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## Abstract

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# NONISOTHERMAL PROCESSES

## THERMAL CRACKING OF METHANE

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Fast high-temperature processes accompanied by chemical interaction of the components represent, from the standpoint of chemical kinetics, a new field of investigation. The specificity of chemical processes occurring under these conditions lies not only in the fact that the rate of chemical transformation at temperatures of thousands of degrees reaches very high values and that the chemical reaction itself begins and ends within small fractions of a second. In contrast to processes occurring at ordinary and moderately elevated temperatures, in the region of high temperatures it becomes difficult, and even practically impossible, to carry out the process under isothermal conditions. The process proceeds nonisothermally, with changing values of the constants of the elementary stages, and in order to characterize the reaction regime it becomes necessary to introduce a new concept–the rate of temperature change, as a measure of the nonisothermicity of the process.

The study of chemical processes occurring under nonisothermal conditions is associated with difficulties both in the experiment and in the treatment of experimental data. Only recently has it been possible to show the applicability of the method of rapid adiabatic compression and expansion of a gas mixture, developed by Ryabinin ($^1$), specifically as a quantitative method for studying homogeneous reactions occurring at high rates of temperature change, reaching $10^7$ deg/sec ($^2$).

In the present communication we give the results of an investigation of the high-temperature (1400—2500° K) thermal cracking of methane, obtained by means of the method of adiabatic compression and expansion ($^2$). Mixtures with argon and nitrogen containing from 1 to 5.4% methane were investigated. The component content was chosen so that, for all the mixtures studied, the dependence of the ratio of heat capacities at constant pressure and constant volume $\left(\frac{c_p}{c_v}\right)$, and hence also the dependence of the temperature of the system on the degree of compression $\alpha$, in the range from $\alpha_{\max} = 18$ to $\alpha_{\max} = 24$, was the same (to within 5°). This made it possible to compare quantitatively the data obtained for mixtures with different initial methane contents. The

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

results of one series of experiments are presented in Fig. 1, which illustrates the accumulation of reaction products as a function of the maximum degree of compression. It is seen from the figure that hydrogen and ethane are formed first, and only then, at higher degrees of compression, is the formation of ethylene and acetylene observed. Soot formation becomes noticeable only beginning with $\alpha_{\text{max}} \sim 29$—30.

To determine the sequence of formation of the reaction products, small (0.2%) additions of ethane and ethylene were introduced into the initial mixture in different series. The results of these experiments, carried out with mixtures containing 3% methane, are shown in Fig. 2. It is seen from the figure that ad-

the addition of ethane (Fig. 2, *I*) considerably increases the content of ethylene and acetylene, which in this case are formed at substantially lower degrees of compression ($\alpha_{\text{max}} = 15$-16 instead of 19-20), and that by the time the introduced ethane additive has been consumed ($\alpha_{\text{max}} \sim 25$) the content of ethylene and acetylene approaches the values found in experiments with the pure mixture. With the addition–

**Fig. 1.** Accumulation of methane-cracking products as a function of the degree of compression. Initial mixture (in percent): $CH_4$ 5.4, Ar 94.6. 1 –hydrogen, 2 –ethane, 3 –ethylene, 4 –acetylene

–of ethylene (Fig. 2, *II*) a substantial increase in the acetylene content is observed; acetylene is already formed at $\alpha_{\text{max}} = 16$. The amount of ethane in the reaction products does not change, and the corresponding ethane-accumulation curves for the pure mixture and with the addition of ethylene coincide. As the introduced ethylene additive is consumed, the acetylene content approaches the value found for the pure mixture. The results of experiments with additives make it possible to draw a conclusion about the following sequence of product formation

$$\begin{gathered} CH_4 \to C_2H_6 \to C_2H_4 \to C_2H_2 \to \\ \to \text{soot}. \end{gathered} \tag{10}$$

Obviously, in the initial stage of the reaction, when the consumption of ethane may be neglected, the accumulation of hydrogen is connected only with the reaction $CH_4 \to C_2H_6$, whose rate can be described by the expression

