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Abstract

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ALKYLATION OF PHENOL WITH ACETYLENE UNDER ELEVATED PRESSURE

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In previous works (1–5) we were the first to carry out and study in detail the reaction of alkylation of phenol with acetylene at atmospheric pressure. As solvents for phenol we used water and ethyl alcohol (2); it was shown that water promotes a more selective course of the reaction. It was found (3) that in an aqueous medium acetylene reacts with phenol through the stage of formation of acetaldehyde. The yield of 1,1-(4,4′-dioxy)-diphenylethane in this reaction does not exceed 50% of that calculated stoichiometrically:

$$\mathrm{CH \equiv CH + 2\,C_6H_5OH \rightarrow HO{-}C_6H_4{-}CH(CH_3){-}C_6H_4{-}OH}$$

To determine the influence of pressure and to establish the optimum conditions for alkylation under pressure, experiments were carried out in a rotating autoclave.

Conducting the reaction at elevated pressure has the following advantages: the concentration of acetylene in the gas phase is many times higher than at atmospheric pressure; in the liquid phase the concentration of acetylene increases owing to the increased solubility of acetylene, and acetylene losses are insignificant.

A substantial drawback of carrying out the reaction in a rotating autoclave is the impossibility of maintaining the pressure at a definite level.

The conditions and methods for using acetylene under pressure were first studied by A. E. Favorskii and M. F. Shostakovskii (6) in the vinylation reaction, and also in the works of A. D. Petrov and L. I. Antsus (7) on the reaction of hydropolymerization of acetylene; there are a number of patents for syntheses of vinyl ethers of high-molecular products under the pressure of acetylene diluted, for safety, with nitrogen.

But the safety of the course of the reaction, as was initially proved by the works of Soviet investigators, can be ensured without resorting to special diluents of acetylene; during the reaction the dilution of acetylene occurs through vapors of the substance of the reaction mixture. The advantage of this method is the

Fig. 1. Dependence of the rate of acetylene absorption on temperature (A) and the amount of catalyst (B)

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absence of nitrogen consumption and the high rate of the process owing to the higher concentration of acetylene in the reaction zone.

The method was successfully applied in our work as well. All experiments were carried out in a rotating autoclave made of stainless steel, with a capacity of 250 cm^3. The temperature inside the autoclave was measured with an iron-constantan thermocouple and a millivoltmeter. The rate of rotation of the autoclave and the temperature were regulated by rheostats.

A mixture of phenol, solvent, catalyst $H_3PO_4 \cdot BF_3$, and HgO was charged into the autoclave. The autoclave was first purged with acetylene from a cylinder to remove air. After purging it was filled with acetylene to a pressure of

pressure of 20 atm and set in rotation. At the same time, electric heating was switched on. Since acetylene was absorbed at a high rate, by the time the required temperature was reached the pressure in the autoclave had fallen sharply.

Therefore, in subsequent experiments the corresponding temperature was first attained, and then acetylene was introduced.

After the reaction was completed, the temperature in the autoclave was maintained at about 70° in order to reduce the viscosity of the reaction products and facilitate their discharge.

The reaction products were separated from the aqueous layer and cooled. The crystals that separated were filtered off on a vacuum filter, washed with cold water to remove phenol, dried, and weighed. The melting point of the crystals after recrystallization from water was in all cases 120–122°. A mixture of the crystals with pure 1,1-(4,4′-dioxy)-diphenylethane gave no depression of the melting point.

Fig. 1. Dependence of the rate of acetylene absorption on temperature (A) and the amount of catalyst (B)

The optimum reaction conditions were judged from the yield of crystals and from the rate of acetylene absorption.

To study the effect of temperature, experiments were carried out in aqueous solution in four temperature intervals: 18–20°, 70–80°, 90–100°, and 110–120°.

The reaction time (66 min) and the ratio of the reaction components remained constant in all cases. A mixture of 50 g of phenol, 50 ml of distilled water, 2 g of HgO, and 20 ml of $H_3PO_4 \cdot BF_3$ was kept for 24 hours, with vigorous stirring, after which it was used for the reaction.

The rate of the reaction was judged from the rate of acetylene absorption, which was determined from the change in pressure per unit time (atm/min).

The dependence of the rate of acetylene absorption on temperature is shown in Table 1 and in Fig. 1A. From Fig. 1A it is evident that the maximum rate of acetylene absorption occurs in the temperature interval 110–112°, and the minimum at 18–20°. The maximum reaction rate occurs at a pressure of 20–16 atm. The higher the temperature, the lower the pressure corresponding to the minimum absorption rate.

