# Chemistry

N. M. Nazarova, Academician A. A. Balandin, and L. Kh. Freidlin

1958

SovietRxiv

**Abstract**

**Full Text**

## Chemistry

**N. M. Nazarova, Academician A. A. Balandin, and L. Kh. Freidlin**

# Catalytic Alkylation of *n*-Butane with Ethylene at High Temperatures and Pressures

Earlier ([1–3]) it was established that at elevated temperatures (450°) and pressures (500 atm), catalytic alkylation of normal paraffinic hydrocarbons with olefins can be carried out on alumina. At temperatures and pressures below these, propylene and butylene-1 mainly polymerize. Continuing research in this direction, in the present work we studied the alkylation of butane with ethylene.

The experiments were carried out under flow conditions; the apparatus scheme, experimental procedure, and analysis are described in work ([1]). A 90% ethylene was used (the remainder was ethane) and butane containing 4.6% impurities of gaseous hydrocarbons. Alumina and aluminosilicate were used as catalysts. The alumina, active in the dehydration reaction of isopropyl alcohol, had the following characteristics: specific surface area by adsorption of methyl alcohol (calculated by BET) 355 $m^2$/g, apparent density 0.89 g/$cm^3$, total pore volume 0.86 $cm^3$/g. The alumina was impregnated with potassium bifluoride (10% by weight of $Al_2O_3$), treated with 50% sulfuric acid, and washed with water. Before the experiment the catalyst was calcined at 430° in a stream of air.

The aluminosilicate was an industrial spherical cracking catalyst with the following characteristics: specific surface area 310 $m^2$/g; total pore volume 0.69 $cm^3$/g; average pore radius 40 Å; $Al_2O_3$ 8.8 wt.%, $SiO_2$ 88.3 wt.%.

The alkylates obtained were fractionated on a column with an efficiency of 70 theoretical plates.

Individual narrow fractions were freed from unsaturated compounds by chromatographic separation on silica gel and analyzed by the method of combined light scattering (CLS). The yield of alkylate was calculated on the ethylene taken into the reaction. The space velocity is expressed in liters of gas per 1 liter of catalyst per hour, and the yields of individual alkylate fractions in volume percent.

The results of the experiments carried out show that in the reaction of butane with ethylene, as with propylene and butylene, a complex mixture of hydrocarbons is formed.

The expected hexane fraction—the product of addition of butane to ethylene—is larger than the other alkylate fractions, and its unsaturation is considerably lower than that of the other fractions.

Table 1 gives the experimental conditions, alkylate yields, and characteristics of the fractions obtained. In experiment No. 1 at 450°, 500 atm, and 15.7 wt.% ethylene in the initial mixture with butane, the alkylate yield was 84%, and the degree of ethylene conversion 82%. Approximately half of the alkylate (51.8 vol.%) distilled below 125°. The hexane fraction (b.p. 60—70°) formed

24.2%, about 50% of it is accounted for by the narrow fraction 61-63°; the bromine number of the latter is 7.8 (see Fig. 1, *I*). In experiments Nos. 2 and 3, carried out on the same portion of catalyst and under analogous conditions, but with a lower ethylene content in the mixture

**Table 1**

| No. of experiment | Temp., °C | Pressure, atm | Ethylene content in mixture, % | Duration of experiment, min | Space velocity | Ethylene conversion, % | Alkylate yield, wt. % | <60° yield, % | 60–65° yield, % | 60–65° bromine number | 65–70° yield, % | 65–70° bromine number | 70–115° yield, % | 70–115° bromine number | 115–120° yield, % | 115–120° bromine number |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Catalyst — treated aluminum oxide** | | | | | | | | | | | | | | | | |
| 1 | 450 | 500 | 15.7 | 280 | 1300 | 82 | 84 | 2.5 | 16.0 | 7 | 8.2 | 28 | 15.5 | 20 | 8.3 | 7 |
| 2 | 450 | 500 | 10.0 | 230 | 1500 | 77 | 75 | 3.0 | 28.0 | 6 | 9.3 | 30 | 10.3 | 57 | 14.5 | 24 |
| 3 | 450 | 500 | 9.3 | 170 | 1200 | 75 | 68 | 15.4 | 17.7 | 19 | — | — | — | — | — | — |
| 4 | 450 | 300 | 10.6 | 65 | 1600 | 66 | 66 | 7.5 | 19.5 | 26* | 8.7 | — | — | — | — | — |
| 5 | 450 | 600 | 9.3 | 190 | 1000 | 76 | 87 | 7.3 | 26.5 | 15 | 12.6 | 38 | — | — | — | — |
| 6 | 460 | 300 | 12.5 | 100 | 1200 | 74 | 81 | 3.7 | 11.2 | 28* | 8.2 | — | — | — | — | — |
| 7 | 450 | 200 | 12.5 | 290 | 1500 | 61 | 27 | | | | | | | | | |
| **Catalyst — untreated aluminum oxide** | | | | | | | | | | | | | | | | |
| 8 | 450 | 450 | 12.1 | 160 | 550 | 81 | 135 | 5.2 | 29.0 | 8 | 10.8 | 30 | 12.2 | 48 | 7.2 | 21 |
| 9 | 450 | 300 | 11.0 | 160 | 1200 | 69 | 69 | 5.2 | 19.7 | 17 | 9.4 | 33 | 19.7 | — | 9.8 | — |

