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Abstract

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ON THE MECHANISM OF FORMATION OF SECONDARY PRODUCTS IN THE HIGH-TEMPERATURE CRACKING OF ETHANE

The present work is devoted to an investigation of the mechanism of formation of the principal secondary products in the high-temperature cracking of ethane to ethylene. The formation of CH_4, C_2H_2, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8, and C_4H_6 was studied. The mechanism of the formation of ethylene from ethane at 770–890° was studied by us earlier ([1]), using a specially developed method for studying the kinetics of high-temperature reactions ([2]). It was found that, under the conditions studied, the formation of C_2H_4 proceeded mainly by a molecular route. Indications were also obtained that the hydrocarbons C_3 and C_4 were formed with the participation of radicals. To clarify the regularities of the formation of secondary products, we carried out a study of the cracking of ethane with additions of ethylene labeled with carbon C^{14}, in a turbulent reactor ([2]) at temperatures of 800–880° and a pressure of 90 ± 3 mm Hg. Corundum was used as the heat carrier in all experiments, and in experiment No. 18, powdered quartz. The procedure for carrying out the experiments, the chromatographic analysis, and the determination of the radioactivity of the products obtained was analogous to that described in detail in ([1]). All experiments were carried out on a mixture of composition 99.5% C_2H_6 + 0.45% C_2H_4. The activity of the initial C_2H_4 was $1.33 \cdot 10^6$ imp/cm$^3 \cdot$ min, and that of the initial mixture $6 \cdot 10^3$ imp/cm$^3 \cdot$ min.

The most complete data were obtained in experiments at 880°, where it was possible to determine the concentrations and specific activities of the secondary products. This made it possible to elucidate the mechanism in greatest detail precisely at this temperature. Tables 1 and 2 give the compositions of the products obtained and their specific and absolute activities. The yield of the secondary products of cracking and their specific activity do not depend on the heat-carrier material; this is shown by the data of experiment No. 18, in which quartz was used as the heat carrier. From the data of Table 2 it is seen that the specific activities

Table 1*

Compositions of the products of cracking of C_2H_6 (vol. %)

Experiment No.	Temp., °C	kt**	α	C_2H_6	C_2H_4	H_2	CH_4	C_2H_2	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8	C_4H_6
3	866	0.287	1.21	64.23	17.54	17.14	0.66	0.073	0.124	0.082		0.082	0.073
4	870	0.54	1.39	45.7	25.46	26.3	1.9	0.124	0.113	0.152	0.09	0.032	0.127
6	880	0.45	1.37	49.25	23.2	25.1	1.9	0.133	0.082	0.113	0.0615	0.022	0.108
7	880	0.43	1.38	50.5	22.5	24.6	2.9						
8	880	0.54	1.36	48.74	24.10	24.8	1.7	0.156	0.121	0.125	0.08	0.032	0.135
5	880	0.64	1.39	42.00	26.86	28.6	1.8	0.174	0.102	0.159	0.06	0.006	0.207
9	895	0.63	1.47	40.84	25.7	30.9	1.87	0.147	0.083	0.147	0.09	0.03	0.159
18	898	1.21	1.55	29.8	34.30	33.7	2.3	0.367	0.044	0.183	0.043	0.02	0.283
14	836	0.12	1.11	80.3	9.7	9.4	0.56						
12	845	0.14	1.13	76.8	11.2	11.3	0.50						
13	846	0.195	1.15	72.6	12.8	12.25	0.75						
11	842	0.23	1.18	68.71	15.5	14.95	0.62	0.026	0.092	0.069		0.089	0.039
15	800	0.07	1.06	88.2	6.1	5.4	0.3						
17	801	0.107	1.08	84.7	8.00	6.8	0.5						
16	803	0.14	1.12	78.2	10.5	10.74	0.56						

* The accuracy of the analytical determination of the concentrations of C_2H_6, C_2H_4, H_2, and CH_4 was ±1-2% (relative), and for C_2H_2, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8, and C_4H_6 present in small amounts, ±10% (relative).

** The quantity $kt = C_0/\alpha C + 1$, where k is the total rate constant for decomposition of C_2H_6, t is the reduced reaction time, C_0 is the initial concentration and C the current concentration of C_2H_6, and α is the coefficient of increase in the number of moles during cracking; it characterizes the depth of reaction.

