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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE KINETIC REGULARITIES OF THE HIGH-TEMPERATURE CRACKING OF ETHANE

This article describes a study of the overall kinetics of ethane cracking in the temperature range 800–900°. The investigation of cracking at such high temperatures, which until now has not been carried out with sufficient accuracy for kinetic experiments and under strictly specified conditions, is of considerable theoretical and definite practical interest ([1]).

Increasing the temperature and the corresponding sharp reduction of the reaction time to 0.5–0.005 sec required the development of a special experimental procedure. In particular, in order to heat the cracking gas sufficiently rapidly and to maintain a constant temperature along the length of the reaction zone, intensive heat exchange with a "fluidized bed" ([2]) of a powdered heat carrier (corundum)* was used. The experiment was divided into two parts: 1) cracking proper and 2) analysis of the products. For the analysis we used a chromatographic method developed by us and described in ([3]). In those cases where individual gases, for example isobutane, were present in such small amounts that they were not recorded in the chromatographic analysis, the method of radioactive indicators was used. For this purpose, small quantities of methane labeled with C^{14} were added to the initial ethane.** The radiocarbon entered into the composition of the gases formed during cracking and was determined in the corresponding fraction after adsorption separation of the cracking products, to which the appropriate inactive gases were added.***

Fig. 1. Diagram of the apparatus: **1** —quartz reactor, **2** —heat carrier (corundum), **3** —preheater, **4** —thermocouples, **5** —vessel with the initial mixture, **6, 9, 14** —manometers, rotameters, **8** —vessel with carbon dioxide, **11** —condenser, **12** —pumping line, **13** —valve, **15** —vessel for regulating the pressure in the valve, **16** —line to the gas-sampling system.

The schematic arrangement of the principal elements

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* It should be noted that at the temperatures considered, the role of surfaces becomes obviously secondary.

** The authors express their gratitude to Yu. B. Kryukov and L. I. Liberov for providing the labeled methane.

*** A detailed consideration of the distribution of activities among the cracking products will be given in a subsequent paper.

of the experimental setup is shown in Fig. 1. Vessel 5 contained a mixture of ethane with small additions (about 2%) of radioactive methane. Within the accuracy of chromatographic analysis, the indicated gases contained no impurities. During the experiment the gas from 5 was directed through preheater 3, whose temperature was maintained at 350–400°, into reactor 1. The lower part of the reactor was filled with corundum particles, whose diameter varied, depending on the gas-flow rate, from 0.1 to 0.8 mm. As was already indicated, during the experiments a "fluidized bed" was realized in the reactor, and complete or nearly complete mixing of the reaction mixture took place. This circumstance was confirmed by visual observation and by comparison with the hydrodynamic criterion for formation of a fluidized bed. However, the chief argument indicating the presence of mixing in the reactor is the very strict fulfillment, for the monomolecular overall cracking reaction, of relations obtained on the assumption of complete or nearly complete mixing in the reactor zone.

For rapid cooling of the cracking products after their exit from the fluidized bed, carbon dioxide at room temperature was fed into the reactor from above in a weight ratio to the reaction mixture of from 3 to 12. The temperatures in the reactor in the fluidized bed and above the fluidized bed after introduction of the carbon dioxide

Table 1

Run No.	Composition of initial gas, vol. %	Reduced contact time, t	Pressure in reactor, mm Hg	Temperature, °C	Increase in volume, α	Exit-gas composition, vol. % C_2H_6	Exit-gas composition, vol. % C_2H_4	Exit-gas composition, vol. % CH_4	Exit-gas composition, vol. % H_2	Exit-gas composition, vol. % coke (CO_2)
35	98% C_2H_6 + 2% CH_4	0.0578	90	765	1.06	86.6	5.4	2.6	5.05	0.35
43	98% C_2H_6 + 2% CH_4	0.0796	90	773	1.055	88.7	4.4	2.5	4.3	0.1
38	98% C_2H_6 + 2% CH_4	0.140	92	771	1.075	84.3	6.9	2.8	5.4	0.4
41	98% C_2H_6 + 2% CH_4	0.185	88	770	1.13	79.7	8.6	2.5	8.6	0.3
42	98% C_2H_6 + 2% CH_4	0.260	91	770	1.12	76.1	10.3	2.5	10.3	0.4
44	98% C_2H_6 + 2% CH_4	0.415	88	770	1.17	68.7	14.2	3.4	13.3	0.4
46	98% C_2H_6 + 2% CH_4	0.705	91	770	1.23	60	19.5	2.75	16.7	1

Run No.	Composition of initial gas, vol. %	Reduced contact time, t	Pressure in reactor, mm Hg	Temperature, °C	Increase in volume, α	Exit-gas composition, vol. % C_2H_6	Exit-gas composition, vol. % C_2H_4	Exit-gas composition, vol. % CH_4	Exit-gas composition, vol. % H_2	Exit-gas composition, vol. % coke (CO_2)
48	98% C_2H_6 + 2% CH_4	0.82	89	773	1.36	51	22.4	4.1	21.7	0.8
28	98% C_2H_6 + 2% CH_4	0.008	130	843	1.04	89	4.5	1.96	4.1	0.4
29	98% C_2H_6 + 2% CH_4	0.026	82	838	1.17	69.4	14.3	3.05	13.1	0.2
32	98% C_2H_6 + 2% CH_4	0.0415	92	841	1.25	59.5	18.3	4	17.9	0.3
30	98% C_2H_6 + 2% CH_4	0.0625	92	837	1.27	55.7	21.1	3.9	19.0	0.3
33	98% C_2H_6 + 2% CH_4	0.0735	93	837	1.38	45.2	25.6	4.4	24.1	0.4
31	98% C_2H_6 + 2% CH_4	0.0875	90	834	1.45	45.2	21.2	4.8	28.0	0.7

