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Initiation Step of Methane Pyrolysis*1

Takayuki YANO and Kenji KURATANI

Institute of Space and Aeronautical Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo

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Equimolar mixtures of CH_4 and CD_4 were pyrolyzed at 1560°K by a reflected shock wave. From the isotope distribution of H_2, HD and D_2 which are components of the product in early stage, the initiation step of methane pyrolysis is concluded to be the splitting to a methyl radical and a hydrogen atom.

Recently, the vacuum ultraviolet photolysis(1) and the radiolysis(2) of methane were recognized to begin with the decomposition to a methylene radical and a hydrogen molecule. The reaction mechanism of the methane pyrolysis, especially the initiation step of this reaction, however, has not been settled yet and two hypotheses have been discussed during these thirty years. One of which(3) suggested the same mechanism as proposed in the case of the ultraviolet photolysis and the radiolysis, while the splitting to a methyl radical and a hydrogen atom was assumed by the others.(4)

It is the purpose of this paper to study the thermal

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2) P. Ausloos and S. G. Lias, *ibid.*, **38**, 2207 (1963); V. Aquilanti, *J. Phys. Chem.*, **69**, 3434 (1965).

3) L. Kassel, *J. Am. Chem. Soc.*, **54**, 3949 (1932); L. Belchetz and F. K. Rideal, *ibid.*, **57**, 1168 (1935); V. Kevorkian, C. E. Heath and M. Boudart, *J. Phys. Chem.*, **64**, 964 (1960).

4) F. O. Rice, M. D. Dooley, *J. Am. Chem. Soc.*, **57**, 2747, (1934); G. B. Skinner and R. A. Ruehrwein, *J. Phys. Chem.*, **63**, 1736 (1959); P. S. Shantarovich and B. V. Pavlov, *Zhur. Fiz. Khim.*, **30**, 811 (1956).

decomposition of the equimolar mixture of methane and tetradeuteromethane around 1560°K using a single pulse shock tube and to decide which of these two aforementioned hypotheses is correct.

Experimental

The shock tube used in this study is similar to a magic hole type developed at Cornell University[5] (the detail of this tube will be described in near future). Mixtures of 6% each of CH_4 and CD_4 in argon were heated by the reflected shock wave to 1560+30°K for dwell times of about 1 msec. The reaction mixture was withdrawn to an evacuated vessel and its composition was determined by the gas chromatographic analysis. Isotope mixtures of hydrogen molecules were separated using an alumina column coated with $MnCl_2$ of 5 m length at 77°K and detected by a cathalometer (He was used as carrier gas.) Hydrocarbons were separated by a 3 m activated charcoal column at 150°C and analyzed by a flame ionization detector. CH_4 and CD_4 were supplied by Takachiho Chemicals Co. and Merck respectively, and used without further purification.

Results and Discussion

It is well known that methane is converted into ethane in the early stage of the reaction and ethane formed is decomposed further into ethylene, acetylene, *etc.* in the later stage. The presence of one mole of ethane in products corresponds to the formation of one mole of hydrogen, and similarly the findings of one mole each of ethylene and acetylene are equivalent to the production of two and three moles of hydrogen respectively. Therefore, it is the proper requirement to suppress the occurence of the secondary reactions such as ethylene and acetylene formations in order to study the initiation step of methane pyrolysis in terms of the isotopic distribution of the produced hydrogens. The another restriction is concerned with the deviation from the ideal behavior of gases behind a reflected shock wave. The use of high dilution with argon is essential to avoid this difficulty, but the limitation by the sensitivity of our analytical apparatus should be also taken into account. From these reasons, the aforementioned experimental conditions about temperature range, dwell time and concentration of reactants were adopted.

In order to confirm the experimental accuracy, yields of reaction products of three experimental runs are compared and mass balances in regard to hydrogen are testified. In Table 1 $\sum H_2$ means sum of observed values of H_2, D_2 and HD, and $\sum(C_2H_6+2C_2H_4+3C_2H_2)$ corresponds also to the total yield of hydrogen expected from the formation of these hydrocarbons. The agreement between these two values is satisfactory and we believe that analytical accuracy of our experiment is sufficient, though the chromatographic separation of the small amount of H_2, HD, and D_2 is rather troublesome, since the tailing of an individual peak interferes the distinct separation between the adjacent peaks.