Table 2

Specific activities (a) (imp/min per 1 mm gas pressure in the counter) and concentrations of active products (A) (in imp/min per 1 cm^3 of gas obtained)*

Experiment No.	T-re, °C	kt	CH_4 a	CH_4 A	C_2HC_4 a	C_2HC_4 A	C_2HC_2H a	C_2HC_2H A	C_2HC_3H a	C_2HC_3H A	C_3HC_3H a	C_3HC_3H A	C_3HC_6H a	C_3HC_6H A	$C_4HC_{10}H$ a	$C_4HC_{10}H$ A	C_4HC_4H a	C_4HC_4H A	C_4HC_6H A
15	800	0,07	211	10	67506	560	–	6,3	–	1,3	–	4,1	–	1,84	–	5,3	–	7,7
17	801	0,107	240	13,8	48606	230	–	4,4	–	1,9	–	10	–	1,0	–	1,7	–	7,25
16	803	0,14	270	23,8	36105	980	–	4,5	–	1,6	–	6,1	–	3,0	–	4,7	–	12,4
14	840	0,12	136	12,0	40006	120	–	10,5	–	4,4	–	10,6	–	3,3	–	6,1	–	13,8
12	845	0,14	115	9,0	34306	060	–	10,0	–	2,9	–	10,65	–	1,0	–	3,7	–	10,3
13	846	0,195	162	19,2	29406	270	–	10,0	–	1,9	–	8,0	–	2,2	–	2,1	–	16,9
11	842	0,23	160	15,6	24006	230	250	10,5	290	4,22	176	19,2	–	–	–	–	434	25
3	866	0,287	–	–	20705	740	260	29,6	148	2,9	192	25,1	420	5,5	–	–	–	–
4	875	0,54	–	–	12855	120	160	31,2	195	3,5	121	27,3	500	7,2	1090	5,5	290	59,0
6	878	0,45	104	32	13254	840	204	42,7	220	2,8	131	23,5	560	5,5	940	3,3	256	4,37

Experiment No.	T-re, °C	kt	CH_4 a	CH_4 A	C_2H_6 a	C_2H_6 A	C_2H_4 a	C_2H_4 A	C_2H_2 a	C_3H_8 A	C_3H_8 a	C_3H_6 A	C_3H_6 a	C_4H_{10} A	C_4H_{10} a	C_4H_8 A	C_4H_8 a	C_4H_6 A
7	880	0,43	114	52	1440	5100	–	–	–	–	–	–	–	–	–	–	–	–
8	880	0,54	180	45,7	1300	4900	1860	45,5	213	4,06	1140	22,4	400	5,5	1160	5,8	2740	58,1
5	880	0,64	–	–	1185	5000	1785	49,5	185,5	2,3	1060	26,0	510	5,0	640	0,6	2400	78
9	895	0,54	170	50	1130	5120	1330	31,2	196	3,46	960	27,3	–	7,2	–	5,50	2200	59
18	898	1,21	75	27,2	860	4650	1250	71,5	235	1,6	900	24,6	390	2,65	–	2,5	1730	77

* The specific activity of C_2H_6 was 4–5 imp/mm · min at 880°, 2–3 imp/mm · min at 840°, and 1–2 imp/mm · min at 800°. The accuracy of determining the specific activities of all products was $±$3%. In those experiments in which it was not possible to measure the specific activities of C_2H_2, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8, and C_4H_6, which were present in small amounts, the determination of the total activities of these products was carried out as follows: inactive gases were added to the reaction mixture; the mixture was separated chromatographically and the total activity of the individual hydrocarbons was determined. In order to calculate the fraction of radioactive molecules for each hydrocarbon, it is necessary to multiply the corresponding value of a by the coefficient $2.5 \cdot 10^{-9}$.

C_2H_2, C_3H_6, and C_4H_8 are close to the specific activity of ethylene, from which it may be concluded that these products are formed with the participation of one molecule of ethylene. The specific activity of divinyl in all experiments is approximately twice the specific activity of C_2H_4. Evidently C_4H_6 is formed with the participation of two molecules of C_2H_4 or of products obtained from ethylene and having the same specific activity (for example, from C_2H_4 and C_2H_2), and not from C_4H_6. The specific activities of methane, ethane, propane, and butane are comparatively small and, consequently, these products are formed chiefly from low-activity ethane and the products of its transformations. Thus, from consideration of the specific activities of the products it is immediately possible to draw a conclusion about a qualitative difference in the pathways of formation of saturated, unsaturated, and diene hydrocarbons in the cracking of ethane. From the data on the concentrations of active products in the reaction mixture it follows that the main directions of ethylene consumption are the formation of acetylene, methane, propylene, and divinyl. Reverse hydrogenation of ethylene to ethane proceeds only to an insignificant extent: less than 0.01 of the fraction of C_2H_4 is converted into ethane. It should be noted that the rate constant of the reaction ${}^*C_2H_4 + H_2 \rightarrow \rightarrow C_2^*H_6$ proves, with good accuracy, to be equal to the product Kk, where K is the equilibrium constant for the reaction under consideration and k is the rate constant of ethane dehydrogenation by the molecular path. Consequently, the reaction written above corresponds to the actual path of formation of $C_2^*H_6$ under the conditions investigated.

