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Methane Pyrolysis Stimulated by Admixture of Atomic Hydrogen: 2. Mechanism Analysis and Kinetics Calculation

I. E. Baranov, S. A. Demkin, V. K. Zhivotov, I. I. Nikolaev,
V. D. Rusanov, and N. G. Fedotov¹

Kurchatov Institute Russian Research Center, pl. Kurchatova 1, Moscow, 123182 Russia

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Abstract—The kinetics of methane pyrolysis stimulated by the introduction of atomic hydrogen into the reaction medium from an arcjet plasma source was analyzed. Numerical simulation of the reaction kinetics demonstrated that the thermal pyrolysis at lower temperatures (1800 K or lower) followed the radical chain mechanism with short chains (a chain length of 2 or 3), and the addition of atomic hydrogen considerably increased the rate of the process. An analysis of the kinetics of pyrolysis in a stirred reactor showed that acetylene was formed immediately after methane degradation without the buildup of by-products in the reaction medium.

This work is a continuation of our studies on the stimulation of hydrocarbon pyrolysis by the introduction of radicals into the reaction medium from an external source by mixing. An experimental study of this process was reported in [1]. In this work, we analyzed the experimental results in order to determine the reaction mechanism and theoretically calculated the kinetics of methane pyrolysis stimulated by the addition of radicals.

The experimental apparatus and procedure was described in detail previously [1]. In the test process, radicals acted as both a heat-transfer agent and a reactant. This effect weakened the temperature dependence of the reaction rate and allowed us to conduct the process at lower temperatures and to directly affect the pyrolysis chemistry in order to inhibit the formation of by-products. An arc discharge was chosen as a source of radicals, and an argon mixture with hydrogen was used as a plasma gas. The pyrolysis stimulated by admixture of atomic hydrogen proceeds as follows: Passing through an arc, hydrogen dissociates into atoms, and an exhaust jet consisting of a mixture of argon with atomic hydrogen flows from the plasma generator. Then, the jet is mixed with a hydrocarbon, heats the compound, and simultaneously induces its decomposition. After the completion of the thermal reaction in the gas moving in the reaction tube, its temperature falls to the level at which reactions stop (self-quenching takes place).

Methane was used as a hydrocarbon in this study. This gas was chosen because the methane pyrolysis kinetics are easy to calculate. The kinetic scheme of this process can be described with a high degree of adequacy by 20–60 reactions, whereas a simulation of the

pyrolysis, for example, of butane needs 200–300 reactions to be taken into account.

PYROLYSIS MECHANISM BASED ON EXPERIMENTAL RESULTS

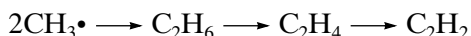
To draw conclusions concerning the kinetics and mechanism of methane conversion, let us analyze the product composition in the first two sets of experiments [1] with a relatively high energy input of 3–4 eV per methane molecule. We use the following method of analysis [2]: plotting the fractions of individual complex hydrocarbons (ethane, ethylene, and acetylene) as functions of conversion. In studying the conversion process, comparative experiments were performed with two plasma gases, namely, pure argon and an argon–hydrogen mixture. Figure 1 shows the resulting plots for experiments with a plasma jet containing atomic hydrogen. The corresponding curves obtained in the experiments with a bare argon-plasma (radical-free) jet were analogous in shape. This can be explained by the fact that the thermal mechanisms of methane degradation were powerful enough in the first two sets of experiments with a comparatively higher energy input per methane molecule. Therefore, in this section, we analyze the pyrolysis mechanism disregarding the differences between the hydrogen atom-activated pyrolysis and plain thermal pyrolysis.

In terms of an approximation described in [2], conversion can be considered as the extent of reaction and, hence, a certain effective time. Therefore, the plots in Fig. 1 can be represented as kinetic curves. Let us analyze these curves in terms of the given method. The fraction of acetylene remained almost constant as the degree of conversion increased by a factor of 20; thus suggesting that the formation of acetylene is not related

¹ E-mail: iv3000@mail.ru

to the buildup of intermediate products (ethane and ethylene) in the system. A maximum amount of ethane was detected at low conversions. The fraction of ethane decreased with conversion, and the fraction of ethylene increased proportionally to this decrease. In terms of the approximation [2], we can state that ethane is rapidly formed together with acetylene at a low conversion; then, it is converted into ethylene with increasing conversion.

