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Abstract

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ON THE REGULARITIES OF THE TRANSFORMATIONS OF ETHYLENE AND ACETYLENE DURING HIGH-TEMPERATURE DECOMPOSITION OF HYDROCARBONS

Most published studies on the thermal decomposition of ethylene are devoted to the investigation of its transformations either at temperatures below 800°, or in shock waves at temperatures above 1000° (1-5). The temperature interval 800-1000° remains the least studied.

In connection with this, we carried out an investigation of the thermal decomposition of ethylene with additions of C_2H_2, labeled with radiocarbon C^{14}, in the temperature interval 800-1000° at a pressure of 100 mm Hg. Study of the distribution of radioactivity among the pyrolysis products of C_2H_4 made it possible to elucidate the pathways and regularities of the transformations of C_2H_2 under the conditions of thermal decomposition of C_2H_4. The experiments were conducted in a flow vacuum apparatus with a metallic reactor according to the procedure described in (6). The thermal decomposition reaction of ethylene was carried out in a boiling bed of heat-transfer medium, for which finely ground quartz was used. The experiments were performed under conditions of complete mixing of the reactants. The reaction products were analyzed chromatographically.

Two series of experiments were carried out on mixtures of the following compositions: 99.44% C_2H_4 + 0.56% C_2H_2 and 97.3% C_2H_4 + 2.7% C_2H_2. The specific radioactivities of C_2H_2 in the initial mixtures were: $5.1 \cdot 10^6$ and $1.1 \cdot 10^6$ imp/cm$^3 \cdot$ min; the specific radioactivity of the entire mixture in both cases was $285 \cdot 10^4$ imp/cm$^3 \cdot$ min.

The reaction mixture was separated chromatographically into individual components, and then their specific radioactivity was determined with the aid of internal-fill counters. The specific radioactivity of the coke deposited during the reaction on the surface of the heat-transfer medium was determined by burning it in an oxygen atmosphere at 500-600°.

Thermal decomposition of ethylene under the experimental conditions proceeds

Figure 1

Figure 1: Figure 1

(6) by a first-order law with rate constant k_1, whose Arrhenius dependence in the temperature interval considered is as follows*:

$$\lg k_1 = (11.35 \pm 0.2) - (60\,000 \pm 1500)/4.58\,T\ \text{sec}^{-1}. \qquad (1)$$

The principal reaction products under the conditions studied are H_2, CH_4, C_2H_2, C_4H_6, C_6H_6, and coke. Ethane, propylene, allene, methylacetylene, vinylacetylene, toluene, and cyclopentadiene are obtained in considerably smaller amounts (6). Since in the present work the investigations were carried out in a reactor with complete mixing of the products, from the ratio of the specific radioactivities of the i-th products and C_2H_2 ($a_i/a_{C_2H_2}$) it is possible directly to estimate the degree of participation of C_2H_2 in the formation of these products. Thus, if $a_i = a_{C_2H_2}$, then one molecule of C_2H_2 participates in the formation of the i-th product,

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* It should be noted that the numerical values of the rate constants for the decomposition of pure ethylene and of ethylene in the system of cracked ethane (7) coincide within the limits of experimental error.

if $a_i < a_{C_2H_2}$, there are pathways for formation of the i-th product without participation of C_2H_2, etc. Figure 1 shows the ratios $a_i/a_{C_2H_2}$ at various temperatures and degrees of conversion. Since at low temperatures all $a_i < a_{C_2H_2}$ (except $2a_{\text{coke}} \approx a_{C_2H_2}$), there are pathways for the formation of all products without participation of C_2H_2. With increasing temperature, degree of conversion,

Fig. 1. Dependence of $a_i/a_{C_2H_2}$ on temperature (in the case of methane and coke, the ordinate shows $2a_{CH_4}/a_{C_2H_2}$ and $2a_{\text{coke}}/a_{C_2H_2}$).
1 –methane (a); 2 –ethane (b) and ethylene (c); 3 –propylene (d); 4 –divinyl (e); 5 –vinylacetylene (f); 6 –cyclopentadiene (g); 7 –allene (h) and methylacetylene (i); 8 –benzene (k) and toluene (l)

