CATALYTIC ALKYLATION OF ISOBUTANE WITH ETHYLENE UNDER PRESSURE AT HIGH TEMPERATURES

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Original article submitted July 16, 1958

The reaction of isobutane with ethylene in the presence of such catalysts as aluminum chloride [1] or hydrogen fluoride with boron trifluoride added [2] forms an alkylate, the hexane fraction of which consists mainly of 2,3-dimethylbutane. The yield of hexane fraction represents ~45% of the liquid product. In contrast to this, the thermal alkylation [3] of isobutane with ethylene under pressure (510°, 315 atm) forms an alkylate whose hexane fraction consists mainly (80%) of 2,2-dimethylbutane; 20% of 2-methylpentane is formed simultaneously. The yield of the hexane fraction is ~30%. Thus, under these conditions ethylene adds largely to the tertiary C atom of isobutane to form 2,2-dimethylbutane:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_9\text{CH} = \text{CH}_2 + \text{CH}_2 = \text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_9,
\end{align*}
\]

and to a lesser extent to a primary C atom:

\[
\begin{align*}
\text{CH}_9\text{CH} = \text{CH}_2 + \text{CH}_3\text{CH}_2\text{CH}_9 \rightarrow \text{CH}_9\text{CH} = \text{CH}_2\text{CH}_3\text{CH}_2\text{CH}_9.
\end{align*}
\]

In high-temperature alkylation (427°, 200 atm) in the presence of a homogeneous catalyst, namely 1-3% of chloro or nitro derivatives of naphthalene [4], the main component of the hexane fraction is also 2,2-dimethylbutane. The yield of hexane fraction is 43%. The reaction of n-butane with ethylene under the same conditions forms 3-methylpentane, i.e., the product of addition to the secondary C atom:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_9 + \text{CH}_2 = \text{CH}_2 \rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{CH}_9.
\end{align*}
\]

In almost half the yield (28%). As we showed [5-8], the addition of an olefin to a normal paraffin in the presence of solid catalysts (aluminum oxide or aluminosilicate) at high temperatures and pressures (450°, 300-500 atm) occurs predominantly at the C atom in position 2, for example:

\[
\begin{align*}
\text{CH}_9\text{CH} = \text{CH}_2 \rightarrow \text{CH}_9\text{CH} = \text{CH}_2\rightarrow \text{CH}_9\text{CH} = \text{CH}_2\rightarrow \text{CH}_9\text{CH} = \text{CH}_2\rightarrow \text{CH}_9.
\end{align*}
\]
In the present work we studied the alkylation of isobutane in the presence of aluminum oxide catalyst at high temperature under pressure. The data obtained show that under these conditions ethylene and propylene react with isobutane predominantly at the tertiary and, to a lesser extent, at the primary carbon atom. It was also possible to isolate an octane fraction which was mainly the alkylation product of the 2,2-dimethylbutane formed. However, at this stage the alkylation occurred at the primary C atom of the unbranched end of the carbon chain:

\[
\text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_3 \rightarrow \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3.
\]

This fact confirmed the stepwise nature of the alkylation process which we established previously [8]. It should be noted that in the presence of sulfuric acid, for example, hydrocarbons with a quaternary C atom (neohexane and 2,2,4-trimethylpentane) do not react with olefins [9]. An octane fraction was also obtained in the thermal alkylation of isobutane with ethylene (9% of the alkylate weight), but its composition was not investigated.

It seemed interesting to compare the yields of the main product of primary alkylation obtained during the alkylation of n-butane and isobutane with ethylene under different experimental conditions. In the presence of aluminum oxide, the product of alkylation of n-butane with ethylene at the secondary C atom (2-methylpentane) was formed in higher yield (29 weight%) than the product from alkylation of isobutane with ethylene at the tertiary C atom, i.e., 2,2-dimethylbutane (20%). On the other hand, in the presence of homogeneous catalysts [4] the yields of the same products were 26 and 43%, respectively.

During thermal alkylation there was comparatively ready addition of olefin to secondary and tertiary C atoms of the paraffin in the reaction of propane and isobutane with ethylene [3]. It was found that under these conditions the yield of the primary product from alkylation at the tertiary carbon atom was greater than that at the secondary carbon atom.

**EXPERIMENTAL**

The experiments were carried out under flow conditions on the apparatus described previously [5]. The aluminum oxide catalyst used was prepared in the following way: aluminum oxide was impregnated with an aqueous solution of potassium bifluoride (10% of the weight of Al_2O_3) and fired in a stream of air at 400° until the hydrofluoric acid had been removed and was then treated twice with sulfuric acid (1:1) and washed to remove SOF_4 [6].

The reaction was carried out with industrial isobutane fraction (81.2% isobutane, 12.4% n-butane, and 6.4% propane) and with ethylene containing 8.7% of ethane. The alkylates obtained in the experiments were freed from isobutane and fractionated on a column with an efficiency of 70 theoretical plates. The content of unsaturates in the alkylate fractions was determined by the bromine method [10]. Individual narrow fractions were separated from unsaturates by chromatography on silica gel and then analyzed by Raman spectroscopy. *

Table 1 gives the experimental conditions, the degree of conversion of ethylene, and the yields of alkylates. This table shows that at 450° the alkylation may be accomplished even at a pressure of 300 atm. With a rise in pressure from 300 to 500 atm (experiments 3 and 4), the alkylate yield rose from 63 to 110%, calculated on the ethylene taken for the reaction. With a rise in the ethylene content of the mixture, the alkylate yield increased (experiments 1-3). The alkylate from experiment 2 was found to contain 24% of hexane fraction (b. p. 47-70°); half of it distilled over the range 48-49°.

Table 2 gives the characteristics of individual fractions of the alkylates obtained in experiments 2 and 4. Figure 1 shows the fractionation curve of the catalyzate from experiment 4. The curve clearly shows three horizontal sections corresponding to the boiling points of the three alkylation products formed. In the alkylate of experiment 4, which was carried out at 500 atm, the content of hexane fraction represented 33% of the catalyze; 60% of this distilled over the range 48-49°.

* The Raman spectral analyses of the fractions were carried out by Yu. P. Egorov and G. K. Gaivoronskaya.