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The Alkylation of n-Butane with Propylene in the Presence of Aluminum Oxide.

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The process of alkylation of branched paraffin^s with olefins in the presence of mineral acids has been studied so extensively that it is now widely used in industry. Normal paraffins under analogous conditions do not react with olefins. Liquid-phase alkylation has a number^o of inherent drawbacks, associated with the large consumption of sulfuric acid and the inconvenience in using such condensing agents as hydrofluoric acid. ⁴ Lavrovskii and Mikhnovskaya /1/ conducted experiments on the condensation of n-heptane with propylene at 400° and 30 atm. in the presence of an aluminosilicate catalyst. Later O'Kelly and Sachanen /2/ found that at high temperatures and pressures in the presence of homogeneous catalysts (Freon, chlorinated ligroin, benzyl chloride, etc.) n-butane, like branched paraffins, is alkylated by ethylene. Experiments, in which the weight ratio of saturated to unsaturated components was 8:1, were conducted under static conditions at a pressure of 220 atm and a temp. of 427°. The quantity of catalyst was varied from 1 to 3.2% dry weight of the reaction mixture. In

that paper no data were given on the alkylation of n-butane with propylene, but it was pointed out that the alkylation of isobutane with propylene was conducted at a higher pressure (300 atm). The authors themselves consider as a disadvantage of this method, the presence in the alkylate of 1 to 2% chlorine, the complete removal of which complicates the process with additional difficult operations.

The data presented show that it is necessary to develop heterogeneous catalytic methods for the complex chemical processing of gaseous and low-boiling hydrocarbons. With the aid of such catalysts not only branched, but also normal hydrocarbons could be treated. In our work this question was studied for the case in which n-butane is alkylated with propylene in the presence of aluminum oxide. Experiments led to a circulating type of apparatus, a diagram of which is given in Fig. 1.

Fig. 1. Diagram of the alkylation apparatus.

From cylinder 1, using gas compressor 2, ^{into} mixer 3, which consists of an autoclave equipped with a mechanical stirrer and inspection port, n-butane and propylene are added in sequence after first being dried over calcium chloride. The liquid mixture of n-butane and propylene, by means of hydraulic compressor 4 (of the system of Vereshchagin and Ivanov) is fed to reactor 5 which has been heated to the required temp. The reactor is fabricated from stainless steel and is 450 mm long, has a 20 mm inside diam and a 17.5 mm wall

thickness. The top of the reactor was hermetically sealed with hydraulic closure 6 operated by pump 7, and is closed below by a fine regulation valve. By means of the latter, reaction products were continuously withdrawn, and the space velocity regulated for the reaction mixture being passed through the apparatus. The reactor was heated in a tubular electric furnace and its temp. measured by thermocouple 8, inserted into a small opening in the body of the reactor to a depth of 150 mm, i.e., level with the catalyst bed. In this work, the propylene was 98% pure, and the butane contained as impurities 2.8% of unsaturated compounds, 0.8% propane, and 0.5% of isobutane. The propylene content of the mixture was varied between the limits 23-30%. The selection of aluminum oxide as catalyst was determined by its freedom from strong cracking and isomerization catalysts, thereby allowing us to follow the chemistry of the process from the composition of the condensate. Immediately before the expt. the catalyst was dehydrated for one hour at 425° in a stream of air. It has an apparent density of 1.02 g/cm^3 , and a total pore vol. of $0.67 \text{ cm}^3/\text{g}$ and the vol. of sorbed liquid benzene from saturated vapors was $0.68 \text{ cm}^3/\text{g}$. In each expt. a fresh 50 ml portion of catalyst was used. Above the catalyst was poured a layer, comprising 80 ml of porcelain tiles, which helped heat the reacting components being fed to the catalyst. At the beginning of the expt., nitrogen was passed through, the fine regulator closed and and the hydraulic compressor turned on. After 5-7 min, when the reacting components built up the required pressure in the reactor, the valve was opened and drops of condensate began to fall through the cooler 9 into the ice-cooled

receiver 10, while the gaseous products pass through gas meter 12 to gas-holder 11. Gas samples for analysis are taken as follows: before the expt. from the clean-out valve located at the inlet to the reactor; and after the expt. from the gas-holder. The condensate was first stripped of butane, and then fractionated through a column with 30 theoretical plates. In this way we collected fractions with the corresponding paraffin boiling points: C₅-C₆ (up to 75°), C₇ (75-100°), C₈ (100-125°) and C₉₋₁₀ (125-175°). The individual fractions were analyzed for unsaturates by the bromine method. Sp. gr. and refractive index were also measured. The experiments were conducted at temperatures of 400, 450 and 500° at pressures of 100, 300, 600, 1000 and 1500 atm. Space velocities for the butane-propylene liquid mixture were varied from 1.9 to 4.0 liters/liter-hour. The duration of an expt. was 1-3 hours.

