KINETIC METHOD OF APPLYING LABELED ATOMS IN THE STUDY OF PROPANE CRACKING

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KINETIC METHOD OF APPLYING LABELED ATOMS IN THE STUDY OF PROPANE CRACKING

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According to present-day concepts, the reactions of thermal decomposition of hydrocarbons are chain reactions proceeding with the participation of free radicals.

It is known that the principal products of propane cracking are methane, ethylene, hydrogen, and propylene; ethane is formed in smaller amounts. The formation of these products, according to Rice' s theory (^{1}) of the decomposition of organic compounds, takes place according to the following scheme:

$$\text{a) } CH_3CH_2CH_3 \rightarrow \dot{C}H_3 + \dot{C}_2H_5;$$

$$\text{b) } \dot{C}H_3 + CH_3CH_2CH_3 \rightarrow CH_4 + \dot{C}H_2CH_2CH_3;$$

$$\text{c) } \dot{C}H_2CH_2CH_3 \rightarrow C_2H_4 + \dot{C}H_3;$$

$$\text{d) } \dot{C}_2H_5 \rightarrow C_2H_4 + \dot{H};$$

$$\text{e) } \dot{H} + CH_3CH_2CH_3 \rightarrow H_2 + CH_3\dot{C}HCH_3;$$

$$\text{f) } CH_3\dot{C}HCH_3 \rightarrow C_3H_6 + \dot{H};$$

$$\text{g) } \dot{C}H_3 + \dot{C}H_3 \rightarrow C_2H_6.$$

The use of labeled atoms in the study of cracking makes it possible to answer the question of whether the indicated products of propane cracking are final products or undergo further transformations. By introducing into the initial propane

Fig. 1

Figure 1: Fig. 1

a small amount of one of the reaction products labeled with the radioactive carbon isotope C^{14}, and observing the activity in one or another of the reaction products, it is possible to draw certain conclusions about the mechanism of cracking.

The present work was undertaken in order to study the behavior of ethylene formed during the cracking of propane. In the work we used the kinetic method of applying labeled atoms (2,3), developed by one of the authors. The application of this method makes it possible to establish the sequence of formation of some products from others, and also to calculate the rates of formation and consumption of individual reaction products and, on the basis of knowledge of the rates of elementary processes, to estimate the concentrations of intermediate products and radicals.

We studied the cracking of propane under static conditions in a quartz reaction vessel of volume 725 ml in the temperature range 530–580°. Propane was synthesized by us from propyl bromide through a magnesium-organic compound. After purification, the propane contained 0.5% ethane and 1–1.5% propylene. Labeled ethylene $C_2^{14}H_4$, prepared from $BaC^{14}O_3$ (4), was added to the initial propane in an amount of 1%. The specific activity of the introduced ethylene was 38.8 μC/mmol. The initial pressure of the mixture in the reaction vessel was the same in all experiments—354 mm.

The cracking products were separated by chromatography (5,6) and burned to CO_2, which was absorbed by barium water. From the barium carbonate, samples were prepared for measuring the activity on an end-window counter. Figure 1 presents kinetic curves for the decomposition of propane containing 0.5% ethane and 1% labeled ethylene at different temperatures. The activation energy of the overall cracking process changes from 68,000 cal/mole for 3% conversion of propane to 72,500 cal/mole for 14% conversion.

Fig. 1. Kinetic curves of the reaction of thermal decomposition of propane: 1 –580°, 2 –554°, 3 –532°

Radiometric analysis of the cracking products showed that, in addition to ethylene, ethane has high specific activity. Figure 2 gives the change in the specific activity of ethylene (1) and ethane (2) with the depth of conversion for 3 series of experiments at different temperatures. The specific activity of ethylene α decreases as a result of dilution of the labeled ethylene by inactive ethylene formed during cracking. The specific activity of ethane β at the initial moment of time is equal to zero, since the initial mixture contains unlabeled ethane; then β increases, passing through a maximum. The maximum of the specific activity of ethane lies on the curve of the change in the specific activity of ethylene; in accordance with the general theory of the kinetic method, this indicates that

Fig. 2

Figure 2: Fig. 2

ethane is formed directly from ethylene.

Fig. 2. Change in the specific activity of ethylene (1) and ethane (2) in the course of the reaction: a and b $-T = 532°$; c and d $-554°$; e and f $-580°$; a, c, and e $-C_2H_6$; b, d, and f $-C_2H_4$

Figure 3 shows the relationship between the amount of ethylene converted during the reaction and the amount of ethane formed. The amount of ethylene formed, C', without taking into account its consumption (1), was calculated by means of the kinetic method according to the formula

$$C' = \int C \, d \ln \alpha, \tag{1}$$

where C is the concentration of ethylene in the course of the reaction, corresponding to the specific activity of ethylene α.

Curve 2 shows the accumulation of ethylene measured in the experiments; curve 3, the accumulation of ethane in the course of the reaction. The amount of ethylene converted—the difference between curves 1 and 2—corresponds to the amount of ethane formed within the accuracy with which the amounts were measured.

of ethane and ethylene, and the balance is closed with respect to the activity of the introduced ethylene and the active cracking products. This confirms that, in the cracking of propane, ethane is formed mainly from ethylene, and not by recombination of methyl radicals, as had previously been assumed. It should be noted that, as the extent of reaction increases, the discrepancy between the amount of ethylene converted and the ethane formed exceeds the experimental errors. This indicates the possibility that, at deeper stages of cracking, other products are formed from ethylene.