Let us consider relevant reactions in more detail. Methane degradation after mixing with a heat-transfer-agent jet results in the formation of radicals: $\text{CH}_4 \rightarrow \text{CH}_3\cdot + \text{H}\cdot$. Atomic hydrogen rapidly (see the calculated kinetics below) reacts with methane to afford $\text{CH}_3\cdot$. Thus, the resulting products are primarily formed by the combination reaction of $\text{CH}_3\cdot$. In the majority of kinetic schemes (for example, those by Kassel [3] and Frenclach [4]), the combination is followed by the consecutive formation of ethane, ethylene, and acetylene



and their buildup in the reaction medium.

As shown in Fig. 1, the fraction of acetylene is constant and independent of the buildup of ethane and ethylene. It may be assumed that, after methane degradation, a portion of the resulting radicals rapidly converts into acetylene ($2\text{CH}_3\cdot \rightarrow \text{C}_2\text{H}_2$) without the buildup of intermediate products in the reaction medium (unlike the Kassel and Frenclach reaction schemes). This process can occur via the double degradation of excited ethane and ethylene molecules $2\text{CH}_3\cdot \rightarrow \text{C}_2\text{H}_6^* \rightarrow \text{C}_2\text{H}_4^* \rightarrow \text{C}_2\text{H}_2$ (where the asterisk denotes a vibrationally excited molecule). In the combination reaction of $\text{CH}_3\cdot$ radicals, the bond energy (260 kJ/mol), which is not withdrawn via a collision with a third body (a low pressure of the process) or by emission, results in the excitation of the resultant ethane, thus facilitating its degradation to ethylene and then to acetylene by decreasing the activation energy. If energy is removed by a third body or via emission, ethane is formed, which can be seen in Fig. 1 at low conversions. The ethane is slowly converted (reaction (2) in the scheme below) into ethylene. The ratio between the rates of quenching of excited ethane and its conversion into acetylene can be found from the ratio between acetylene and ethane concentrations at low conversions in Fig. 1. It is equal to 3. In the kinetic calculations, the formation and rapid decay of excited ethane is described by the overall reactions $\text{CH}_3\cdot + \text{CH}_3\cdot = \text{C}_2\text{H}_5\cdot + \text{H}\cdot$ and $\text{CH}_3\cdot + \text{CH}_3\cdot = \text{C}_2\text{H}_4 + \text{H}_2$. The quenching of excited ethane is described by the reaction $\text{CH}_3\cdot + \text{CH}_3\cdot + \text{M} = \text{C}_2\text{H}_6 + \text{M}$. The calculation of the kinetics of these processes with the use of NIST data (see the next section) gave a ratio between the reaction rates of excited ethane degradation and the reaction rate of ethane quenching equal to 2–5 over the temperature range 1700–2300 K. This value is consis-

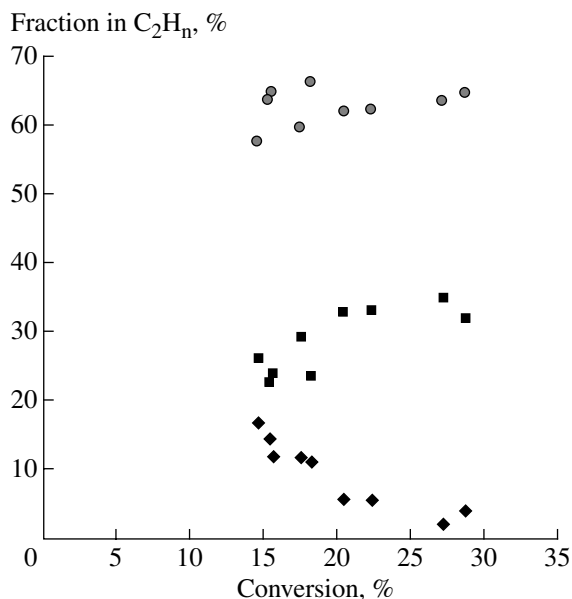
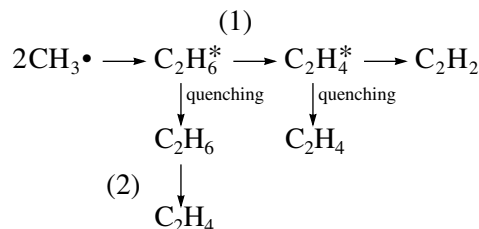


