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Abstract

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ON THE SIGNIFICANCE OF CHAIN REACTIONS IN HIGH-TEMPERATURE CRACKING OF ETHANE

The article considers the question of the share of the chain reaction in the cracking of ethane in the temperature range 770-900°. For lower temperatures this problem has recently been studied intensively (^{1}-^{3}, ^{8}). However, the mechanism of cracking and pyrolysis reactions, especially at the high temperatures used in technology (^{4}), cannot be regarded as fully elucidated.

To solve the problem posed, measurements were made of the activities of various products obtained in the cracking of a mixture of ethane with additions of methane labeled with radiocarbon C^{14}. The procedure for carrying out these

Table 1

t, sec.	Temp. in °C	C_2H_6	C_2H_4	C_3	C_4	CO_2 (coke)
0,14	770 ± 3	$7,1 \pm 3,3$	$5,4 \pm 1,5$	15,8	0,14	$2,8 \pm 0,1$
0,185	770 ± 3	$8,6 \pm 3,7$	$7,9 \pm 1,9$	38	0,65	–
0,260	770 ± 3	$14,4 \pm 5,6$	$13,8 \pm 2,8$	42,5	1,64	$3,94 \pm 0,2$
0,415	770 ± 3	$19 \pm 4,7$	$22 \pm 1,9$	74	3,5	$6,35 \pm 0,4$
0,82	770 ± 3	$24 \pm 5,6$	$52 \pm 3,7$	131	10,3	$17,2 \pm 0,9$
0,008	840 ± 3	$10,8 \pm 5$	$9,32 \pm 0,5$	–	–	$5,05 \pm 0,1$
0,026	840 ± 3	$80,5 \pm 5$	$67,2 \pm 2$	–	–	$14,4 \pm 0,6$
0,0415	840 ± 3	$80,5 \pm 3$	$93,5 \pm 5$	–	–	$28,8 \pm 0,3$
0,0625	840 ± 3	86 ± 4	107 ± 3	–	–	$30,7 \pm 1,5$
0,0735	840 ± 3	75 ± 4	135 ± 5	–	–	–
0,0078	890 ± 3	87	146,5	248	9,75	0,35

t, sec.	Temp. in °C	C_2H_6	C_2H_4	C_3	C_4	CO_2 (coke)
0,0117	890 ± 3	99	162	271	13,9	4,25
0,0152	890 ± 3	126	247	400	24,2	17,3
0,0156	890 ± 3	124	254	402	24	14,2
0,0192	890 ± 3	138	297	477	39,5	–

$$\frac{\text{Activity of the gases obtained}}{\text{Activity of the initial mixture}} \cdot 10^5 \ast$$

* In those cases where the error in measuring the activity is not indicated, it does not exceed 3%.

experiments is described in article (^{5}). The data obtained for three temperatures: 770, 840, and 890°, are given in Table 1. In processing the results it was taken into account that the experiments under consideration were carried out under conditions of complete or nearly complete mixing in a "boiling" bed (^{5}). This makes it possible to reduce the problem to the solution of a system of algebraic equations.

Keeping the notation adopted in (5), let us additionally introduce into consideration the following elementary processes*:

$$\mathrm{C_2H_6} \to 2\mathrm{CH_3}; \tag{1}$$

$$\mathrm{CH_4} \to \mathrm{H} + \mathrm{CH_3}; \tag{1'}$$

$$\mathrm{R}_i + \mathrm{R'H} \to \mathrm{R}_i\mathrm{H} + \mathrm{R'}; \tag{2}$$

$$\mathrm{R}_i + \mathrm{R}_j \to \mathrm{R}_i\mathrm{R}_j; \tag{3}$$

$$\mathrm{C_2H_5} \to \mathrm{C_2H_4} + \mathrm{H} \tag{4}$$

with constants equal, respectively, to k_1, k_1', $k_{2(\mathrm{R}i)}$, $k_{3(\mathrm{R}i,\mathrm{R}_j)}$ ($= k_3$ when $\mathrm{R}_i\mathrm{R}_j \neq \mathrm{H}$), and k_4.

In what follows the quantities

$$k_2 = \sum_{\mathrm{R}i} k_{2(\mathrm{R}i)} \frac{[\mathrm{R}_i]}{[\mathrm{R}]} \qquad \left(\mathrm{R} = \sum_{\mathrm{R}i} \mathrm{R}_i\right) \tag{5}$$

and the averaged value of the recombination constant $\bar{k}_3$ will also be used.

A special analysis, carried out taking into account the circumstance that in the reaction mixture the activity of methane is much greater than the activities of the other gases, whereas the total concentration $[CH_4] \ll [M]$, and using a number of experimental estimates**, gives the following expressions for the dependence of the concentrations of various active products on time t (active products are denoted by *):

$$\Delta = [CH_4^*]_0 - a[CH_4^*] =$$

$$= k_2[CH_4^*]_0[R]\,t\,\frac{(1+\bar{k}_3 t[R])}{1+k_{2(CH_3)}[M]\,t+\bar{k}_3[R]\,t}; \tag{6}$$

$$[C_2H_6^*] = \frac{k_3[CH_3][CH_3^*]}{1+\bar{k}t}; \tag{7}$$

$$[C_3^*] = \frac{k_3[CH_3^*][C_2H_5]}{1+tf_{C_3}(t)}; \tag{8}$$

$$[C_4^*] = \frac{k_3[C_2H_5^*][CH_5]}{1+tf_{C_4}(t)}, \tag{9}$$

where, in the approximation used,

$$[R] = \frac{1}{4\bar{k}_3 t}\left[\sqrt{1+16\,k_1\bar{k}_3 t^2[C_2H_6]}-1\right];$$