| No. of experiment | Temp., °C | Pressure, atm | Ethylene content in mixture, % | Duration of experiment, min | Space velocity | Ethylene conversion, % | Alkylate yield, wt. % | <60° yield, % | 60–65° yield, % | 60–65° bromine number | 65–70° yield, % | 65–70° bromine number | 70–115° yield, % | 70–115° bromine number | 115–120° yield, % | 115–120° bromine number |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 450 | 500 | 12.8 | 40 | 1000 | 75 | – | – | – | – | – | – | – | – | – | – |
| 11 | 450 | 300 | 12.0 | 240 | 850 | 65 | 103 | 6.8 | 21.2 | 15 | 8.3 | 43 | 13.0 | 23 | 7.6 | 25 |
| **Catalyst – aluminosilicate** | | | | | | | | | | | | | | | | |
| 12 | 430 | 250 | 7.0 | 120 | 1500 | 52 | 30 | Bromine number of alkylate 17 | | | | | | | | |
| 13 | 450 | 500 | 10.2 | 110 | 1400 | 68 | 50 | 4.8 | 17.8 | 12* | 6.2 | – | 16.3 | – | 14.4 | – |

* The bromine number was determined for the 60–70° fraction.

ethylene in the mixture (9–10%), the yield of alkylate and the degree of ethylene conversion were somewhat lower. However, 70% of the combined alkylate of these experiments distilled up to 125°, and the content of the hexane fraction proved to be 37.3%; ~60% of it boiled off at 62–63° (Fig. 1, *II*). The bromine number of this narrow fraction was 5.8. During the distillation of the alkylates, in addition to the narrow fraction 60–63°, narrow fractions with boiling points of 67–70° and 117–119° were also isolated. On the fractionation curves *I* and *II* (Fig. 1) of the alkylates, these correspond to the horizontal sections *a* and *b*. In the combined alkylate of experiments Nos. 2 and 3, these fractions were contained in amounts of 9 and 11 vol. %, respectively. By chromatographic separation on silica gel, all three narrow fractions were freed from unsaturated compounds and were studied by the method of combined light scattering. Table 2 gives the boiling points, $n_D^{20}$, $d_4^{20}$, and spectral frequencies of these fractions; according to the API spectral atlas, the observed frequencies of these fractions correspond to their containing, respectively: 3-methylpentane, *n*-hexane, and 3-methylheptane. The values found for their $n_D^{20}$ and $d_4^{20}$ are also close to

**Fig. 1.** Fractionation curves of alkylates: *I*—experiment No. 1, *II*—experiments Nos. 2 and 3.

reported in the literature ([7]). In the Raman spectrum of the broad fraction 70-100°, which after separation from the unsaturated compounds had $n_D^{20}$ 1.3915 and $d_4^{20}$ 0.6927, frequencies corresponding to the spectrum of 3,3-dimethylpentane were found:

347 (1); 374 (1); 411 (1); 455 (1); 695 (5); 702 (2); 856 (1); 913 (1); 934 (1); 1005 (1);

1015 (10); 1057 (10); 1081 (1); 1196 (1 sh); 1220 (1); 1240 (1); 1447 (3); 1469 (2) :

By analogy with thermal alkylation ([4,5]) or with the reaction in the presence of homogeneous catalysts ([6]), it could have been expected that, on a solid catalyst as well, the interaction of butane with ethylene could be carried out at a lower pressure than with propylene and butylene. The results of experiments Nos. 4 and 6 (Table 1) confirmed this assumption. It is interesting to note that on a catalyst that had operated for some time, an alkylate was obtained with a higher content of the narrow fraction with b.p. 60–65°. Thus, in the alkylate of experiment No. 4, carried out in the presence of a fresh portion of catalyst, it contained 17.7 vol.%, whereas in experiment No. 6 it contained 26.5 vol.%.

**Table 2**

| B.p., °C | $n_D^{20}$ | $d_4^{20}$ | Spectrum frequencies, $cm^{-1}$ | Identified hydrocarbon |
|---|---|---|---|---|
| 60–63 | 1.3750 | 0.66284 | 442 (2); 736 (0); 750 (2); 766 (0);816 (23); 879 (1); 952 (1 sh);966 (1 sh); 989 (1 sh); 1018 (0);1039 (2); 1050 (2); 1156 (1 sh);1174 (1 sh); 1355 (0); 1447 (5);1463 (5) | 3-methylpentane |

| B.p., °C | $n_D^{20}$ | $d_4^{20}$ | Spectrum frequencies, $cm^{-1}$ | Identified hydrocarbon |
|---|---|---|---|---|
| 67–70 | 1.3755 | 0.6619 | 317 (0); 334 (0); 371 (1); 403 (0);826 (2 sh); 871 (2); 893 (4); 901 (4);1040 (4); 1082 (10); 1140 (1);1305 (4); 1440 (7); 1460 (7) | *n*-hexane |
| 116–119 | 1.3996 | 0.7101 | 454 (0); 745 (0); 762 (1); 821 (2);874 (1); 905 (1); 961 (4); 978 (0);1040 (1); 1064 (0); 1083 (0);1147 (1); 1168 (1); 1222 (0);1288 (0); 1302 (2); 1352 (1 sh);1444 (7); 1464 (7). | 3-methylheptane |

When the pressure was lowered to 300 atm, the yield of alkylate changed little, but the bromine number of the hexane fraction increased somewhat.