Fig. 1. Dependence of the relative amounts of C_2H_n hydrocarbons in the effluent gas on the extent of reaction (conversion). Plasma gas: argon + hydrogen. (\diamond) C_2H_6 , (\blacksquare) C_2H_4 , and (\circ) C_2H_2 .

tent with that obtained from the experimental data under discussion.

To summarize, an analysis of the experimental data suggests the following mechanism of methane pyrolysis through excited states under the experimental conditions in a stirred reactor at 0.1 atm:



In addition to the above approach, we can analyze the data presented in Fig. 1 using another approach: the calculation of an adiabatic pyrolysis process in a stirred reactor. The mixing of a jet from an arc plasma torch with methane occurs rapidly (as estimated, in 10^{-4} s), as compared with the characteristic time of methane conversion in the reaction zone downstream from the mixer (see the calculation of the kinetic of pyrolysis below). Therefore, the mixing and heating of methane can be considered as an instantaneous process, and the kinetics of pyrolysis in a stirred reactor can be calculated as an adiabatic process of the conversion of methane heated to an effective temperature. This temperature can be calculated from the heat balance of mixed gases.

The formation of $\text{CH}_3\cdot$ occurs after mixing; for this reason, the temperature rapidly decreases and the combination of $\text{CH}_3\cdot$ results in pyrolysis products. As fol-

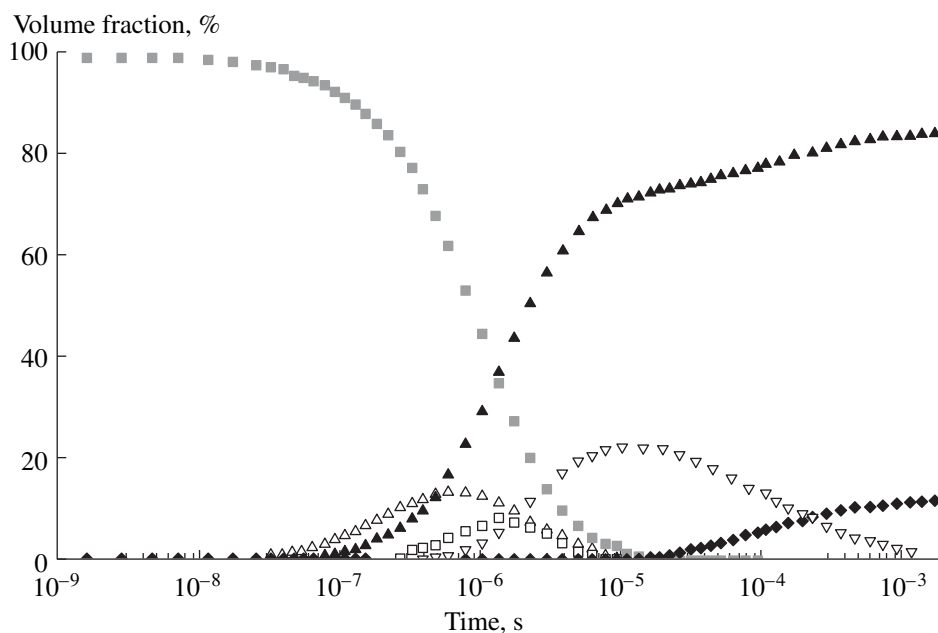


Fig. 2. Composition of the reaction mixture in methane pyrolysis at 2300 K and 0.1 atm (calculated kinetics): (■) CH₄, (▲) H₂, (△) CH₃, (□) C₂H₄, (▼) C₂H₂, and (◆) C_{soot}.

lows from calculations, a considerable portion of the products, including acetylene, is formed rapidly, 5×10^{-4} s after mixing. In this case, the temperature decreases to 1600–1700 K and remains at this level for a long enough time (to 0.1 s). At this temperature, ethane can more slowly be converted into ethylene in the reaction medium. Thus, the kinetic behavior predicted by the simulation of the adiabatic pyrolysis process is consistent with the methane conversion scheme specified above.