On the basis of the radical-chain scheme of hydrocarbon cracking, the following pathway for the formation of ethane from ethylene may be represented:

$$C_2^{14}H_4 + \dot{H} \rightarrow \dot{C}_2^{14}H_5; \tag{2}$$

$$\dot{C}_2^{14}H_5 + C_3H_8 \rightarrow C_2^{14}H_6 + \dot{C}_3H_7; \tag{3}$$

$$\dot{C}_2^{14}H_5 + H_2 \rightarrow C_2^{14}H_6 + \dot{H}. \tag{4}$$

Fig. 3. Consumption of ethylene and formation of ethane during propane cracking: **1**—amount of ethylene formed (without allowing for its consumption); **2**—accumulation of ethylene; **3**—accumulation of ethane during the reaction. The symbols are the same as in Fig. 2.

Reaction (2) proceeds readily, with activation energy $E < 5000$ cal/mole (^{7}). Further conversion of ethyl radicals consists of reactions of $\dot{C}_2H_5$ involving abstraction of H atoms from the saturated molecules $\mathrm{C_3H_8}$ or $\mathrm{H_2}$.

Knowledge of the rate w_2 of the elementary process (2), or, equivalently, the rate of ethylene consumption, makes it possible to estimate the concentration of H atoms in the zone of thermal decomposition of propane. We determine w_2 as the difference between the rate of ethylene formation w_1 and the total accumulation of ethylene with time $\frac{d(\mathrm{C_2H_4})}{dt}$.

$$w_2 = -[\mathrm{C_2H_4}]\,\frac{d\ln\alpha}{dt} - \frac{d[\mathrm{C_2H_4}]}{dt}, \tag{5}$$

where

$$w_1 = -[\mathrm{C_2H_4}]\,\frac{d\ln\alpha}{dt}. \tag{6}$$

However, from equation (5) and Fig. 3 it is seen that an estimate of w_2 as the difference between two rates close in magnitude cannot be made sufficiently accurately, although the ethylene-consumption rates obtained in this way are close in magnitude to the rate of formation of ethane from ethylene, as should be expected from the above considerations regarding the ratio of the amounts of ethylene converted and ethane formed.

Taking into account that the rate of ethane consumption under the conditions of our experiments is small, we can use the kinetic method to calculate the rate of formation of ethane from ethylene

$$w_{\mathrm{C_2H_6}} = \frac{1}{\alpha}\,\frac{dI_{\mathrm{C_2H_6}}}{dt}, \tag{7}$$

where $I_{\mathrm{C_2H_6}} = \beta[\mathrm{C_2H_6}]$ is the total activity of ethane.

The mean value of $w_{\mathrm{C_2H_6}}$ is close to the rate of ethane formation that can be obtained from the slope of the experimental curve for ethane accumulation. Using, for estimating the concentration of H atoms by reaction (2), the rate of ethane formation $w_{\mathrm{C_2H_6}}$,

$$w_2 = w_{\mathrm{C_2H_6}} = f k_0 e^{-E/RT}[\mathrm{C_2H_4}][\mathrm{H}] \tag{8}$$

and substituting $f = 0.01$, $k_0 = 10^{-10}$ $\text{cm}^3 \cdot \text{sec}^{-1} \cdot \text{molecule}^{-1}$, $E =$ 5000 cal/mol, we obtained the values of [H] given in Table 1.

To estimate the concentration of normal propyl radicals we used the rate w_1 of ethylene formation, calculated from formula (6). As follows from Rice' s scheme, normal propyl radicals decompose with formation of ethylene and a methyl radical

$$n\text{-}\dot{\text{C}}_3\text{H}_7 \xrightarrow{w_1} \text{C}_2\text{H}_4 + \dot{\text{C}}\text{H}_3. \tag{9}$$

The rate of this process, equal to the rate of ethylene formation, may be written as:

$$w_1 = k_0 e^{-E/RT} [n\text{-}\dot{\text{C}}_3\text{H}_7]. \tag{10}$$

For calculating $[n\text{-}\dot{\text{C}}_3\text{H}_7]$ we took the value $E = 28000$ cal/mol. Table 2 gives the concentration values obtained.

The estimates made in this work by means of the kinetic method for the concentrations of radicals and atoms in the reaction zone indicate the possibility of further development of this method toward the study of the elementary stages of complex processes.

Table 1

Concentration of H atoms during propane cracking, $T = 580°$

Propane conversion, %	$[\text{H}] \cdot 10^{-10}$, atoms/cm^3
3.5	4.2
6	2.9
8	2.3
10	2
13	1.6
16	1.3
18	1.2
20	1.1

Table 2

Concentration of $n\text{-C}_3\text{H}_7$ radicals during propane cracking, $T = 580°$

Conversion, %	$[n\text{-C}_3\text{H}_7] \cdot 10^{-10}$, molecules/cm^3
2	4.9
3.5	4.1
6	2.6

Conversion, %	$[n\text{-}C_3H_7] \cdot 10^{-10}$, molecules/cm^3
10	2.0
13	1.7
16	1.6

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