CATALYTIC CRACKING OF ETHYLIDENEDIISOPROPYLBENZENE

1957

SovietRxiv

Abstract

Full Text

CHEMISTRY

V. L. VAISER, V. D. RYABOV, and B. I. KRYVELEV

CATALYTIC CRACKING OF ETHYLIDENEDI-ISOPROPYLBENZENE

(Presented by Academician A. V. Topchiev, 3 VIII 1956)

The study of the catalytic cracking of ethylidenediisopropylbenzene was undertaken by us in connection with work on obtaining styrenes from diarylethanes. Such a study was also of interest from the standpoint of elucidating the chemistry and certain regularities of the catalytic cracking of this complex aromatic hydrocarbon; there is no information in the literature concerning this process. If the catalytic cracking of unsymmetrical diphenylethane ([1]) and ditolylethane ([2]) leads mainly to the formation of an aromatic hydrocarbon and the corresponding styrene, then the cracking of ethylidenediisopropylbenzene should be a more complex phenomenon because of the presence of isopropyl groups.

Ethylidenediisopropylbenzene was obtained by the alkylation reaction of isopropylbenzene with acetylene in the presence of the catalyst $H_3PO_4 \cdot BF_3$ ([3]). It is an oily, fluorescent liquid: b.p. 180—190°/10 mm; $d_4^{20} = 0.9655$; $n_D^{20} = 1.5465$; viscosity ν_{50} 9.1 cSt.

All cracking experiments were carried out at $600 \pm 5°$ in a quartz tube heated by a powerful electric furnace.

A temperature of 600° was chosen because it is optimal for the cracking of other diarylethanes, in particular for the cracking of ditolylethane, as we established in previous work ([2]).

The temperature was measured with a chromel-alumel thermocouple, the junction of which was located inside the catalyst bed. Cracking was carried out in the presence of a diluent—water—which in this case lowers the partial pressure of the product being cracked, reduces the contact time, and interacts with coke on the catalyst, thereby preventing rapid loss of activity of the latter.

It is known that at high temperatures water vapor causes a decrease in the total activity of an aluminosilicate catalyst, which is explained by a reduction in its surface area ([4]); however, the specific catalytic activity does not decrease in this case. In heterogeneous catalytic reactions, the use of the full surface of the catalyst depends on the ratio of the reaction rate to the diffusion rate.

The cracking of diarylethanes, especially at high temperatures (550—600°), apparently proceeds in the diffusion region, as a result of which mainly the external surface of the catalyst is used. Therefore, a decrease in the total surface area of

the catalyst under the action of water vapor should not substantially affect the rate of the cracking reaction, as we also observed.

The cracking experiments were carried out in a conventional apparatus. Accurate feeding of the feedstock and water was accomplished by means of clock mechanisms. Ethylidenediisopropylbenzene (hereinafter $C_{20}H_{28}$) was mixed in a three-way junction with water vapor heated in a stainless-steel steam superheater to 200—250°. The resulting mixture entered the cataly-

···-tic tube. The amount of catalyst in all experiments was 50 cm^3; the length of the catalyst layer was 17 cm.

The catalyzates were separated from water and, after appropriate treatment, were distilled under vacuum to separate the light cracking products from $C_{20}H_{28}$. Each time, the light cracking products were analyzed for their content of alkylstyrenes by titration with bromine in a solution of glacial acetic acid according to Rosenmund, after which they were distilled into fractions in a column with a dephlegmator. The gas was analyzed in a VTI apparatus.

Four catalysts were tested: the aluminosilicate catalyst "Gudri" and three activated clays—bentonite, askangel, and kaolin. The results of the experiments are given in Table 1.

Table 1

Catalyst	Space velocity	Contact time, sec.	Conversion to light products, %	Alkylstyrene content, %	Initial boiling point of catalyzate, °C	Amount of gas, l
"Gudri"	0.8	0.064	71	66.5	135	6.5
Bentonite	0.78	0.054	57.4	66.0	150	4.5
Askangel	0.8	0.065	67.4	51.5	138	4.0
Kaolin	0.8	0.064	57.3	57.5	135	3.5

Note. Temperature $600 \pm 5°$. Molar dilution

$$\frac{\text{mol. } H_2O}{\text{mol. } C_{20}H_{28}} = 60 \pm 5.$$

It is seen from Table 1 that the aluminosilicate catalyst "Gudri" possesses the greatest activity. In its presence, the conversion of $C_{20}H_{28}$ and gas formation were maximal. The composition of the gases in the different experiments varied within the following limits:

Fig. 1. a –distillation curve, b –curve of n_D^{20} values of the fractions

Figure 1: Fig. 1. a –distillation curve, b –curve of n_D^{20} values of the fractions

	Vol. %		Vol. %
CO_2	2–6	Ethylene	2–4
O_2	1–3	Propylene	40–60
CO	3–8	Higher olefins	–
		$C_nH_{2n} + N_2 + H_2$	30–40

The presence in the gas of a large amount of unsaturated hydrocarbons indicates the complexity of the course of the process, associated with reactions of hydrogen redistribution and cleavage of the isopropyl group.