$$[CH_3^*] = \frac{k_2[CH_4^*][R]\,t}{1+k_{2(CH_3)}[M]\,t+\bar{k}_3 t[R]};$$

$$[CH_3] = \frac{2k_1[C_2H_6]\,t+k_2[CH_4][R]\,t}{1+k_{2(CH_3)}[M]\,t+\bar{k}_3 t[R]}; \tag{10}$$

$$[C_2H_5] = \frac{k_2[C_2H_6][R]\,t}{(1+k_{2(C_2H_5)}[M]\,t+\bar{k}_3 t[R])+k_4 t}.$$

* The influence of the possible participation in the reaction of an additional molecule M may be included in the corresponding constant, since the experiments were carried out at the same pressure.

** Mainly those experimental results were used according to which the activity of C_3 exceeds the activity of all the other products formed (Table 1), and according to which the decomposition of $C_2H_6^*$ is not the main path for the formation of active ethylene. The nature of the dependence of the various products on t was also taken into account.

and $f_{C_3}(t)$ and $f_{C_4}(t)$ denote the destruction functions of C_3^* and C_4^*, respectively, with $[C_3^*](1 + tf_{C_3}(t)) \cong [C_3^*] + 2[C_2H_4^*] + 2[C_4^*] - 2kt[C_2H_6]$.

In this case the rate constant of the chain reaction k_c, proceeding through elementary act (4), can be expressed in the form

$$k_c = \frac{k_4[C_2H_5]}{[C_2H_6]} = \frac{k_4 t \cdot k_2[R]}{1 + k_{2(C_2H_5)}[M]t + \bar{k}_3 t[R] + k_4 t}. \tag{11}$$

The data obtained make it possible to find directly the upper limit of k_c by means of the inequality

$$k_c < \frac{k_2 k_4 t[R]}{(1 + \bar{k}_3 t[R] + k_{2(CH_3)}[M]t} \ll \frac{[C_3^*]}{[C_4^*]} \frac{[C_2H_4^*]}{t[CH_4^*]}. \tag{12}$$

Substitution of the experimental values into (12) gives $k_c/k <\sim 0.05$ at 770° and $k_c/k <\sim 0.05 \div 0.1$ at 890°. Thus, even a preliminary estimate shows that the fraction of the chain reaction in the total cracking process is, within the framework of the generally accepted scheme, very small in the case considered.

To determine exact values of k_c and to establish the magnitudes of the elementary constants, it proves necessary additionally to invoke thermodynamic considerations relating k_1 and k_3; moreover, it is sufficient to find the value of $k_1\bar{k}_3$, which enters into the expression for $[R]$. The available tabulated data on thermodynamic functions (^{6}) make it possible to calculate the equilibrium constants* $K_I = (k_1')^2/k_1k_3$ and $K_{II} = k_1/k_3$, which are equal, respectively, to 0.10 and $1.8 \cdot 10^9$ at 770°; 4.6 and $2.4 \cdot 10^{10}$ at 840°; 70 and $1.13 \cdot 10^{11}$ at 890°.

Assuming the presence only of bimolecular recombination, we have grounds to substitute $k_1' = 10^{13} e^{-101/RT}$. Combining then K_I and K_{II}, we find a value of k_3 equal to $7.1 \cdot 10^{-13}$ at 770°; $6 \cdot 10^{-13}$ at 840° and $4.5 \cdot 10^{-13}$ at 890°. Substitution of the indicated k_3 into the expression for K_{II} gives, for k_1, values close to those determined in work (^{7}). The value of k_3, obtained under the assumption of a double collision in recombination, has a steric factor of the order of 10^{-3} and differs little from the standard value for a triple collision at the pressure studied; therefore we adopted $k_1\bar{k}_3$ equal to $2.8 \cdot 10^{-16}$ at 770°, $2.14 \cdot 10^{-15}$ at 840° and $9.33 \cdot 10^{-15}$ at 890°. These values are obtained by substituting into K_I the chosen value k_1' with a factor of $\sim 1/3$. Combining the formulas given above, one can further obtain from the experimental data values of $k_{2(CH_3)}$ equal to $2.2 \cdot 10^{-16}$ at 770° and $4 \cdot 10^{-16}$ at 890°, which corresponds to an activation energy of 12 ± 2 kcal and a steric factor of the order of 10^{-3}.

The possibility of such small steric factors in reactions of type (2) was pointed out earlier ([8],[9]). For the value k_2/k_3, the values obtained are $2.8 \cdot 10^{-3}$ at 770° and $3.3 \cdot 10^{-2}$ at 890°. Such a large increase in the latter value should apparently be associated with an increase in the fraction of H radicals. For the same reason, the ratio $k_3/\bar{k}_3$ increases approximately from unity at 770° to 2.5 at 890°. Estimation of $\bar{k}_3$ from the experimental data gives, in agreement with the preceding considerations, a value of $\sim 5 \cdot 10^{-13}$. The pre-exponential factor for k_4 proves to be 10^3 times smaller than the standard value. Substitution of the constants determined above into expression (4) gives for the ratio k_c/k a value of the order of 0.03.

* The constants of the various recombination processes are equated; concentrations are written in molecules/cubic centimeter.

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

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