**Fig. 2.** Effect of ethane and ethylene impurities. The dashed curves show the accumulation of products in the pure mixture. The solid curves show the same with addition of ethane (left) and ethylene (right). 1, 1a —ethane; 2, 2a —ethylene; 3, 3a —acetylene. Composition of mixtures (in percent): $CH_4$ 3.0, Ar 89.0, $N_2$ 8.0; $CH_4$ 3.0, Ar 89.5, $N_2$ 7.3, $C_2H_6$ 0.2; $CH_4$ 3.0, Ar 89.4, $N_2$ 7.4, $C_2H_4$ 0.2

$$\frac{d[\mathrm{H_2}]}{dt} = K_0[\mathrm{CH_4}]^n e^{-\frac{E}{RT}}. \tag{2}$$

Substituting $[CH_4]$, $T$, and $dt$ in accordance with the expressions describing the dynamics of compression of the gas mixture in an adiabatic apparatus (2), and integrating under the assumption that the reaction order $n$ does not vary with temperature,

we arrive at the expression

$$[\mathrm{H_2}] = 2K_0[\mathrm{CH_4}]_0^n A I(\alpha_{\max}), \tag{3}$$

where $H_2$ is the amount of hydrogen formed, $[CH_4]_0$ is the methane content in the initial gas, $A$ is a constant determined by the parameters of the adiabatic apparatus, and $I(\alpha_{\max})$ is the integral

$$I(\alpha_{\max}) = \int_{\alpha=1}^{\alpha_{\max}} \frac{\alpha^{n-2} e^{-\frac{E}{RT_0\alpha^{\gamma-1}}}}{\sqrt{\alpha_{\max}^{\gamma-1} - \alpha^{\gamma-1}}}\, d\alpha, \tag{4}$$

whose value is determined by the values of $\gamma = c_p/c_v$, $n$, the activation energy $E$, and the limits of integration.

Expressions (3) and (4) make it possible, with the aid of the experimental data obtained by us (Fig. 3), to find the reaction order, the activation energy, and the pre-exponential factor $K_0$. The reaction order is determined as the slope of the dependence $\lg[\mathrm{H_2}]$—$\lg[\mathrm{CH_4}]_0$ at constant $\alpha_{\max}$.

The corresponding calculations (see Fig. 3) show that $n = 1$. To calculate the activation energy one may use the fact that, for identical initial mixtures, when $[\mathrm{CH_4}]_0 = \mathrm{const}$, proportionality between the amount of hydrogen $H_2$ formed at various degrees of compression and the value of the integral $I(\alpha_{\max})$ is fulfilled only for $E$ equal to the activation energy of the reaction. Therefore any other values of $I(\alpha_{\max})$, found for other $E$ not equal to the activation energy, do not satisfy expression (3) and, accordingly, do not allow the experimental data to be expressed by a linear function.

**Fig. 3.** Accumulation of hydrogen upon compression of mixtures with different methane contents. Initial stage of the reaction. Composition of the initial mixture (in percent): 1 —$CH_4$ 1.0, Ar 83.1, $N_2$ 15.9; 2 —$CH_4$ 2.0, Ar 86.0, $N_2$

Fig. 3. Accumulation of hydrogen upon compression of mixtures with different methane contents. Initial stage of the reaction. Composition of the initial mixture (in percent): 1 $-CH_4$ 1.0, Ar 83.1, $N_2$ 15.9; 2 $-CH_4$ 2.0, Ar 86.0, $N_2$ 12.0; 3 $-CH_4$ 3.0, Ar 89.0, $N_2$ 8.0; 4 $-CH_4$ 5.4, Ar 94.6. Inset—determination of the reaction order. Black points—for $\alpha$max = 22; open points—for $\alpha$max = 23.

Figure 3: Fig. 3. Accumulation of hydrogen upon compression of mixtures with different methane contents. Initial stage of the reaction. Composition of the initial mixture (in percent): 1 $-CH_4$ 1.0, Ar 83.1, $N_2$ 15.9; 2 $-CH_4$ 2.0, Ar 86.0, $N_2$ 12.0; 3 $-CH_4$ 3.0, Ar 89.0, $N_2$ 8.0; 4 $-CH_4$ 5.4, Ar 94.6. Inset—determination of the reaction order. Black points—for $\alpha$max = 22; open points—for $\alpha$max = 23.

