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# Chemistry

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**Abstract**

**Full Text**

**Chemistry**

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## INVESTIGATION OF THE NITRATION REACTION OF ISOPROPYLCYCLOHEXANE WITH NITRIC ACID

In work <sup>(1)</sup> the principal literature data on the nitration of cyclane hydrocarbons published before 1948 were set forth. Subsequently, studies were published devoted to the mechanism of nitration of cyclohexane <sup>(2, 4)</sup> and to the reaction of cyclohexene with dilute nitric acid <sup>(4)</sup>.

The present work is devoted to the results of our investigation of the nitration reaction of isopropylcyclohexane with nitric acid under various process conditions.

### Experimental Part

**Starting material and procedure.** The starting product for nitration was isopropylcyclohexane, b.p. 152-154°,  $d_4^{20} = 0.8006$ ,  $n_D^{20} = 1.4410$ . Nitric acid of specific gravity 1.3, 1.2, and 1.075 was used as the nitrating agent (concentration, respectively, 48, 28, and 11%). The nitration process was carried out in a 500 ml round-bottom flask fitted with a ground-in reflux condenser, equipped with a thermometer immersed in the liquid. The reaction flask was heated in a glycerol bath.

Calculated amounts of the hydrocarbon and nitric acid were placed in the reaction flask. The reaction mixture was heated at a definite temperature for the specified duration of the experiment. After the end of the experiment, the upper layer of the reaction mixture, consisting of a mixture of the nitro product and unreacted hydrocarbon, was washed, dried, and subjected to distillation on a vacuum column. The crude nitro product freed from unreacted starting material was separately fractionated on the same column, but at a considerably lower residual pressure. The isolated fractions were then analyzed.

To establish the structure of the reaction products, part of the obtained nitro-product fractions was reduced to the corresponding amino derivatives. The reduction was carried out in an autoclave of I. A. Musaev's design and in the presence of Raney nickel under high hydrogen pressure. The amino compounds thus obtained were analyzed.

The nitration experiments with isopropylcyclohexane were carried out at temperatures of 50-55, 80-85, and 105-110°. The duration of the experiment was chosen as 5, 10, 15, and 20 hours, and the concentration of nitric acid as 11%

Fig. 1

Figure 1: Fig. 1

( $d = 1.075$ ), 28% ( $d = 1.2$ ), and 48% ( $d = 1.3$ ). The molar ratios of hydrocarbon to nitric acid were varied from 1 : 1.25 to 1 : 2.5. In all, more than 40 experiments were conducted. Below we shall discuss the results of investigating the influence of individual factors on the nitration process.

**Effect of temperature.** Figure 1 presents the results of experiments in which nitration was carried out with acid of specific gravity 1.3 at a molar ratio of hydrocarbon to acid of 1 : 2.5.

From the character of the curves in Fig. 1A it is evident that, with an increase in the reaction temperature, the percentage conversion of the starting material rises sharply, reaching 60.8% at a temperature of 105°; however, an increase in the yields of the crude nitro product and the mononitro product is observed only up to a temperature of 80°, after which a further rise in temperature leads to a decrease in yield. Consequently, under the conditions of our experiments the optimum temperature for the nitration reaction of isopropylcyclohexane is 80–85°, at which

**Fig. 1.** Dependence of the nitration reaction of isopropylcyclohexane on temperature (A), on process duration (B), and on the relative amount of nitric acid (C).

**1** –hydrocarbon conversion, **2** –yield of crude petroleum product as a percentage of converted hydrocarbon, **3** –yield of mononitro compound as a percentage of converted hydrocarbon

the yield of mononitro product reaches 72.8% of theory (although the conversion is 25.1%). This should evidently be explained by the development, under these reaction conditions, of oxidation, as well as by the deepening of the nitration reaction with the formation of di- and polynitro products.

Thus, in the nitration reaction of cyclanes with nitric acid, a change in the reaction temperature affects not only the quantitative aspect of the conversion, but also to a large extent determines the direction of the reaction and the nature of its final products.

**Effect of process duration.** In this part of the investigation we carried out a series of experiments on the nitration of isopropylcyclohexane with nitric acid of specific gravity 1.3 at a temperature of 80–85° and at a molar ratio of hydrocarbon to acid of 1 : 2.5. The reaction times adopted were 5, 10, 15, and 20 hours. The experimental results are presented in Fig. 1B.

Consideration of the character of the curves in Fig. 1B shows that, under the conditions of our experiments, the optimum duration of the nitration reaction is 15 hours. With increasing process duration, the relative importance of the oxidation reaction increases.

**Effect of the molar ratio of the reacting components.** To clarify this question, a series of experiments was carried out on the nitration of isopropylcyclohexane with nitric acid of specific gravity 1.3 at a temperature of 80–85° and a process duration of 15 hours, the molar ratio of hydrocarbon to nitric acid being varied from 1 : 1.25 to 1 : 2.5. The results of the experiments are shown in Fig. 1C. The character of the curves in Fig. 1C shows that, with a decrease in the relative amount of nitric acid, the percentage conversion of the initial hydrocarbon decreases, while the yield of crude nitro product and mononitro compound...

in percent, based on converted starting material, remains almost unchanged. Thus, under the conditions of our experiments the optimum molar ratio of hydrocarbon to nitric acid is 1 : 2.5.

**Influence of the concentration of nitric acid.** The experiments we carried out showed that, at the same relative mass of nitric acid, the nitration process depends to a considerable degree on the concentration of the latter. Thus, if, in nitration with nitric acid of specific gravity 1.3, the conversion of isopropylcyclohexane is 61%, and the yield of crude nitro product and of the mononitro compound (in percent, based on converted hydrocarbon) averages, respectively, 76.1 and 46.8%, then, other conditions being equal, even with a threefold longer duration, the action of nitric acid of specific gravity 1.075 leads to the formation of only traces of nitro product.

To summarize, it may be noted that the optimum conditions for the reaction of nitration of isopropylcyclohexane with nitric acid in the liquid phase are: temperature 80–85°, duration—15 hours, nitric acid concentration 48% ( $d = 1.3$ ), and a molar ratio of hydrocarbon to nitric acid equal to 1 : 2.5. Under these conditions the conversion of the hydrocarbon is 57%, and the yields of crude nitro product and of mononitroisopropylcyclohexane, in percent based on converted hydrocarbon, are respectively 98.3 and 78.6.

The established dependence of the course of the nitration reaction of isopropylcyclohexane on various factors can, it seems to us, be explained by the dynamics of the amount of nitrogen dioxide formed from nitric acid under different conditions, since lowering the temperature and decreasing the duration of the reaction, as well as the concentration and relative mass of nitric acid, reduces the ability of nitric acid to decompose into nitrogen oxides. To confirm the latter, we undertook a special experiment on the nitration of isopropylcyclohexane in the presence of a small amount of ammonium sulfite. For this purpose, a mixture of 43.6 g of isopropylcyclohexane, 9 g of ammonium sulfite, and 113.5 g of nitric acid of specific gravity 1.3 was heated at 80–85° for 8 hours. Although the process was carried out under conditions that had proved optimum for the nitration reaction of isopropylcyclohexane, the experiment did not lead to the formation of even traces of nitro product.

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

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