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ALKYLATION OF BENZENE WITH PROPYLENE IN THE PRESENCE OF A SERIES OF PHOSPHORIC ACIDS CONTAINING FLUORINE AND BORON FLUORIDE

The study of the alkylation of benzene with ethylene in the presence of orthophosphoric, monofluorophosphoric, and difluorophosphoric acids saturated with boron fluoride showed that catalysts based on fluorine compounds and boron fluoride are extremely active in the reaction of alkylation of benzene with ethylene ([1]). It was therefore of interest to study the catalytic properties of these compounds in the reaction of alkylation of benzene with propylene.

The alkylation of benzene with propylene was carried out in the same apparatus as the alkylation of benzene with ethylene ([1]).

A series of experiments established that neither monofluorophosphoric nor difluorophosphoric acids cause the alkylation reaction of benzene with propylene at room temperature. When the experiments were carried out at 80°, an alkylate was obtained in a yield of 56% of the theoretical value. Thus, in the alkylation of benzene with propylene, even at a temperature of 80°, the catalytic activity of monofluorophosphoric acid is comparatively low.

However, introduction of a fluorine atom into the molecule of phosphoric acid somewhat increases the catalytic activity of the acid, since in the alkylation of benzene with isobutylene at a temperature of 20° an alkylate was obtained in a yield of 70% of theoretical, consisting of 45–49% tert-butylbenzene and 51–55% di-tert-butylbenzene. According to literature data ([2]), alkylation of benzene with isobutylene in the presence of orthophosphoric acid is possible at temperatures above 60°.

Although the introduction of fluorine into the molecule of phosphoric acid somewhat increases the activity of the catalyst, this increase in activity is nevertheless insufficient. Therefore the authors of this article studied in greater detail the reaction of alkylation of benzene with propylene in the presence of monofluorophosphoric and difluorophosphoric acids saturated with boron fluoride. In parallel, for comparison, experiments were carried out on the alkylation of benzene with propylene in the presence of orthophosphoric acid saturated with boron fluoride, and sulfuric acid.

The authors studied the duration of operation of these catalysts in the reaction of alkylation of benzene with propylene. It should be noted that the duration of operation of an acid in the alkylation reaction (and consequently its consumption) is a very important characteristic determining the technical suitability of a catalyst. It was therefore proposed to determine the activity of catalysts from the yield of alkylate per unit weight of catalyst.

The experiments were carried out at a temperature of 20°. For each experiment, 40 ml of catalyst, 156 g of benzene, and 41 g of propylene were taken. Propylene was fed into the reactor at a rate of 3.5 l/hour. After each experiment the alkylate obtained was decanted from the catalyst, and the acid was used in the following experiment.

Data on the yield of alkylates and the consumption of a series of catalysts in the alkylation of benzene with propylene are given in Table 1.

It is seen from Table 1 that, of the catalysts studied, the most active in the reaction of alkylation of benzene with propylene is monofluorophosphoric acid saturated with boron fluoride. The catalysts studied may be arranged in the following series in decreasing order of their catalytic activity:

$$\mathrm{H_2PO_3F \cdot BF_3 > HPO_2F_2 \cdot 0.5\,BF_3 > H_3PO_4 \cdot BF_3 > H_2SO_4},$$

i.e., the activity of the catalysts in the reaction of alkylation of benzene with propylene changes in the same way as in the case of alkylation of benzene with ethylene (1).

It was of interest to trace the influence of the catalyst activity on the fractional composition of the alkylate and the change in the fractional composition of the alkylate upon changing the molar ratio of benzene to propylene. For this purpose, experiments were carried out on the alkylation of benzene with propylene in the presence of a number of catalysts. For each experiment, 40 ml of catalyst, 156 g of benzene, and 20.5, 41.0, and 82.0 g of propylene were taken. The quantities of benzene and propylene taken corresponded closely to benzene-to-propylene molar ratios of 4 : 1, 2 : 1, and 1 : 1, respectively. The experiments were conducted at a temperature of 20°; the gas was fed into the reactor at a rate of 3.5 l/hr.

Table 1

Consumption of catalysts in the alkylation of benzene with propylene

Catalyst	Catalyst taken, ml	Catalyst taken, g	Alkylate obtained, g	Catalyst consumption, wt. %
$\mathrm{H_2PO_3F \cdot BF_3}$	40	75.5	2768	2.73
$\mathrm{HPO_2F_2 \cdot 0.5\,BF_3}$	40	71.5	2408	2.97
$\mathrm{H_3PO_4 \cdot BF_3}$	40	76.0	2173	3.50

Catalyst	Catalyst taken, ml	Catalyst taken, g	Alkylate obtained, g	Catalyst consumption, wt. %
H_2SO_4	40	73.5	414	17.80

The results of the experiments showed that, as the activity of the catalysts decreased, the fractional composition of the alkylates changed only slightly.

At a benzene-to-propylene molar ratio of 4 : 1, the alkylate consisted to the extent of 80-85% of fairly pure isopropylbenzene. Decreasing the benzene-to-propylene molar ratio to 2 : 1 and 1 : 1 led to a decrease in the content of monoalkylate in the alkylate to 75-80 and 65-70%, respectively.

