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**Abstract**

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# PATHWAYS OF FORMATION OF PROPYLENE AND ETHYLENE IN THE CRACKING OF ISOBUTYLENE

It is known that, during the thermal decomposition of isobutylene, up to 50% of the initial substance is converted into liquids (olefins, aromatic compounds) ([1]). The first stage in the formation of liquids is apparently the polymerization of the initial olefin to dimers or trimers. The latter, at the usual cracking temperatures (500-700°), are themselves capable of undergoing various transformations, ultimately forming liquid cracking products.

The ratio of carbon to hydrogen in the liquid products of the thermal cracking of isobutylene is approximately equal to unity ([2]), whereas in isobutylene it is equal to two. This makes it possible to assume that, during the formation of liquids, hydrogen and methane may be released into the gas phase; it is also in principle possible that heavier gaseous cracking products, containing 2 and 3 carbon atoms per molecule, may be formed in part. The question of which gaseous products, and in what quantities, can be released from the liquids or in the course of their formation has not been studied at all.

The aim of the present work is to elucidate the pathways of formation of propylene—one of the main gaseous products of the cracking of isobutylene. It could be expected in advance that, if propylene is formed only from isobutylene, the rate of its formation should follow in time the rate of consumption of isobutylene, i.e., it should decrease with time. If, however, propylene is formed not from isobutylene but from liquids or from some unstable intermediate products (but not radicals), the rate of its formation should be equal to zero at the beginning of the reaction and then increase according to the laws of consecutive reactions. If both pathways of propylene formation occur, then a superposition of both these patterns should take place. Precisely such a case was observed in our experiments.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

We studied the change in the rate of formation of propylene during the cracking of isobutylene by means of the isotope kinetic method ($^3$). For this purpose, a small amount of labeled propylene was added to isobutylene, and the concentration and specific activity of propylene were determined during the course of the reaction. The labeled propylene was prepared by dehydration (at 370° over an aluminosilicate catalyst) of *n*-propyl alcohol labeled with carbon $C^{14}$ at the hydroxyl group*. Cracking of a mixture of this propylene (15 mm Hg) and isobutylene (285 mm Hg) was carried out in a static vacuum apparatus at 542°. The course of the specific activity $a$ and the concentration of propylene $[C_3H_6]$ is shown in Fig. 1. The rate $w_1$ of formation of propylene, calculated from the formula

$$w_1 = -2.3[C_3H_6]\, d\lg a/dt,$$

is given in Fig. 2.

* E. D. Fedorov took part in the synthesis of the labeled propylene.

The values of the derivative $d\lg\alpha/dt$ and the concentration $[\mathrm{C_3H_6}]$ were taken from the smoothed curves in Fig. 1.

It is evident that at the beginning of the reaction the rate $w_1$ is not equal to zero and that it increases over the course of 10–12 min, i.e., approximately up to 20% conversion of isobutylene.

The increase in $w_1$ found by us indicates that an appreciable amount of propylene during the cracking of isobutylene is formed not from isobutylene, but from certain intermediate cracking products, evidently from liquids. At time $t = 0$ there are no intermediate products, and the total rate of formation of propylene $w_1^0$ at this moment is equal to the rate of formation of propylene from isobutylene. The difference $w_1 - w_1^0$ is a measure of the rate of formation of propylene from intermediate products.

**Fig. 1.** Dependence of the concentration (1) and specific activity (2) of propylene on time. The lower abscissa axis gives the percentages of conversion of isobutylene

**Fig. 2.** Dependence of the rate $w_1$ of formation of propylene on time

It must be kept in mind that the rate of consumption of isobutylene is approximately constant up to 20-30% conversion ($^4$).

Fig. 3

Figure 3: Fig. 3

As can be seen from Fig. 2, the rate of formation of propylene in the region of 10–14 min passes through a maximum and begins to decrease. Since the maximum lies in the region of high percentages of conversion, where the reaction is complicated by a number of side processes, we consider it premature to draw any quantitative conclusions from this fact.

In several experiments, along with the specific activity of propylene, the activity of ethylene was determined. The results of these experiments are shown in Fig. 3. To interpret these results it is necessary to know the ratio of the specific activities of propylene and the ethylene formed from it.

**Fig. 3.** Dependence of the specific activity of propylene (1) and ethylene (2) on time

Special experiments on the cracking of labeled propylene, used in our work ($T = 600^\circ$, $p_0 = 300$ mm Hg), showed that in the interval from 14 to 45% conversion the ethylene obtained had the same activity per carbon atom as the initial propylene.*

As can be seen from Fig. 3, the activity of ethylene in the experiments on the cracking of isobutylene is considerably lower than the activity of propylene over the entire investigated range of conversion of isobutylene.

This means that only part of the ethylene is formed from propylene. Possible two other pathways for the formation of ethylene—directly from isobutylene or from the liquids.

On the basis of our experimental data it is impossible to conclude which of these pathways predominates. The possibility of ethylene formation from the liquids is indicated by the fact that propylene can be obtained from them.

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* This interesting result can evidently be explained only by assuming that, in the process of catalytic dehydration of *n*-propyl alcohol, the $^{14}C$ label in the propylene obtained was uniformly distributed over all carbon atoms. There is no reason to think that in the initial alcohol the label had already been uniformly distributed over all carbon atoms; however, we did not specifically investigate this question.

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

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