In Table 2, experimental results on additional runs as well as the above described runs are summarized. The relative yields of HD and D_2 to H_2 are shown in this table along with those of ethylene and acetylene to ethane. As shown in Table 2 there are considerable scatters of experimental values, but the average value of the relative yields of H_2 : HD : D_2 is estimated to be 1 : 1.7 : 0.6. As already pointed out, hydrogen molecules are produced not only by the primary process from methane to ethane but also by the secondary processes from ethane to ethylene and acetylene, and

TABLE 1. MASS BALANCES OF PRODUCTS (VOLUME PER CENT IN PRODUCTS)

Run No.	H_2	D_2	HD	$\sum H_2$	C_2H_6	C_2H_4	C_2H_2	$\sum(C_2H_6+2C_2H_4+3C_2H_2)$
20	0.014	0.026	0.011	0.051	0.015	0.009	0.004	0.045
21	0.017	0.028	0.014	0.060	0.025	0.008	0.005	0.056
22	0.015	0.023	0.012	0.050	0.019	0.007	0.003	0.044

TABLE 2. RELATIVE YIELDS OF PYROLYZED PRODUCTS AT $T_5=1560\pm30$°K AND DWELL TIME FOR 1 msec

Run No.	HD/H_2	D_2/H_2	C_2H_4/C_2H_6	C_2H_2/C_2H_6	$1-R$
16	1.6	0.6	1.11	0.32	0.56
17	1.6	0.5	0.60	0.17	0.65
18	1.7	0.4	0.76	0.21	0.63
19	1.7	0.5	0.63	0.22	0.63
20	1.9	0.8	0.63	0.26	0.62
21	1.6	0.8	0.33	0.19	0.62
22	1.5	0.8	0.38	0.18	0.63

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5) J. E. Klepeis, Thesis, Graduate School of Aeronautical Eng., Cornell University (1961); A Lifshitz, S. H. Bauer and E. L. Resler, Jr., *J. Chem. Phys.*, **38**, 2056 (1963).

the contribution of the primary process relative to the overall reaction is represented by the ratio $(1-R)$, where

$$R = [(C_2H_4) + 2(C_2H_2)]/[(C_2H_6) + 2(C_2H_4) + 3(C_2H_2)]. \qquad (1)$$

If we assume the elimination of molecular hydrogen in the initiation step, then the following reaction scheme corresponding to the primary process will be formulated,

$$CH_4 \rightarrow CH_2 + H_2$$
$$CH_2 + CH_4 \rightarrow CH_3 + CH_3$$
$$CH_3 + CH_3 \rightarrow C_2H_6$$

That is, from this scheme only H_2 and D_2 are produced. Then, even if we further assume the elimination of atomic hydrogen from any step among the processes from ethane to ethylene and acetylene, the observed high yield of HD cannot be explained, since the contribution of the primary process relative to the overall reaction is rather large and the values of $(1-R)$ exceed 0.6 in all experimental runs.

From this consideration, we conclude qualitatively that the initiation steps of methane pyrolysis are the elimination of atomic hydrogen,

$CH_4 \rightarrow CH_3 + H$ yields of H atom a mol

and

$CD_4 \rightarrow CD_3 + D$ yields of D atom b mol

To explain the observed values of $H_2 : HD : D_2$ semiquantitatively, it is necessary to take into account the isotope effect on the reaction rates. If we assume the relative rate of the first step is equal to $a : b$, the amounts of hydrogen molecules produced from the primary processes will be represented as follows,

$H + CH_4 \rightarrow H_2 + CH_3$ yield of H_2 $a/2$,
$H + CD_4 \rightarrow HD + CD_3$ yield of HD $a/2$,
$D + CH_4 \rightarrow HD + CH_3$ yield of HD $b/2$,
$D + CD_4 \rightarrow D_2 + CD_3$ yield of D_2 $b/2$.