The yield of monoalkylate (calculated as isopropylbenzene) at a benzene-to-propylene molar ratio of 2 : 1 was fairly high in all experiments and amounted to 89-91% of the theoretical. When the benzene-to-propylene molar ratio was decreased, as was to be expected, the yield of monoalkylate in all experiments decreased owing to a considerable increase in the amount of polyalkylation products.

The results obtained make it possible to conclude that the optimum benzene-to-propylene ratio for all the catalysts studied by us is 2 : 1. Increasing this ratio is hardly expedient, since it will lead to a considerable increase in the size of the apparatus with a comparatively small increase in the total content of monoalkylate in the alkylation products.

The fractions of isopropylbenzene and diisopropylbenzene obtained in the presence of a number of catalysts contained no unsaturated compounds. The latter were present in insignificant amounts only in the residues from distillation of the alkylates; moreover, as the activity of the catalyst decreased, the bromine numbers of the residues increased somewhat (from 0.1-0.3 when $H_2PO_3F \cdot BF_3$ was used as the catalyst to 1.4-1.8 in the case of H_2SO_4).

In the alkylation of hydrocarbons with olefins, the rate of addition of benzene or of an isoparaffinic hydrocarbon to the olefin is of great importance. This rate depends on the structure of the saturated and unsaturated hydrocarbons, on the activity of the catalysts, on the temperature of the experiments, on the degree of mixing of the reaction mixture, and on other factors.

In this connection, a series of experiments was carried out on the alkylation of benzene with propylene at different rates of gas passage into the reactor. The experiments were carried out with the most active of the catalysts studied—monofluorophosphoric acid saturated with boron fluoride—and with the least active catalyst—sulfuric acid.

For each experiment, 40 ml of catalyst, 156 g of benzene, and 41 g of propylene were taken. The experiments were carried out at a temperature of 20°. The results of the experiments are given in Table 2.

Table 2

Alkylation of benzene with propylene with $H_2PO_3F \cdot BF_3$ and H_2SO_4 at different rates of olefin feed into the reactor

Experiment no.	Gas feed rate, l/hr	Yield of alkylate, % of theory	Fractional composition of alkylate, wt. %	Fractional composition of alkylate, wt. %	Fractional composition of alkylate, wt. %	Fractional composition of alkylate, wt. %	Fractional composition of alkylate, wt. %	Bromine number of residue
			85–150°	150–154°	154–200°	200–210°	residue	
Catalyst $H_2PO_3F \cdot BF_3$								
1	3.5	88.5	3.5	73.0	4.3	5.2	14.0	0.1
2	22.5	90.3	4.1	76.0	4.9	5.0	10.0	0.4
3	30.0	91.0	4.3	74.2	5.7	5.8	10.0	0.3
Catalyst H_2SO_4								
4	3.5	89.5	5.2	79.0	6.2	4.3	5.3	1.8
5*	22.5	88.0	7.0	70.0	5.3	10.0	7.7	1.0
6	30.0	81.5	4.3	71.3	6.2	10.4	7.8	13.3

* For the reaction, 45.5 g of propylene was taken.

As can be seen from Table 2, increasing the rate of passage of propylene into the reactor in the presence of $H_2PO_3F \cdot BF_3$ from 3.5 to 30.0 l/hr does not appreciably change the yield of alkylate or the content of the isopropylbenzene fraction in the alkylate. In the presence of sulfuric acid (the less active catalyst), as the rate of passage of propylene increased, there was, it is true, a slight decrease in the yield of alkylate and a decrease in the content of the isopropylbenzene fraction in the alkylate.

Table 3

Basic properties of the isopropylbenzene fraction

	Isopropylbenzene fraction	Pure isopropylbenzene
B.p., °C	150–154	152.39
d_4^{20}	0.8644	0.8618
n_D^{20}	1.4934	1.4915
M	120.5	120.19
Bromine number	0	–

	Isopropylbenzene fraction	Pure isopropylbenzene

Unsaturated compounds were detected in small amounts only in the residues from distillation of the alkylates. The content of unsaturated compounds increased sharply when sulfuric acid was used as the catalyst at a propylene passage rate into the reactor of 30 l/hr (experiment no. 6). At the same time, the yield of alkylate decreased somewhat.

When the temperature of the experiment in the alkylation reaction of benzene with propylene was raised to 80° in the presence of monofluorophosphoric acid saturated with boron fluoride, a very slight increase was observed in the yield of alkylate and in the content in it of the isopropylbenzene fraction. At the same time, at this temperature, a fairly significant evolution of boron fluoride from the catalyst was observed, which rapidly lowered its activity.

As already indicated, in the alkylation of benzene with propylene in the presence of a number of catalysts, the main product of the reaction, judging by the tempe-

at the boiling temperature was isopropylbenzene with an admixture of a small amount of polyalkylate. A small amount of intermediate fractions was obtained. Distillation of these fractions established that they consisted of isopropylbenzene and diisopropylbenzene.

The principal properties of the isopropylbenzene fractions obtained by us, together with the constants of pure isopropylbenzene, are given in Table 3.

It is seen from Table 3 that the properties of the isopropylbenzene fraction are very close to the constants of pure isopropylbenzene.

The structure of the diisopropylbenzene fraction was established by oxidizing this fraction with a 20% solution of nitric acid. Terephthalic acid was isolated from the oxidation products and identified. No other oxidation products could be detected. Consequently, the alkylate fraction consists mainly of *p*-diisopropylbenzene.

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References

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