Let us now dwell on the specific pathways of formation of the individual products. From the fact that the specific activities and concentrations of C_3H_8 and C_4H_{10}

are relatively small, it follows that their formation occurs, in accordance with (1), predominantly through recombination of low-activity radicals CH_3 and C_2H_5.

According to (2), we have:

$$[C_3H_8] = \frac{k_1[CH_3][C_2H_5]\,t}{1 + k_{C_3H_8}t}; \tag{1}$$

$$[C_4H_{10}] = \frac{k_1[C_2H_5]^2\,t}{1 + k_{C_4H_{10}}t}. \tag{2}$$

* Molecules containing radioactive carbon C^{14} are marked with an asterisk.

where k_1 is the rate constant of the radical recombination reaction, and $k_{C_3H_8}$ and $k_{C_4H_{10}}$ are the overall rate constants of the decomposition reactions of C_3H_8 and C_4H_{10}. The formulas for the formation of labeled products are written analogously. Combining equations (1) and (2), we find that at 880° and for the ratio $(1 + k_{C_4H_{10}}t)$ to $(1 + k_{C_3H_8})$ equal to ~ 1.5, the ratio $[C_2H_5] : [CH_3]$ is ~ 1.5. Using the value of k_1 obtained in (1), at 880° we obtain, in agreement with an independent calculation (1), $[C_2H_5] = 2 \div 4 \cdot 10^{14}$ radicals/cm^3, since, by estimate, $2 < (1 + k_{C_4H_{10}}t) \leq 4$. Analysis of the data obtained shows that the formation of propylene and butylene proceeds according to the scheme:

$$\begin{aligned} C_2H_6 + R &\xrightarrow{k_2} C_2H_5 + RH, & C_4H_9 &\xrightarrow{k_5} C_4H_8 + H, \\ C_2H_5 &\xrightarrow{k_3} C_2H_4 + H, & C_4H_9 &\xrightarrow{k_6} C_3H_6 + CH_3, \\ C_2H_5 + C_2H_4 &\xrightarrow{k_4} C_4H_9, & C_4H_9 &\xrightarrow{k_7} C_2H_4 + C_2H_5. \end{aligned}$$

Neglecting the consumption of C_4H_9* (i.e., using unity in the denominators), we have:

$$[C_3H_6] = k_6[C_4H_9]t = \frac{k_6 \cdot k_2 \cdot k_4[C_2H_4][C_2H_6][R]t}{(k_5 + k_6 + k_7)k_3}, \tag{3}$$

$$[C_4H_8] = k_5[C_4H_9]t = \frac{k_5 \cdot k_2 \cdot k_4[C_2H_4][C_2H_6][R]t}{(k_5 + k_6 + k_7)k_3}. \tag{4}$$

From the ratio of the specific activities of C_3H_6 and C_3H_8, C_4H_8 and C_4H_{10}, it follows that, under the conditions studied, there was no appreciable formation of C_3H_6 from C_3H_8 or of C_4H_8 from C_4H_{10}. At a temperature of 880°, propylene and butylene were also not formed by recombination of C_2H_3 with CH_3 and C_2H_5. Otherwise, the concentration $[C_4H_8]$ would have been greater than $[C_3H_6]$, since $[C_2H_5] \gg [CH_3]$. In reality, however, at 880°, $[C_4H_8] \ll [C_3H_6]$. This fact can readily be explained if it is assumed that the formation of both

C_3H_6 and C_4H_8 occurs mainly in the decomposition of C_4H_9. The preferential formation of C_3H_6 from C_4H_9, and not from C_3H_7, is due, on the one hand, to the fact that $[C_4H_9] > [C_3H_7]$, since $[C_2H_5] \gg [CH_3]$, and, on the other hand, to the greater ease of breaking the C–C bond as compared with breaking the C–H bond**. Using the experimental data and the values of [R], k_2, and k_3 obtained in (1), and also assuming $k_6 : (k_5 + k_6 + k_7) \simeq 2/3$, from equations (3) and (4) one can estimate the value of the rate constant for the reaction of radical "addition" to the olefin, k_4, which at 880° is equal to $9 \cdot 10^{-16}$ (molecule$^{-1} \cdot$cm$^3 \cdot$sec^{-1}), i.e., twice as large as the rate constant of the substitution reaction. The ratio k_6/k_5, determined from equations (3) and (4), is equal to 5 at 880°, 3 at 840°, and 1 at 800°. Since the activation energy E_6 is less than E_5, the ratio k_6/k_5 should not have increased with increasing temperature, but should have decreased. Evidently, at the lower temperatures studied there are other pathways for obtaining C_4H_8, in particular recombination of C_2H_3 and C_2H_5.