The rapid formation of acetylene through the double degradation of excited ethane and ethylene molecules (or, in other words, the formation of acetylene without the buildup of ethane and ethylene by-products in the reaction medium) is inconsistent with the calculation results obtained in terms of the Kassel [3] and Frenclach [4] kinetic mechanisms. Consequently, the kinetic analysis of methane pyrolysis based on the experimental data is of particular interest.

CALCULATION OF THE METHANE PYROLYSIS KINETICS

Methane is practically the only hydrocarbon for which the rate constants of almost all elementary reactions pertaining to pyrolysis have been experimentally measured. This is due to a relatively small number of substances formed in the pyrolysis of methane and, correspondingly, a small number of reactions (~50). Data on the pyrolysis of methane are summarized in the NIST database [5]. With the use of this database and the Workbench kinetic computation software [6], we made calculations for the isothermal processes of methane pyrolysis at 2300 and 1730 K. In accordance with the above calculations of the adiabatic process and the estimated temperature after mixing heat-transfer-agent and reactant jets, the above temperatures adequately represent the temperature range of pyrolysis under conditions of a stirred reactor.

Table 1. Rates of the main elementary reactions of methane pyrolysis at 2300 K and 0.1 atm

Entry	Reaction	W [cm ³ s]	Classification
1	CH ₄ = CH ₃ · + H·	8×10^{22}	Chain initiation
2	CH ₄ + H = CH ₃ · + H ₂	6×10^{22}	Exchange
3	CH ₃ · + H ₂ = CH ₄ + H·	1×10^{22}	
4	C ₂ H ₄ = C ₂ H ₂ + H ₂	2×10^{22}	C ₂ H ₂ formation
5	CH ₃ · + CH ₃ · = C ₂ H ₄ + H ₂	3×10^{22}	Combination
6	C ₂ H ₅ · + M = C ₂ H ₄ + H· + M	1×10^{22}	Chain with methane decomposition
7	CH ₃ · + CH ₃ · = C ₂ H ₅ · + H·	8×10^{21}	

Table 2. Rates of the main elementary reactions of methane pyrolysis at 1730 K and 0.1 atm

Entry	Reaction	W [$\text{cm}^{-3} \text{ s}$]	Classification
1	$\text{CH}_4 = \text{CH}_3\cdot + \text{H}\cdot$	8×10^{19}	Chain initiation
2	$\text{CH}_4 + \text{H}\cdot = \text{CH}_3\cdot + \text{H}_2$	4×10^{20}	Exchange
3	$\text{CH}_3\cdot + \text{H}_2 = \text{CH}_4 + \text{H}\cdot$	3.2×10^{20}	
4	$\text{CH}_3\cdot + \text{CH}_3\cdot = \text{C}_2\text{H}_4 + \text{H}_2$	6×10^{19}	Combination
5	$\text{CH}_3\cdot + \text{CH}_3\cdot + \text{M} = \text{C}_2\text{H}_6 + \text{M}$	7×10^{19}	Exchange
6	$\text{C}_2\text{H}_6 = \text{CH}_3\cdot + \text{CH}_3\cdot$	3×10^{19}	
7	$\text{CH}_3\cdot + \text{CH}_3\cdot = \text{C}_2\text{H}_5\cdot + \text{H}_2$	2.5×10^{19}	Chain with methane decomposition
8	$\text{CH}_3\cdot + \text{CH}_4 = \text{C}_2\text{H}_5\cdot + \text{H}_2$	5×10^{19}	
9	$\text{C}_2\text{H}_5\cdot + \text{M} = \text{C}_2\text{H}_4 + \text{H}\cdot + \text{M}$	8×10^{19}	
10	$\text{CH}_3\cdot + \text{CH}_4 = \text{C}_2\text{H}_4 + \text{CH}_3\cdot$	2.7×10^{19}	
11	$\text{C}_2\text{H}_4 = \text{C}_2\text{H}_2 + \text{H}_2$	3×10^{19}	C_2H_2 formation

Let us consider the process of pyrolysis at a comparatively high temperature of 2300 K. Figure 2 shows the concentrations of reaction products and intermediates. The time of methane decomposition at 2300 K is 10^{-6} s.