and the content of C_2H_2 in the reaction mixture, all ratios $a_i/a_{C_2H_2}$, except $2a_{\text{coke}}/a_{C_2H_2}$ and $2a_{CH_4}/a_{C_2H_2}$, increase monotonically. Throughout the temperature interval investigated, $2a_{CH_4}$, $a_{C_2H_4}$, $a_{C_2H_6}$, a_{C_3H}, and $a_{C_4H_6}$ remain substantially smaller than $a_{C_2H_2}$; $a_{C_3H_4}$ approach $a_{C_2H_2}$, the specific activity of cyclopentadiene a_{C_5H} and vinylacetylene $a_{C_4H_4}$ approaches $2a_{C_2H_2}$, and that of benzene and toluene approaches $3a_{C_2H_2}$. The curves for the temperature dependence of $2a_{\text{coke}}/a_{C_2H_2}$ and $2a_{CH_4}/a_{C_2H_2}$ have a minimum at 900°. The fact that $a_{C_6H_6}/a_{C_2H_2}$ varies within the range from 0 to ~ 3 indicates that in the system under consideration at least two pathways for benzene formation occur at comparable rates: reactions involving only acetylene molecules and the products of its transformations (for example, $C_2H_2 + C_4H_4 \to C_6H_6$), and reactions without participation of acetylene. Since traces of cyclohexene, which disappeared as the temperature was raised, were detected in the reaction products at temperatures below 900°, this compound was apparently an intermediate in the formation of labeled benzene. In addition, the occurrence of reactions forming C_6H_6 with participation of both C_2H_2 and C_2H_4 molecules is not excluded.

Since over the entire temperature interval investigated C_2H_2 did not take a substantial part in the formation of CH_4 and C_4H_6, the corresponding rate constants for formation of these products in the thermal decomposition of C_2H_4 may be calculated from the formulas*

$$[\mathrm{CH_4}] = k_2[\mathrm{C_2H_4}]\tau; \qquad (2)$$

$$[\mathrm{C_4H_6}] = k_3[\mathrm{C_2H_4}]^2\tau/(1 + k_4\tau). \qquad (3)$$

* Earlier, in the cracking of ethane with additions of labeled ethylene, it was shown (7) that $a_{\mathrm{C_4H_6}}/a_{\mathrm{C_2H_4}} = 2$, i.e., that divinyl is formed by the overall reaction of two ethylene molecules. Since the kinetic curve for accumulation of divinyl has a maximum and the quantity $[\mathrm{C_4H_6}]/[\mathrm{C_2H_4}]^2\tau$ decreases with increasing τ, under the experimental conditions relatively fast reactions of thermal decomposition of divinyl occur, proceeding by first order with the rate constant k_4 (6).

The Arrhenius dependences of the constants k_2 and k_3 (Fig. 2) can be represented as follows:

$$\lg k_2 = (11.75 \pm 2) - (67000 \pm 10000)/4.58\,T \quad (\mathrm{sec}^{-1}), \qquad (4)$$

$$\lg k_3 = (-6.7 \pm 2) - (63000 \pm 10000)/4.58\,T \quad (\mathrm{molecule}^{-1} \cdot \mathrm{cm}^3 \cdot \mathrm{sec}^{-1}). \qquad (5)$$

Acetylene is unstable under the conditions studied and reacts with the formation of various products. In this process the main part of the radioactivity of C_2H_2 (from 0.5 to 0.75 of the initial radioactivity) passes into coke; benzene, vinylacetylene, ethylene, and methane (Table 1). The rate constant of the overall first-order transformation of C_2H_2, k_d, can be calculated from data on the consumption of labeled C_2H_2:

$$A^0_{C_2H_2}/aA_{C_2H_2} = 1 + k_d\tau, \qquad (6)$$

where $A^0_{C_2H_2}$ and $A_{C_2H_2}$ are the concentrations of labeled C_2H_2 in the initial mixture and in the reaction products; the quantity $A_{C_2H_2}$ is equal to $a_{C_2H_2}$

multiplied by the fraction of C_2H_2 in the reaction products; $k_d = \sum k_i C_i$. It is very interesting that the curve of the dependence of $\lg k_d$ on $1/T$ has a characteristic minimum at 900° and cannot be represented by the Arrhenius formula (Fig. 3). The rate constant of the overall decomposition of acetylene, k_d, can be expressed as the sum $k_d = k_c^* + k_g$, where k_c^* is the rate constant for the formation of coke from acetylene, determined by the formula

$$k_c^* = A_{\text{coke}} / A_{C_2H_2} \tau, \tag{7}$$

and k_g is the rate constant for the formation from acetylene of the remaining gaseous products. The course of the curve of the dependence of $\lg k_c^*$ on $1/T$ also does not correspond to the Arrhenius formula and has a minimum at 900° (Fig. 3). The value k_g, on the contrary, changes monotonically with temperature, with an apparent activation energy of $\sim$ 10 kcal/mole (Fig. 3).

