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Abstract

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ON THE MECHANISM OF ETHYLENE FORMATION IN THE CRACKING OF ISOBUTYLENE

(Presented by Academician V. N. Kondrat̕ ev on 27 V 1960)

The study of the mechanism of thermal cracking of olefins (T = 500—700°C) is greatly complicated by the presence of polymerization reactions. Further transformations of the products of these reactions may significantly distort the spectrum of primary products. Usually the primary products are found by extrapolating the molar fractions of the individual products to zero percent conversion. However, it is not evident in advance that this method can be applied unconditionally in such complex systems.

Hard and Eilers (^{1}) studied the cracking of isobutylene in a jet. Using the extrapolation method, they found that methane, propylene, and ethylene are primary cracking products. In studying the thermal cracking of isobutylene under static conditions (^{2}), using the extrapolation method, we also found that, along with methane, propylene, isobutane, and hydrogen, ethylene is a primary cracking product.

However, the structure of the isobutylene molecule is such that it is very difficult to imagine how an ethylene molecule can be formed directly from it or from the radical
$CH_2 : CH(CH_3)\dot{C}H_2$. This circumstance led Hard and Eilers to conclude that applying the extrapolation method to ethylene gives incorrect results and that, in the cracking reaction of isobutylene, ethylene is formed entirely from propylene.

In our work (^{3}) we studied the thermal decomposition of isobutylene with additions of labeled (C^{14}) propylene and showed that only an insignificant part of the ethylene is formed from propylene. In the same work we established that propylene in the indicated reaction is formed not only directly from isobutylene, but also as a result of the decomposition of the polymerization products of isobutylene. It was natural to suppose that ethylene too could be formed in this way.

For the final resolution of the question of the mechanism of ethylene formation, we studied the cracking of isobutylene with additions of labeled ethylene*. To the initial isobutylene we added 0.2% labeled C_2H_4 and carried out cracking of 300 mm of the mixture at 545°.

The cracking products were separated on a column with silica gel-ASM. Unlabeled ethylene was added to the separated ethylene, and it was then burned over CuO in a stream of nitrogen to CO_2. The CO_2 was absorbed by $Ba(OH)_2$, and the activity of the $BaCO_4$ precipitates was measured on an end-window counter.

Figure 1 shows the change in the concentration (a) and specific activity (b) of C_2H_4 during cracking.

The rate of ethylene formation was calculated by formula (^{4}):

$$w = -2.3[C_2H_4]\frac{d\lg a}{dt}.$$

Figure 2 gives the dependence of the rate of ethylene formation on time. At the initial moment of time the rate is not equal to zero, from which it follows that ethylene is formed in part directly from isobutylene.

Below, the pathways of ethylene formation in the process of thermal cracking of isobutylene are shown schematically:

$$\begin{tikzcd}
 & \text{propylene} \arrow[dr] & \\
\text{isobutylene} \arrow[ur] \arrow[rr] \arrow[dr] & & \text{ethylene} \\
 & \text{polymerization products} \arrow[ur] &
\end{tikzcd}$$

Fig. 1.
Fig. 2.

As for the mechanism of ethylene formation directly from isobutylene, it may be represented in the following way:

$$CH_3 + CH_2{=}C\left(\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right) \rightarrow CH_3{-}CH_2{-}\dot{C}\left(\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right) \rightarrow$$

$$\rightarrow \dot{C}H_2{-}CH_2{-}CH\left(\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right) \rightarrow C_2H_4 + iso\text{-}C_3H_7.$$

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* The labeled ethylene was kindly provided to us by the laboratory of labeled atoms headed by M. B. Neiman.

Methyl radicals are undoubtedly present in the reaction zone. Unfortunately, there are no experimental data from which one could draw a sufficiently reliable conclusion that reactions of radical isomerization do indeed occur under the conditions of hydrocarbon cracking.

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CITED LITERATURE

1. C. D. Hurd, L. K. Eilers, *Ind. and Eng. Chem.*, **26**, 776 (1934).
2. Yu. I. Lyadova, V. I. Vedeneev, V. V. Voevodskii, DAN, **114**, 1269 (1957).
3. V. D. Moiseev, Yu. I. Lyadova, V. I. Vedeneev, M. B. Neiman, V. V. Voevodskii, DAN, **123**, 292 (1958).
4. M. B. Neiman, ZhFKh, **28**, 1235 (1954).

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

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