With a further decrease in pressure to 200 atm (experiment No. 7), both the yield of alkylate (to 27%) and the yield of the hexane fraction (to 11.2%) decreased sharply.

Experiments Nos. 8–11 were carried out with alumina that had not been treated with potassium bifluoride. Analysis of the alkylates from experiments Nos. 8 and 11 (Table 1) and the curves of their fractionation (Fig. 2) show that the yield of alkylate and its fractional composition differ little from those obtained in the presence of treated alumina.

Fig. 2. Fractionation curves of alkylates: I—experiment No. 8, II—experiment No. 11

Figure 1: Fig. 2. Fractionation curves of alkylates: I—experiment No. 8, II—experiment No. 11

**Fig. 2.** Fractionation curves of alkylates: *I* —experiment No. 8, *II* —experiment No. 11

From the experimental data obtained it follows that ethylene adds

adds chiefly at the second C atom of butane, forming 3-methylpentane:

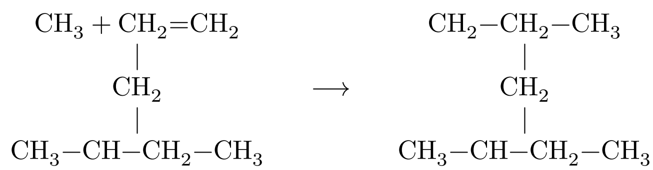
$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} + CH_2{=}CH_2 \longrightarrow \begin{array}{l} \quad CH_3 \\ \quad\;\; | \\ CH{-}CH_2{-}CH_3 \\ \quad\;\; | \\ \quad CH_2 \\ \quad\;\; | \\ \quad CH_3 \end{array}$$

and, to a lesser extent, at the first C atom, with formation of *n*-hexane:

$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} + CH_2{=}CH_2 \longrightarrow \begin{array}{l} CH_2{-}CH_2{-}CH_3 \\ \quad\;\; | \\ \quad CH_2 \\ \quad\;\; | \\ \quad CH_2 \\ \quad\;\; | \\ \quad CH_3 \end{array}$$

In the presence of an aluminosilicate catalyst it is also possible to carry out the reaction with ethylene at a lower pressure (250 atm.) (experiments Nos. 12 and 13). The bromine number of the alkylate is small (Table 2), but the yield is low (~30%). When the pressure is increased to 500 atm., the alkylate yield does not increase appreciably (50%).

In the course of alkylation, along with the expected products, higher-boiling hydrocarbons are also formed. It could be assumed that they consist mainly of the product of repeated alkylation. In the reaction with ethylene, the stage of repeated alkylation of the 3-methylpentane formed is particularly clearly visible (Fig. 1, *II*). However, at this stage addition proceeds predominantly at the first, and not at the second, C atom:



Comparison of the results of the present work with those obtained earlier in the alkylation with propylene and butylene shows that the interaction of *n*-butane with ethylene proceeds according to a scheme common to all the hydrocarbons we have studied, but at a lower pressure and with a higher yield of the expected hydrocarbon fraction.

We express our gratitude to Yu. P. Egorov and G. K. Gaivoronskaya for recording and interpreting the spectra of the hydrocarbon fractions.

A. I. Palii and V. N. Zharov took part in the work.

Institute of Organic Chemistry
im. N. D. Zelinskii
Academy of Sciences of the USSR

Received
26 IV 1958

## CITED LITERATURE

1. L. Kh. Freidlin, A. A. Balandin, N. M. Nazarova, DAN, **96**, 1011 (1954).
2. L. Kh. Freidlin, A. A. Balandin, N. M. Nazarova, Yu. P. Egorov, [[unclear: journal/series]], **105**, 1270 (1955).
3. L. Kh. Freidlin, A. A. Balandin, N. M. Nazarov, DAN, **109**, No. 1 (1956).
4. F. E. Frey, H. J. Hepp, *Ind. and Eng. Chem.*, **28**, 1439 ([[unclear: year]]).
5. C. S. Oberfell, F. E. Frey, *Oil and Gas J.*, **38**, No. 28, 50 (1939); **38**, No. 29, 70 (1939).
6. A. A. O' Kelly, A. N. Sachanen, *Ind. and Eng. Chem.*, **38**, 462 (1946).
7. R. D. Obolentsev, *Physical Constants of Hydrocarbons of Liquid Fuels and Oils*, 1953.

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