The data presented in Table 1 show that a complex mixture of hydrocarbons is formed in this process. About 60-70% of these products boil below 175°. The principal processes appear to be those of polymerization and alkylation. At 400° polymerization predominates, as confirmed by the small proportion of the heptane fraction in the condensate (about 11 vol. %), and by the higher degree of unsaturates in all condensate fractions. As the temp. is increased to 450-500°, the yield of alkylation products increases significantly, the unsaturation of the condensate decreases, the heptane fraction increases, and the higher boiling products decrease in quantity. Increase of pressure from 300 to 1000 atm at 400°, from 600 to 1500 atm at 450°, or from 100 to 600 atm at 500°, has no significant effect on the course of the process. However when the pressure was reduced from 600 to 100 atm at 450°

significant effect on the course of the process. However when the pressure was reduced from 600 to 100 atm at 450^o, the rate of condensate formation decreased and the proportion of unsaturates increased (experiments 4,6 and 12).

Increasing the space velocity of the mixture across the catalyst from 2.6 to 4.0 increases the proportion of heptane fraction in the condensate, decreases the unsaturates in the latter, and reduces the quantity of high-boiling products (experiments 4,5 and 6).

Reducing the propylene concentration in the feed mixture has no significant effect on the proportion of unsaturates in the condensate, but it does lead to an increase in the quantity of the heptane fraction, and to a decrease in the quantity of high-boiling products. Thus when the feed mixture contains 17% propylene, heptane constitutes 33% of the product, and the residue boiling above 175^o is only 24% of the total. Analogous results were obtained with 10% propylene in the feed mixture (Expt. 9).

Table 1

(key)

- 1) Expt. No.
- 2) Temp. (°C)
- 3) Pressure (atm)
- 4) Space velocity
- 5) Properties of condensate fractions
- 6) Vol. % in catalyzate

- 7) Bromine No
- 8) Residue
- 9) Expt. in absence of aluminum oxide

The yield of liquid products in the process, based on propylene introduced was 115% in expt. 6 at 450° and 600 atm; 150% in expt. 8 at 450° and 1000 atm; and 137% in expt. 13 at 500° and 600 atm; but was 87% in expt. 7 when aluminum oxide was omitted. Among the gaseous products only 5% of cracking products were observed. As was shown by the work of Frey and Hipp /3/ propane is alkylated with ethylene at 504-510° at a pressure of 300 atm in the absence of catalyst. In this connection, we conducted expt. 7 on the alkylation of n-butane with propylene in the absence of catalyst at 450° and 600 atm, the remaining conditions being similar to those of experiments 4 and 6. Fig. 2 shows condensate fractionation curves derived from experiments 6,7 and 8. Comparison of the results obtained

Fig. 2. Fractionation of condensates.

I- Expt. 8; II- Expt. 6; III- Expt. 7.

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in these experiments shows that in the presence of aluminum oxide the heptane fraction is 2-2.5 times as high. This indicates the catalytic role of aluminum oxide in the alkylation process. Thermal alkylation occurs simultaneously with the catalytic process. Since on distillation of the condensates

in all experiments, the hydrocarbon fraction boiling in the narrow range 895-925° is easily separated, the attempt was made to isolate individual hydrocarbons from the heptane fraction. For this purpose 20.3 ml of the fraction boiling at 75-100°, obtained from several experiments, was passed twice through a 40 g silica gel column to remove the olefins from it /4/. We recovered 19 ml of saturates, from which, after distillation through a column yielded the following three fractions: I 3 ml boiling at 80-91°, d_4^{20} 0.6888, n_D^{20} 1.3882; II 12 ml boiling at 91-92°, d_4^{20} 0.6879, n_D^{20} 1.3900; III 3.5 ml residue, d_4^{20} 0.6894, n_D^{20} 1.3904.

Fraction II, comprising 59% of the heptane fraction, corresponds in properties to 3-methylhexane. By the method of combinational light-scattering it was confirmed that this fraction contained, in effect, only the hydrocarbon 3-methylhexane which was identified by the frequencies: 329 (4 broad, doublet), 379 (1 broad), , etc. This provides confirmation that in the process under investigation, n-butane reacts with propylene according to the equation:

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An analogous scheme was given for the thermal alkylation of propane by ethylene /3/, where the condensate contained 52% 2-methylbutane, as well as for the alkylation of n-butane with ethylene in the presence of homogeneous catalysts /2/.

By means of a special expt. conducted at 450° and 600 atm, we showed that on passage of n-butane alone through the catalyst, without propylene admixture, 11.2% of the n-butane

was converted into isobutane, but no condensate was formed. Approximately the same quantity of isobutane was found in the gaseous product of the alkylation process under analogous conditions in experiments 4 and 6. These circumstances and 3-methylhexane formation confirm that isobutane is not an intermediate product in the alkylation of n-butane in the presence of aluminum oxide. It is known that the thermal alkylation of isobutane with propylene yields 2,2-dimethylpentane /2/.

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