Fig. 2. Dependence of $\lg k_3$ and $\lg k_2$ on $1/T$.

Table 1

Conditions of the experiments and concentration of labeled reaction products A_i

T, °C	Conversion depth, %	C_2H_2, %	CH_4	C_2H_6	C_2H_4**	C_2H_2	C_3H_8	allene	methylacetylene	C_4H_8	C_4H_4	C_5H_6	C_6H_6	$C_6H_5CH_3$	coke
865	13.8	1.04	674	39	500	5692	69	38	67	531	544	493	277	26	16482
900	15.5	2.58	225	27	853	14688	64	63	131	717	891	426	690	–	3165
939	21.6	4.67	476	11	1444	11024	61	66	142	512	876	596	1450	98	8301
952***	36.9	9.19	478	–	1593	9797	–	–	–	313	934	98	1830	75	5354
1018***	71.9	16.65	601	–	1273	5908	9	21	39	46	354	41	1115	9	9834

* Values of A_i are found from the formula $A_i = \frac{a_i}{7.37} C_i$, where C_i is the percentage concentration of the i-th component of the mixture.

** As a blank experiment showed, during chromatographic separation of the reaction products, 0.03% of radioactive acetylene is entrained by ethylene. In this connection the concentrations of labeled ethylene are somewhat overestimated.

*** Experiment with addition of 2.7% C_2H_2. In the remaining experiments, the addition was 0.56% C_2H_2.

The results of this work show that acetylene plays a very important role in coke-formation reactions during high-temperature transformations of hydrocarbons. At the highest and lowest of the investigated temperatures, the ratio $2a_{\text{coke}}/a_{\text{C}_2\text{H}_2}$ is close to unity, i.e., the greater part of the carbonaceous deposits is formed as a result of acetylene transformations. At the same time, since at low temperatures all a_i are small, it should be assumed that under these conditions coke is formed during decomposition, polymerization, or condensation directly

Fig. 3. Dependence of $\lg k_d$, $\lg k_c^*$, and $\lg k_g$ on $1/T$

Figure 2: Fig. 3. Dependence of $\lg k_d$, $\lg k_c^*$, and $\lg k_g$ on $1/T$

from C_2H_2. At temperatures of 950-1000°, the ratio $2a_{\text{coke}}/a_{C_2H_2} = 0.5$. Thus, under these conditions a substantial part of the carbonaceous deposits is formed not through acetylene, but as a result of transformations of ethylene and other hydrocarbons having low specific radioactivities. The apparent rate constant for the formation of nonradioactive coke, k_c^0, calculated from the formula

Fig. 3. Dependence of $\lg k_d$, $\lg k_c^*$, and $\lg k_g$ on $1/T$

$$k_c^0 = (1 - 2a_{\text{coke}}/a_{C_2H_2})[\text{coke}]/[C_2H_4]\tau, \tag{8}$$

has an activation energy of about 80 kcal/mole. Such a high value of the activation energy indicates that coke is formed as a result of decomposition reactions. The numerical value of k_c^0 at temperatures of 950-1000° is 2-3 times smaller than k_c^*.

Since in the present work and in (6) complete data have been obtained on the formation and decomposition of acetylene under the conditions studied, one may attempt to determine the rate constant for the formation of C_2H_2 from ethylene, k_5', taking its decomposition into account:

$$[C_2H_2] = k_5'[C_2H_4]\tau/(1 + k_d\tau). \tag{9}$$

However, the value k_5', calculated by formula (9), does not remain constant with variation in the extent of conversion. At the same time, the value k_5, calculated by the formula

$$[C_2H_2] = k_5[C_2H_4]\tau \tag{10}$$

without taking into account the subsequent decomposition of acetylene, is constant within the experimental error, and its dependence on temperature is expressed by the Arrhenius formula

$$\lg k_5 = (15.34 \pm 1.0) - (86\,000 \pm 10\,000)/4.58\,T \ (\text{sec}^{-1}). \tag{11}$$

Thus, it turns out that C_2H_2 added to the initial C_2H_4 decomposes at a considerably higher rate than the C_2H_2 formed in the course of the reaction. This very interesting circumstance, the full explanation of which requires further investigation, may be connected with the formation in the reaction process of an excited triplet state of C_2H_2 (4).

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