The interrelated formation of acetylene and divinyl*** is described

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* In the present work, when considering pathways for the formation of secondary products involving free radicals, we, in agreement with the results of (1), assume that at the high temperatures studied the main pathway for the disappearance of the radicals C_3H_7 and C_4H_9 is decomposition, and not substitution or recombination reactions. This is confirmed, in particular, by the total activity of C_3H_8, which is approximately an order of magnitude lower than the activity of C_3H_6. At 880°, the main pathway for the disappearance of C_2H_5, according to (1), is also decomposition. At the lower temperatures studied, neglecting other pathways for the disappearance of C_2H_5 leads to an overestimate of $[C_2H_5]$ by no more than a factor of two.

** In processing the results in (1), the possibility of formation of C_3H_6 from C_4H_9 was not taken into account. This led to a somewhat overestimated value of the ratio $[C_2H_5]/[CH_3] = 4$, compared with the value 1.5 obtained in the present work.

*** A special experiment, in which 0.2% labeled C_2H_2 was added to the initial mixture, confirmed that C_4H_6 is formed not from two C_2H_2 molecules, but from a C_2H_2 molecule and C_2H_4. The specific activities of C_2H_4, C_2H_2, and C_4H_6 in this experiment were respectively 2370, 800, and 3140 imp/mm $\cdot$ min.

by the following overall equations:

$$[C_2H_2] = \frac{k_8[C_2H_4]t}{1 + k_9[C_2H_4]t} \tag{5}$$

$$[C_4H_6] = k_9[C_2H_2][C_2H_4]t. \tag{6}$$

The rate constant for the reaction of formation of C_2H_2 from C_2H_4 (k_8) was found to be 0.65 s^{-1} at 880°, 0.17 s^{-1} at 840°, and 0.04 s^{-1} at 800°. This variation of k_8 with temperature corresponds to an activation energy of $\sim$ 95 kcal. The effective rate constant for the reaction of C_2H_2 with C_2H_4 with formation of C_4H_6 (k_9), determined from the independent equations (5) and (6) at 880°, is equal to $1.6 \cdot 10^{-16}$ molecule$^{-1} \cdot cm^3 \cdot s^{-1}$ and changes hardly at all when the temperature is lowered. At 840 and 800°, the value of k_9 calculated from equation (5) was approximately twice the value of k_9 obtained from equation (6). Possibly, at lower temperatures other reactions begin to play a substantial role in the disappearance of C_2H_2, for example, the addition of alkyl radicals to C_2H_2. The detailed mechanism of the very interesting reaction of divinyl synthesis is complex and apparently includes steps involving free radicals. This is indicated by the fact that the concentration $[C_4H_6]$ in the products is higher than the equilibrium concentration for the process $C_4H_6 \rightleftarrows C_2H_2 + C_2H_4$. The established independence of the constant k_9 from the depth of conversion shows that only chemically highly reactive radicals, the concentration of which is stationary, can act as intermediate compounds in the indicated reaction.

The specific activity of C_2H_5 ($a_{C_2H_5}$) should be equal to half of $a_{C_4H_{10}}$. From the ratio of $a_{C_3H_8}$ and $a_{C_4H_{10}}$, one can determine a_{CH_3} and, consequently, the specific activity of CH_4 formed in substitution reactions involving CH_3. Thus, in experiment No. 18, where $a_{C_4H_{10}}$ was measured especially accurately, $a_{CH_3} = 40$ imp/mm $\cdot$ min, while $a_{CH_4} = 75$ imp/mm $\cdot$ min. Thus, about one half of the CH_4 was not formed through CH_3. Since the concentration of active $CH_4{}^*$, A_{CH_4}, is relatively large, it cannot be assumed that CH_4 is formed to a significant extent by decomposition of high-molecular active products present in small quantities. Evidently there is a reaction of CH_4 formation involving C_2H_4, possibly by molecular processes, as is also indicated in work ([3]). With increasing temperature, a_{CH_4} falls, which indicates a decrease in the fraction of the reaction of formation of CH_4 through C_2H_4. The specific activity of coke, measured in the form of CO_2 (a_{CO_2}), at 880° is $\sim$ 630–640 imp/mm $\cdot$ min, i.e., $1/2\, a_{C_2H_4}$. Hence it may be concluded that at 880° coke is formed from highly active unsaturated products. At 840 and 800°, a_{coke} is equal, respectively, to 230 and 90–160 imp/mm $\cdot$ min. At these temperatures, reactions of interaction of unsaturated and condensed hydrocarbons with less active alkyl radicals begin to play a substantial role in coke formation.

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