Run No.	Composition of initial gas, vol. %	Reduced contact time, t	Pressure in reactor, mm Hg	Temperature, °C	Increase in volume, α	Exit-gas composition, vol. % C_2H_6	Exit-gas composition, vol. % C_2H_4	Exit-gas composition, vol. % CH_4	Exit-gas composition, vol. % H_2	Exit-gas composition, vol. % coke (CO_2)
49	96.5% C_2H_6 + 3.5% CH_4	0.0078	89	890	1.19	63.54	18.7	2.2	15.5	0.06
50	96.5% C_2H_6 + 3.5% CH_4	0.0117	101	890	1.23	58.8	20.5	3.2	17.4	0.1
53	96.5% C_2H_6 + 3.5% CH_4	0.0156	93	892	1.34	48.6	24.1	3.4	23.7	0.2
52	96.5% C_2H_6 + 3.5% CH_4	0.0192	95	894	1.345	47.5	25.1	3.7	23.6	0.15
56	97.5% C_2H_6 + 2.5% CH_4	0.0152	90	897	1.38	50.2	22.5	4.2	22.6	0.5

were measured with platinum thermocouples, whose readings were recorded by a fast-acting electronic potentiometer with an accuracy of 2–5°. A special valve, whose design is described in (4), made it possible to maintain a constant pressure in the reactor (approximately 90 mm Hg). The first portions of the cracking products were discarded (blank experiment).

The main composition of the exit gases at three temperatures is given in Table 1.

The reduced reaction time is equal to $t = \frac{V\varepsilon}{vF}$, where V is the volume of the fluidized-

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

layer, v is the mean linear velocity of the gas stream, taking into account thermal expansion, ε is the fraction of free volume, and F is the cross section of the reactor. Since the reaction is carried out under conditions of complete mixing and the composition of the exiting gases coincides with the composition in the reaction zone, which does not vary along the length of this zone, it is sufficient, in order to determine the final concentrations, to write the conservation equation. For ethane this equation has the form

$$[C_2H_6]_0 v_0 F = [C_2H_6] v F + k[C_2H_6] V_\varepsilon, \tag{1}$$

where k is the cracking rate constant, $(C_2H_6)_0$ is the ethane concentration at the inlet and (C_2H_6) at the outlet from the reactor. Equation (1) may be rewritten in the following form, convenient for graphical presentation of the experimental data:

$$y = \frac{[C_2H_6]_0}{\alpha[C_2H_6]} = 1 + kt. \tag{2}$$

Figure 2 plots the dependence $y(t)$ for the three temperatures studied. The value of k proved to be 0.54 at 770°, 7 at 838°, and 31 at 890°. As is seen from Fig. 2, the accuracy of the determination of k is quite high, and the main error in the subsequent determination of the activation energy is associated with the above-mentioned error in the determination of temperature. Figure 3 plots the dependence of $\ln k$ on $1/T$. As is seen from Fig. 3, the quantity

Fig. 2. Dependence $y = \dfrac{[C_2H_6]_0}{[C_2H_6]\alpha} = 1 + kt$: I –at $T = 770°$, $k = 0.54$ sec^{-1}; II –at $T = 838°$, $k = 7$ sec^{-1}; III –at $T = 890°$, $k = 31$ sec^{-1}

Fig. 3. Dependence of $\ln k$ on $\dfrac{1}{T}$: a –experimental data, b –literature data

$$E = -\frac{d \ln k}{d\, 1/T}$$

does not remain constant with increasing T, and rises from the value of 68 kcal, obtained in experiments at lower temperatures, to 82.0 ± 3 kcal. This, on the one hand, indicates a change in the reaction mechanism, in which the share of chain processes evidently decreases ([5]); on the other hand, the value obtained is close to the value of the energy of rupture of the C–C bond in ethane, measured in ([6]). It should be noted that, as is seen from Fig. 2, up to quite high degrees of conversion the known effect of self-inhibition is not manifested.

This circumstance may be interpreted as evidence that self-inhibition at lower temperatures is connected with the influence of the walls. The literature has repeatedly noted the formation, during ethane cracking, of higher

hydrocarbons, in particular C^4. However, their nature was not fully elucidated (7). With the aid of the above-mentioned radioactive-tracer method, it was possible to establish that the cracking products contain, in amounts on the order of tenths of a percent, divinyl, butylenes, and only traces of isobutane, as well as propylene and propane.

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CITED LITERATURE

1. K. P. Lavrovskii, A. M. Brodskii, DAN, **72**, No. 4, 745 (1950); Dokl. at the 4th International Petroleum Congress in Rome, Proceedings of the Congress, 1956; *Khim. nauka i promyshl.*, No. 2 (1957).

2. K. P. Lavrovskii, A. L. Rozental' , *Khim. i tekhnol. topliva*, No. 2, 27 (1956).

3. A. M. Brodskii, R. A. Kalinenko, K. P. Lavrovskii, *Khim. i tekhnol. topliva*, No. 8, 18 (1956); Collection: *Application of Labeled Atoms in Catalysis*, Publishing House of the Academy of Sciences of the USSR, 1957.

4. Yu. B. Sharvin, *Zav. lab.*, No. 10, 1261 (1955).

5. C. N. Hinshelwood et al., *Disc. Farad. Soc.*, No. 10 (1951); *Proc. Roy. Soc.*, A **229**, No. 1117, 143 (1955).

6. F. O. Rice, M. D. Dooley, *J. Am. Chem. Soc.*, **55**, 4245 (1933).

7. M. W. Travers, *Trans. Farad. Soc.*, **33**, 751 (1937).

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