Investigation of the Kinetics and Mechanism of the Thermal Decomposition of Isobutylene

1957

SovietRxiv

Abstract

Full Text

Physical Chemistry

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Investigation of the Kinetics and Mechanism of the Thermal Decomposition of Isobutylene

(Presented by Academician N. N. Semenov, January 14, 1957)

One of us (^{1,2}) proposed a chain mechanism for the thermal decomposition of olefins, based on the concept of redistribution of an H atom between an allylic-type radical and an olefin molecule, with formation of an alkyl radical and a diene:

$$\mathrm{R_1CHCH\dot{C}HCH(R_2)R_3 + R_1CHCHCH_2CH(R_2)R_3 \rightarrow R_1CHCHCHC(R_2)R_3 +}$$
$$\mathrm{+ R_1CH_2\dot{C}HCH_2CH(R_2)R_3}$$

or

$$\mathrm{R_1\dot{C}HCH_2CH_2CH(R_2)R_3.}$$

From this point of view it was possible to explain satisfactorily the composition of the products of the thermal decomposition of olefins of various structures.

These concepts could not be directly extended to the cracking of such simplest olefins as C_3H_6 and i-C_4H_8, because of the absence, in the allylic radicals formed from them, of H atoms capable of entering into a redistribution reaction.

It was proposed (^{2}) that, in the case of C_3H_6 and i-C_4H_8, the formation of the reaction products is always preceded by addition of an alkyl radical to the double bond of the olefin.

It seemed of interest to us to study in detail the thermal decomposition of isobutylene, paying particular attention to obtaining additional data on the chain character of this decomposition and to testing the hypothesis of the possibility of transfer of an H atom from one or another radical to the double bond of an olefin.

Cracking of isobutylene was studied in an ordinary static vacuum apparatus in the temperature range from 542 to 620° and in the pressure range from 100 to 500 mm Hg. To clarify the question of the possibility of transfer of an H atom from a radical to an olefin molecule, experiments were carried out with

Fig. 1

Figure 1: Fig. 1

mixtures of i-C_4H_8 with C_2H_4 in the temperature range from 542 to 600° and in the pressure range from 200 to 600 mm Hg.

Fig. 1. Dependence of the composition of gaseous products on pressure during cracking of i-C_4H_8; $T = 542^\circ$, $\Delta p/p_0 = 0.1$, 1 $-CH_4$, 2 $-C_3H_6$, 3 $-H_2$, 4 $-C_4H_{10}$, 5 $-C_2H_4$.

Preliminary study of the kinetics of the thermal decomposition reaction of isobutylene was carried out from the change in total pressure, which was measured with a membrane manometer. The maximum rates dp/dt, found from the Δp–time curves, are proportional to the initial pressure of i-C_4H_8 in the pressure range from 30-500 mm Hg. This indicates first order of the reaction. The activation energy of the reaction, from the change in maximum rates with temperature, was found to be $E = 49.5 \pm 3$ kcal/mole. Earlier, values of 53.7 kcal/mole had been found in the interval 580-630° (3); and 67 kcal/mole in the interval 780-810° (4).

To study the kinetics of the process from the consumption of isobutylene and the accumulation of products, a thermochromatographic method of gas analysis was used. It showed that the principal gaseous products of isobutylene cracking are C_3H_6, CH_4, i-C_4H_{10}, C_2H_4, H_2, together with small amounts of C_2H_6 and C_3H_8.

The change in the composition of gaseous products with the change in pressure and percent conversion for $T = 542^\circ$ is shown in Figs. 1 and 2. Similar dependences were also obtained for $T = 600, 568, 555^\circ$.

Extrapolation of the curves describing the dependence of the composition of gaseous products on percent conversion to zero percent conversion makes it possible to establish the primary reaction products and their ratios.

In view of the difficulties associated with detailed analysis of the liquids, we estimated their amount and the ratio of carbon and hydrogen in them from the balance between the isobutylene consumed and the gaseous products obtained. The calculation showed that about one third of the consumed isobutylene (with respect to carbon) passes into liquid. With increasing percent conversion, the amount of liquids increases somewhat (up to one half of the consumed isobutylene). With increasing temperature, the fraction of liquids relative to the consumed isobutylene decreases somewhat. The ratio of carbon to hydrogen in the liquid was $\cong 1$.

