experiments. The data obtained in the catalytic experiments are given in Table 3. The experiments were carried out at 100°. The data of Table 3 show that, under the same conditions, transformations in the case of isopropenylcyclopropane proceed considerably more intensively than in the case of isopropylcyclopropane. The weight of the liquid catalyzate in this case does not correspond to the weight of the initial hydrocarbon, since part of the reaction product remains on the catalyst in the form of a polymer. With time, the percentage conversion decreases as a result of poisoning of the catalyst.

Table 4

Hydrocarbons	At 100°, first 30 min.	At 100°, second 30 min.	At 100°, 200 min. of operation	At 150°, 30 min. of operation
Isopropenylcyclopropane	88.2	93.5	52.9	30.0
2-Methylpentadiene-1,3 trans	1.4	0.2	5.1	26.2
2-Methylpentadiene-1,3 cis	2.8	1.0	8.0	18.8

Hydrocarbons	At 100°, first 30 min.	At 100°, second 30 min.	At 100°, 200 min. of operation	At 150°, 30 min. of operation
2-Methylpentadiene-1,4	7.1	4.6	34.0	20.5
Not identified	0.5	0.7	0.0	4.4

The composition of the liquid catalyzates (in percent), obtained in experiments with isopropenylcyclopropane over different periods of catalyst operation at different temperatures, is given in Table 4. These data show that in all experiments the liquid catalyzates contain various 2-methylpentadienes, and the ratio of the isomers changes depending on the operating time and the reaction temperature. At 150°, in addition to 2-methylpentadienes-1,3 and 1,4, an unidentified impurity appears in appreciable amount. It may be assumed that these are 2-methylpentadienes-2,4, formed as a result of migration of the double bond in 2-methylpentadiene-1,4.

The chromatogram of the catalyzate obtained at 100° is shown in Fig. 3.

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