# Academy of Sciences of the USSR Reports

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1960

SovietRxiv

## Abstract

## Full Text

Academy of Sciences of the USSR Reports
1960. Volume 130, No. 3

## CHEMISTRY

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# STUDY OF THE ALKYLATION REACTION OF PHENOL WITH AMYLENES USING CATALYSTS BASED ON BORON FLUORIDE

The procedure for alkylation, the work-up, and the analysis of the reaction products of phenol with amylenes were basically the same as in the alkylation of phenol with isobutylene by means of boron fluoride ([1]). In this case only the method of feeding the amylenes into the reactor was changed; it was carried out with the aid of a burette and a capillary. By means of a glass capillary, the liquid amylenes were introduced directly into the mixture of phenol and catalyst heated to 100°. This method of feeding the amylenes provided the best conditions for contact of the reacting substances.

The amylenes were obtained by catalytic dehydration of isoamyl alcohol over granular aluminum oxide at 380—400°. Dehydration gives 3-methylbutene-1, 2-methylbutene-2, and 2-methylbutene-1. To obtain pure olefins, the mixture of amylenes was treated at 0° with 75% $H_2SO_4$; 3-methylbutene-1, which is not dissolved in $H_2SO_4$, remains in the upper layer, which is separated, treated with a 10% solution of NaOH, washed with water until the wash waters are neutral, dried over calcium chloride, and distilled into fractions. During distillation, the fraction 19—20°/753 mm with $d_4^{20}$ 0.6274 and $n_D^{20}$ 1.3641 was collected, which corresponds to 3-methylbutene-1. From the lower, acidic layer, a fraction 37—38°/753 mm was isolated; $d_4^{20}$ 0.6595 and $n_D^{20}$ 1.3863, which according to literature data corresponds to 2-methylbutene-2.

The first experiments on the alkylation of phenol by means of boron fluoride were carried out separately with 3-methylbutene-1 and 2-methylbutene-2. The results of the study showed that with both the first amylene and the second, alkylates of identical composition are formed in the alkylation of phenol. The principal product at a molar ratio phenol : amylene = 1 : 1 is *n*-tert.-amylphenol. The formation of *n*-tert.-amylphenol when 3-methylbutene-1 is used is possible owing to its isomerization in the course of the reaction to 2-methylbutene-2. A similar regularity is also observed in the alkylation of benzene with 3-methylbutene-1; in this case tert.-amylbenzene is formed. Subsequently, for the alkylation, a

mixture consisting of 3-methylbutene-1 and 2-methylbutene-2 was used. General data on the study of the alkylation reaction of phenol with amylenes in the presence of various catalysts are given in Table 1. The reaction was charged with 94 g of phenol, 70 g of amylenes, and 1.6 g of catalyst (1.7% relative to the weight of phenol). The alkylation reaction of phenol with amylenes was carried out at 100°. After the addition of the entire amount of amylenes, the reaction mass was additionally stirred at 110—120° for 30 min.

The data of Table 1 show that, in the alkylation of phenol with amylenes, the highest yields are obtained in the presence of boron fluoride and catalysts containing boron fluoride (experiments 1, 2, and 3). In this case the yields of *n*-tert.-amylphenol are respectively 95, 90, and 89% of theory. Next in effectiveness in this reaction is 75% $H_2SO_4$—the yield of *n*-tert.-amylphenol is 81% of theory—and in last place is aluminum chloride—the yield of *n*-tert.-amylphenol is 64% of theory.

Table 1

Comparative data on the alkylation of phenol with amylenes using various catalysts
(molar ratio phenol : amylenes = 1 : 1)

| No. of experiment | Catalyst | Composition of reaction mass, % | Composition of reaction mass, % | Composition of reaction mass, % | Yield, % of theory | Yield, % of theory | Yield, % of theory |
|---|---|---|---|---|---|---|---|
| | | phenol | *p*-tert.-amylphenol | liquid products | *p*-tert.-amylphenol | liquid products | total |
| 1 | $BF_3$ | 2 | 95 | 3 | 95 | 3 | 98 |
| 2 | $H_3PO_4 \cdot BF_3$ | 2.5 | 89.5 | 8 | 90 | 8 | 98 |
| 3 | $(C_2H_5)_2O \cdot BF_3$ | 5.5 | 88.5 | 6 | 89 | 6 | 95 |
| 4 | $H_2SO_4$ (75%) * | 8.5 | 81.0 | 10.5 | 81 | 11 | 92 |
| 5 | $AlCl_2 \cdot HSO_4$ | 10.4 | 67.7 | 21.9 | 68 | 22 | 90 |
| 6 | $AlCl_3$ | 11.6 | 64.0 | 24.4 | 64 | 25 | 89 |

* The optimum amount of 75% $H_2SO_4$ under these conditions for the alkylation of phenol with amylenes is 17% by weight of phenol.