Table 1 summarizes the rates of the most important reactions. It can be seen that the principal process at 2300 K is the thermal degradation of methane followed by the combination reaction of $\text{CH}_3\cdot$ radicals to yield ethylene and the subsequent conversion into acetylene. Note that the above analysis of the experimental data suggests the formation of acetylene via the double degradation of excited states without the buildup of ethane and ethylene in the reaction medium. It is in this aspect that the calculation results obtained using the given scheme differ from the experimental data.

Every event of methane decomposition in accordance with reaction (1) is accompanied by an additional degradation involving atomic hydrogen. The interchange of $\text{CH}_3\cdot$ and $\text{H}\cdot$ radicals also occurs in the reaction mixture.

The chain process of methane degradation occurs in accordance with reactions (6) and (7) that involve the exchange of two $\text{CH}_3\cdot$ radicals for two $\text{H}\cdot$ to yield ethylene. Together with reaction (2), they constitute a chain in which the desired product is formed. The fraction of chain processes is small. At 2300 K, 20% of the desired product is formed via the chain mechanism (the ratio of the rate of reaction (7) to the sum of the rates of reactions (7) and (5)).

Let us consider the mechanism of pyrolysis at 1730 K. The main reactions are summarized in Table 2. At this temperature, the role of radical processes is much greater. Under these conditions, the chain process of methane conversion to ethylene involves reactions (7)–(9), as well as the chain including reaction (10). The

chain length of the methane degradation process (reactions (7)–(9)) can be calculated by the equation

$$l = \frac{W(7)}{W(5) - W(6)}.$$

This quantity is equal to 1.5–2. The rate of methane conversion through this chain is comparable with the rate of methane thermal decomposition in reaction (1).

Note that $\text{CH}_3\cdot$ is the principal radical present in the reaction medium (Fig. 2). This is due to the fact that the equilibrium of the exchange reactions $\text{CH}_4 + \text{H}\cdot = \text{CH}_3\cdot + \text{H}_2$ and $\text{CH}_3\cdot + \text{H}_2 = \text{CH}_4 + \text{H}\cdot$ is shifted toward the formation of $\text{CH}_3\cdot$. The chain length of exchange reactions (2) and (3) is approximately 10.

Chain processes play a more significant role at lower temperatures. This is due to the fact that the thermal degradation of methane at these temperatures is strongly impeded by a high activation energy. The characteristic time of methane degradation at 1730 K significantly increased to be equal to 10^{-3} s.

In summary, the results of calculations of the methane pyrolysis kinetics demonstrated that, at temperatures below 2000 K, the pyrolysis process is primarily determined by radical chain reactions involving $\text{CH}_3\cdot$, $\text{H}\cdot$, and $\text{C}_2\text{H}_5\cdot$ radicals. This explains the effect of foreign radicals on the methane conversion process.

CONCLUSIONS

(1) Numerical simulation of the reaction kinetics demonstrated that thermal pyrolysis at low temperatures (1800 K or lower) follows the radical chain mechanism with short chains (a chain length of 2–3) and, consequently, the admixture of atomic hydrogen significantly increases the rate of the process, as observed experimentally [1].

(2) An analysis of the kinetics of pyrolysis in a stirred reactor demonstrated that the formation of acetylene is independent of the buildup of ethane and ethyl-

ene in the mixture. Acetylene forms simultaneously with a certain amount of ethane, which is then partially converted into ethylene. This experimental fact is inconsistent with the Kassel scheme, which implies the consecutive formation of ethane, ethylene, and acetylene. The experimental results suggest that acetylene forms at a rate comparable with the ethane and ethylene formation rates; this can be due to the fact that the methane-to-acetylene reaction occurs via the vibrationally activated states of ethane and ethylene.

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