Experiments on the cracking of i-C_4H_8 showed that up to 10% isobutane is formed as one of the primary products. The amount of isobutane increases with increasing pressure and decreasing temperature. This shows that under our conditions the reaction of addition of an H atom to the double bond of isobutylene takes place.

To clarify further the question of transfer of an H atom to the double bond of an olefin, the cracking of mixtures of i-C_4H_8 with C_2H_4 was studied.

In Table 1, the results of one such experiment at $T = 600^\circ$ and $p = 400$ mm Hg for the mixture i-$C_4H_8 : C_2H_4 = 1 : 1$ are compared with the results of cracking pure i-C_4H_8 and C_2H_4.

Table 1

Substance	p_0, mm Hg	$\Delta p/p_0 \cdot 10^3$	t, min	C_2H_4, conc., mm Hg	C_2H_4, consumed, mm Hg	i-C_4H_8, conc., mm Hg	i-C_4H_8, consumed, mm Hg	Decomp. C_2H_4, %	Decomp. i-C_4H_8, %	H_2, mm Hg	CH_4, mm Hg	C_2H_6, mm Hg	C_3H_6, mm Hg	i-C_4H_{10}, mm Hg
C_2H_4	200	0	2.5	193	7	–	–	3.5	–	–	–	3.5	–	–
i-C_4H_8	200	12.5	2.5	7.2	–	137	63	–	31.5	16.8	38.5	1.9	17.3	4.0
$C_4H_8 : C_2H_4 = 1 : 1$	400	5	2.5	142	58	118	82	29	41	33.6	61.5	34	27.4	3.4

The data presented in Table 1 make it possible to draw a number of conclusions. First of all, they confirm the concept of a chain reaction mechanism; the increase in the rate of consumption of i-C_4H_8 in the presence of C_2H_4 cannot be explained within the framework of ideas about a purely radical or molecular mechanism of the process. The same conclusion can be reached by analyzing the data on the formation of a large amount of ethane (34 mm). On the other hand, the formation of ethane in such large quantities is further evidence of the possibility of a reaction involving transfer of an H atom to the double bond of the olefin.

We believe that our experiments confirm the assumption that, in the cracking of isobutylene, the reaction

$$\dot{R} + i\text{-}C_4H_8 \rightarrow M + C_4\dot{H}_9,$$

takes place, and in a mixture of isobutylene with ethylene the reaction

$$\dot{R} + C_2H_4 \rightarrow M + C_2\dot{H}_5.$$

Fig. 2. Dependence of the composition of gaseous products on the conversion percentage during cracking of $i\text{-}C_4H_8$; $T = 542°$, $p = 300$ mm Hg; 1 –CH_4, 2 –C_3H_6, 3 –$i\text{-}C_4H_{10}$, 4 –H_2, 5 –C_2H_4, 6 –C_2H_6

Figure 2: Fig. 2. Dependence of the composition of gaseous products on the conversion percentage during cracking of $i\text{-}C_4H_8$; $T = 542°$, $p = 300$ mm Hg; 1 –CH_4, 2 –C_3H_6, 3 –$i\text{-}C_4H_{10}$, 4 –H_2, 5 –C_2H_4, 6 –C_2H_6

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Comparison of the data from the analysis of the primary gaseous products and of the composition of the liquids leads to the conclusion that the scheme previously proposed by V. V. Voevodskii for the cracking of C_3H_6 and $i\text{-}C_4H_8$ is insufficient. It was necessary to introduce into the scheme new pathways for the conversion of the $i\text{-}\dot{C}_4H_7$ radical. Such pathways may include the decomposition of $i\text{-}\dot{C}_4H_7$ into $\dot{C}H_3$ and allene, as well as the reaction of transfer of the methyl radical from $i\text{-}\dot{C}_4H_7$ to an isobutylene molecule.

$$CH_2C(CH_3)\dot{C}H_2 + i\text{-}C_4H_8 \rightarrow CH_2CCH_2 + \begin{cases} CH_3CH_2\dot{C}(CH_3)_2 \\ \text{or} \\ \dot{C}H_2C(CH_3)_3 \end{cases}$$

Some confirmation of the possibility of such reactions may be provided by the formation of allene during the cracking of isobutylene, which was observed by Rice and Schwartz (4). Under our conditions allene is unstable. Special experiments with the addition of allene showed that, over a time comparable with the duration of the experiments, it disappears completely from the gas phase.

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Received
12 January 1957

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