The liquid products obtained in the alkylation of phenol with amylenes in the presence of boron fluoride, at an equimolecular ratio of the reacting components,

consist of 15% phenol, 55% tert.-amylphenyl ether, 5% di-tert.-amylphenol, and 25% tert.-amyl ether of tert.-amylphenol.

A study of the effect of the amount of catalyst on the yield and composition of the products of the reaction of phenol with amylenes in the presence of boron fluoride shows that, within the range of 1.8–26% at 100°, a change in the amount of catalyst has only a slight effect on the yield and composition of the alkylation products.

General data from the study of the effect of the amount of catalyst on the reaction are given in Table 2.

Table 2

Effect of the amount of catalyst on the composition and yield of products of the reaction of alkylation of phenol with amylenes
(temperature 100°, molar ratio phenol : amylenes = 1 : 1)

| No. of experiment | Amount of catalyst | Amount of catalyst | Composition of reaction mass, % | Composition of reaction mass, % | Composition of reaction mass, % | Yield, % of theory | Yield, % of theory | Yield, % of theory |
|---|---|---|---|---|---|---|---|---|
| | g | % by weight of phenol | phenol | *p*-tert.-amylphenol | liquid products | *p*-tert.-amylphenol | liquid products | total |
| 7 | 0.8 | 0.9 | 7 | 85 | 8 | 88 | 7 | 95 |
| 8 | 1.6 | 1.7 | 2.5 | 94 | 3.5 | 95 | 3 | 98 |
| 9 | 4.9 | 5.2 | 2 | 95 | 3 | 95 | 3 | 98 |
| 10 | 24.6 | 26.2 | 2 | 96 | 2 | 96 | 2 | 98 |

The process of alkylation of phenol with amylenes, as is evident from the data presented, proceeds under identical alkylation conditions better than that of phenol with isobutylene (1). For example, with the same amount of catalyst, 1.7%, the yield of *p*-tert.-amylphenol reaches 95% of theory, whereas that of *p*-tert.-butylphenol is only 78%. The yield of *p*-tert.-amylphenol at the smallest amount of catalyst studied (0.9%) reaches a rather high value (88%), while that of liquid alkylation products is only 7%. No polymers of amylenes were found in the liquid products.

Increasing the amount of catalyst to 1.7% raises the yield of *p*-tert.-amylphenol to 95% of theory and reduces the yield of liquid products to 3%. A further increase in the amount of catalyst has practically no effect on the yield of the alkylation products. The optimum amount of catalyst in the reaction of alkylation of phenol with amylenes under the conditions studied

is 1.7%. The crude alkylate obtained at a molar ratio phenol : amylene = 1 : 1 has the following composition (in %): phenol 2.5; *n*-tert.-amylphenol 95.7; tert.-butyl phenyl ether 0.6; di-tert.-amylphenol 0.9, and tert.-amyl ether of *n*-tert.-amylphenol 0.3.

If the molar ratio phenol : amylene is decreased to 1 : 2, then the composition of the crude alkylate in this case is as follows (in %): phenol 0; *n*-tert.-amylphenol 21; amyl phenyl ether 2.3; di-tert.-amylphenol 30, and tert.-amyl ether of *n*-tert.-amylphenol 46.7. Decreasing the molar ratio phenol : amylene to 1 : 2 sharply lowers the yield of *n*-tert.-amylphenol and increases the yield of di-tert.-amylphenol and ether products.

The isolated ether products had the following constants: for tert.-amyl phenyl ether $n_D^{20}$ 1.4941, OH absent, $d_4^{20}$ 0.9352, mol. wt. 166; for the tert.-amyl ether of *n*-tert.-amylphenol $n_D^{20}$ 1.5038, OH absent; $d_4^{20}$ 0.9406, mol. wt. 234.5.

Received
13 VII 1959

## CITED LITERATURE

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