From the results of the experiments it is evident that the optimum reaction conditions are a temperature of 110–120° and a pressure of 20–16 atm.

The effect of the amount of catalyst was studied at 110–120°. The treatment of the reaction products was as before. Table 2 presents the results of experiments characterizing the dependence of the yield of 1,1-(4,4′-dioxy)-diphenylethane on the amount of catalyst.

From Table 2 it is evident that, as the amount of catalyst is decreased, the yield decreases only slightly. When the amount of catalyst is decreased from 27.2 to 15.1%, the yield decreases by only 8.5%.

Table 1

Experiment no.	Temperature, °C	Initial pressure, atm.	Change in pressure, Δp (atm.) at time intervals: 1 min.	Change in pressure, Δp (atm.) at time intervals: 2 min.	Change in pressure, Δp (atm.) at time intervals: 2 min.	Change in pressure, Δp (atm.) at time intervals: 2 min.	Change in pressure, Δp (atm.) at time intervals: 4 min.	Final pressure, atm.	Acetylene absorbed, g*	Yield, g	Yield, % of theory
1	18—20	20	4	3	1.0	–	0.5	11.5	1.78	0	–
2	70—80	20	4.5	3.5	2.0	2.0	3.5	3.0	2.35	3	15.8
3	90—100	20	–	–	–	–	–	5.0	1.93	7	44.0
4	110—120	20	7.0	3.5	3.5	1.5	–	2.5	2.05	11	65.0

* The amount of acetylene absorbed was calculated by the transformed Mendeleev–Clapeyron equation, taking into account the compressibility coefficient.

Table 2

Experiment no.	Catalyst*	Initial pressure, atm.	Change in pressure, Δp (atm.) at time intervals: 1 min.	Change in pressure, Δp (atm.) at time intervals: 2 min.	Change in pressure, Δp (atm.) at time intervals: 2 min.	Change in pressure, Δp (atm.) at time intervals: 2 min.	Final pressure, atm.	Acetylene absorbed, g	Yield, g	Yield, % of theory
7	27.2	20	7.0	5.5	3.5	1.5	2.5	2.06	10.4	61.2
8	15.1	20	6.5	5.0	2.0	0.5	3.0	2.16	9.5	53.2
9	8.3	20	8.0	6.0	2.5	0.5	3.0	2.28	8.7	48.0

* The amount of mercuric oxide remained constant and equal to 2 g.

The dependence of the rate of acetylene absorption on the amount of catalyst is presented in Fig. 1 B. The rates of acetylene absorption are approximately the same in all cases.

As the experiments showed, at a temperature of 110–120°, the catalytic aqueous solution during the reaction becomes bright green and transparent (the mercuric oxide dissolves completely; no mercury precipitates were detected).

Upon prolonged standing and heating, the color of the solution and its transparency did not change. In order to study the catalytic activity of this solution, several experiments were carried out at a temperature of 110–120°. Thus, to a solution of spent catalyst (from experiment no. 8) in an amount of 70 cm^3, 50 g of phenol was added. The mixture was placed in an autoclave, where the reaction was conducted for 1.1 hours. From the reaction products, after appropriate treatment, 5 g of crystals were isolated. In the next experiment, 70 cm^3 of spent catalytic solution was also taken, but with the addition of 2 g of mercuric oxide. As a result, 11 g of crystals was obtained. To the catalytic solution after this, another 2 g of mercuric oxide was added, and 7 g of crystals was obtained. The results are summarized in Table 3.

Table 3

Experiment no.	Origin of catalytic solution	Initial pressure, atm.	Change in pressure, Δp (atm.) at time intervals: 1 min.	Change in pressure, Δp (atm.) at time intervals: 2 min.	Change in pressure, Δp (atm.) at time intervals: 2 min.	Change in pressure, Δp (atm.) at time intervals: 2 min.	Final pressure, atm.	Acetylene absorbed, g	Yield, g	Yield, % of theory
10	From experiment no. 8	20	4.0	2.5	0.3	0.5	12	0.99	5	62
11	From experiment no. 10	20	7.5	6.8	2.7	–	2.5	2.06	11	65
12	From experiment no. 11	20	7.0	6.0	3.0	–	3.5	2.02	7	60

It is evident from Table 3 that a catalyst used once has approximately half the activity compared with fresh catalysts (if the activity of the catalyst is judged by the amount absorbed per unit time—

of acetylene), however the yield (in % of theory) based on reacted acetylene remains high, which indicates that side reactions proceed only to a slight extent.

The addition of mercuric oxide to the spent catalytic solution restores its activity. Subsequent use of the catalytic solution with the addition of mercuric oxide leads to a gradual decrease in its activity.

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