A preliminary analysis of the catalyzates showed that they are a complex mixture of alkylstyrenes and products of their hydrogenation.

For a more complete study of the cracking products, part of the mixture of catalyzates from all experiments, in an amount of 40 cm^3, was subjected to distillation on a column with an efficiency of 25 theoretical plates.

Twelve fractions were collected, for which refractive indices, molecular weights, and the percentage content of alkylstyrene were determined. The results of the distillation are shown in Fig. 1,a. The maxima on curve *b* correspond to styrenes, and the minima to aromatic hydrocarbons with saturated side chains.

The results of the distillation and the analysis of each fraction separately allow us to conclude that the following compounds are present in the cracking products: ethylbenzene, styrene, isopropylbenzene, α-methylstyrene, diethylbenzene, ethylstyrene, and isopropylstyrene. Styrene was isolated from the 142 –148° fraction in the form of the dibromide (m.p. 73).

The primary reaction in the cracking of ethylidenediisopropylbenzene is cleavage at the C_{arom}—C_{ethylid} bond, as the weakest one. As a result, one would expect the formation of isopropylbenzene and isopropylstyrene:

$$(CH_3)_2CH—C_6H_4—CH(CH_3)—C_6H_4—CH(CH_3)_2 \rightarrow (CH_3)_2CH—C_6H_5 + (CH_3)_2CH—C_6H_4—CH{=}CH_2.$$

Fig. 1. *a* –distillation curve, *b* –curve of n_D^{20} values of the fractions

These compounds are contained in the cracking products in insignificant amounts. They undergo further transformations. Thus, isopropylstyrene can crack in the following directions:

$$(CH_3)_2CH—C_6H_4—CH=CH_2 \xrightarrow{+2H} CH_3CH_2—C_6H_4—CH=CH_2 + CH_4$$

$$(CH_3)_2CH—C_6H_4—CH=CH_2 \longrightarrow C_6H_5—CH=CH_2 + C_3H_6.$$

Under cracking conditions, isopropylbenzene does not split off the isopropyl group, as indicated by the absence of benzene in the cracking products. The formation of α-methylstyrene could be explained by dehydrogenation of isopropylbenzene, but our experiments on the cracking of isopropylbenzene under conditions analogous to those for the cracking of ethylidenediisopropylbenzene showed that α-methylstyrene is not formed. Probably, α-methylstyrene is a product of transformation of ethylidenediisopropylbenzene itself:

$$(CH_3)_2CH—C_6H_4—CH(CH_3)—C_6H_4—CH(CH_3)_2 \rightarrow CH_2=C(CH_3)—C_6H_5+CH_3CH_2—C_6H_4—CH(CH_3)_2.$$

A possible direction of the cracking of $C_{20}H_{28}$ is also the cleavage of one isopropyl group with the corresponding disproportionation.

hydrogen:

$$(CH_3)_2CH-C_6H_4-CH(CH_3)-C_6H_4-CH(CH_3)_2 \longrightarrow C_8H_6 + C_6H_5-CH(CH_3)-C_6H_4-CH(CH_3)_2$$

and further

$$C_6H_5-CH(CH_3)-C_6H_4-CH(CH_3)_2 \longrightarrow C_6H_5-CH=CH_2 + C_6H_5-CH(CH_3)_2$$

Moscow Petroleum Institute
named after I. M. Gubkin

Received
3 VIII 1956

CITED LITERATURE

1. M. Morton, P. V. Nicholls, *Can. J. Res.*, **26B**, 586 (1948).

2. V. L. Vaizer, V. D. Ryabov, S. Sh. Sokolina, *DAN*, **106**, No. 2 (1956).

3. V. L. Vaizer, *DAN*, **84**, No. 1 (1952).

4. S. K. Makarov, M. A. Kaliko, *Neft. khoz.*, No. 2 (1947).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.