12.0; 3 $-CH_4$ 3.0, Ar 89.0, $N_2$ 8.0; 4 $-CH_4$ 5.4, Ar 94.6. Inset—determination of the reaction order. Black points—for $\alpha_{\text{max}} = 22$; open points—for $\alpha_{\text{max}} = 23$.

From graphs constructed for identical $[CH_4]_0$ in the coordinates $[H_2]$—$I(\alpha_{\text{max}})$ at different $E$, a linear dependence corresponded only to $E = 100$ kcal/mole. Thus the activation energy satisfying equation (3) is $100 \pm 10$ kcal/mole. From the slope of the straight line the value of the pre-exponential factor $K_0$ was found; its magnitude is $1.1 \cdot 10^{13}$ $\text{sec}^{-1}$. These results coincide with the data of ($^3$), who investigated methane cracking by the shock-wave method in a nearby temperature region. In accordance with the data of these authors and with our data, the initial stage of methane cracking is evidently described by the following elementary acts:

$$CH_4 \to CH_3 + H, \tag{5}$$

$$H + CH_4 \to H_2 + CH_3, \tag{6}$$

$$2CH_3 \to C_2H_6, \tag{7}$$

$$CH_3 + CH_4 \to C_2H_6 + H. \tag{8}$$

The study carried out by us of the methane cracking reaction under conditions of adiabatic compression and expansion shows the possibility of studying

mechanism of high-temperature reactions occurring under sharply nonisothermal conditions. It is significant that, in order to find the principal kinetic parameters, such as the reaction order, activation energy, and pre-exponential factor, what are needed are not the values of the reaction rates, but the amounts

Fig. 4. Effect of the degree of nonisothermality of the process on the acetylene content in the reaction products. The rates of the processes represented by curves 1, 2, 3 are related as 1 : 1.35 : 3.12. Initial composition during compression (in percent): $CH_4$ 5.4, Ar 94.6, with pistons of different mass ($m = 401.7$ g, $m_2 = 191.4$ g, $m_3 = 34.9$ g)

Figure 4: Fig. 4. Effect of the degree of nonisothermality of the process on the acetylene content in the reaction products. The rates of the processes represented by curves 1, 2, 3 are related as 1 : 1.35 : 3.12. Initial composition during compression (in percent): $CH_4$ 5.4, Ar 94.6, with pistons of different mass ($m = 401.7$ g, $m_2 = 191.4$ g, $m_3 = 34.9$ g)

of the products formed, which in many cases prove to be a much more easily measurable quantity.

The method of adiabatic compression and expansion ($^2$) makes it possible to characterize quantitatively the nonisothermality of the process by the magnitude of the rate of temperature change and, by changing the mass of the piston, to vary this characteristic. This enabled us to study the content of reaction products formed under different reaction regimes. Fig. 4 illustrates the acetylene content in the reaction products at different rates of the process. It is seen from the figure that shortening the reaction time by a factor of 3.12 or, in other words, increasing the nonisothermality of the process by a factor of 3.12, shifts the maximum accumulation of acetylene by 100-120° into the region of higher temperatures and at the same time increases the maximum acetylene content. These results illustrate the very important conclusion that the concentrations of intermediate substances increase sharply with increasing nonisothermality of the processes.

**Fig. 4.** Effect of the degree of nonisothermality of the process on the acetylene content in the reaction products. The rates of the processes represented by curves **1**, **2**, **3** are related as 1 : 1.35 : 3.12. Initial composition during compression (in percent): $CH_4$ 5.4, Ar 94.6, with pistons of different mass ($m = 401.7$ g, $m_2 = 191.4$ g, $m_3 = 34.9$ g)

It seems to us that rapid high-temperature nonisothermal processes, the kinetics of which are still far from having been studied, should become an object of the closest attention of researchers, since it is precisely along this path that it becomes possible to carry out a reaction with a high content of intermediate substances and to preserve them in the reaction products.

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## REFERENCES

1. Yu. N. Ryabinin, ZhETF, **23**, 461 (1952).

2. A. M. Markevich, V. V. Azatyan, N. A. Sokolova, *Kinetics and Catalysis*, **3**, No. 3, 431 (1962).

3. G. B. Skinner, R. A. Ruchwein, *J. Phys. Chem.*, **63**, 1736 (1959).

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

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