That is, in the primary processes the relative yields of $H_2 : HD : D_2$ are given as

$$H_2 : HD : D_2 = a : a+b : b, \qquad (2)$$

and the methyl radicals produced both in the initiation steps and the abstraction reactions will be combined together to form ethanes. The isotopic distributions of the latters are

$$C_2H_6 : CH_3CD_3 : C_2D_6 = (3a+b)^2 : 2(3a+b)(a+3b) : (a+3b)^2. \qquad (3)$$

As it is well known,⁶⁾ on the way of the secondary processes from ethane to ethylene, a hydrogen atom is removed from the parent molecule by the following mechanism,

$$C_2H_6 \rightarrow CH_3 + CH_3 \qquad (R1)$$
$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \qquad (R2)$$
$$C_2H_5 \rightarrow C_2H_4 + H. \qquad (R3)$$

Here we assume tentatively that these reaction steps are independent on the presence of a large amount of methane in order to simplify the algebraic treatment. Therefore, from an ethane molecule a hydrogen atom is removed and an ethylene molecule is produced. The hydrogen atom produced in the step (R3) reacts with a large excess of methane, and it is converted to the molecular hydrogen,

$$H(D) + CH_4(CD_4) \rightarrow (H_2, HD, D_2) + (CH_3, CD_3). \qquad (R4)$$

In our experiment, not only ethylene but also acetylene are produced step by step,

$$C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2. \qquad (R5)$$

As acetylene is formed from ethylene, the quantity of ethylene, which is equivalent to the amount of the hydrogen atom formed in process (R3), must be the sum of the observed values of ethylene and acetylene. Of course, in a process $C_2H_4 \rightarrow C_2H_2$, atomic or molecular hydrogen may be produced. But in our experiment, the yield of acetylene is relatively small compared with those of ethane and ethylene, and the amount of hydrogen formed in the process from ethylene to acetylene is omitted from the following discussions.

If we assume that the isotope effect on the process (R3) is negligible, H and D atoms are formed in proportion to the hydrogen isotopic distribution in ethane molecules. Since the relative yields of the isomeric ethanes are represented by Eq. (3), the distribution of H and D atoms in ethanes is given by

$$H : D = (3a + b)(4a + 4b) : (a + 3b)(4a + 4b)$$
$$= (3a + b) : (a + 3b). \qquad (4)$$

Therefore, the isotopic distributions of the hydrogen molecules produced by the process (R4) will be represented as

$$H_2 : HD : D_2$$
$$= (3a+b) : (3a+b)+(a + 3b) : (a+3b)$$
$$= (3a+b) : (4a+4b) : (a+3b). \qquad (5)$$

On the other hand, if we assume the same isotope effect on the process (R3) as that on the splitting of methane to a methyl radical and a hydrogen atom, the amounts of the hydrogen atoms liberated in the process (R3) are given as

$$H : D = a(3a+b) : b(a+3b),$$

and the ratios of hydrogen molecules produced by

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6) B. S. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Co., New York (1960), p. 349.

(R4) process are expressed as

$$\begin{aligned} &H_2 : HD : D_2 \\ &= a(3a+b) : a(3a+b)+b(a+3b) : b(a+3b). \quad (6) \end{aligned}$$

The observed isotopic distributions of hydrogen molecules should be expressed as the sum of the contributions of the primary and secondary processes. That is, in the former case, where the isotope effect in the secondary process is ignored, the relative yields of hydrogens are given by combining Eqs. (2) and (5),

$$\begin{aligned} &H_2 : HD : D_2 \\ &= (1-R)a/[2(a+b)] + R(3a+b)/[8(a+b)] : \\ &\quad (1-R)(a+b)/[2(a+b)] + R4(a+b)/ \\ &\quad [8(a+b)] : \\ &\quad (1-R)b/[2(a+b)] + R(a+3b)/[8(a+b)] \\ &= [4a-R(a-b)]/[8(a+b)] : 1/2 : \\ &\quad [4b-R(b-a)]/[8(a+b)] \end{aligned}$$

and in the latter case, where the same isotope effect in the secondary process as in the primary process is assumed, the ratios are expressed by combining Eqs. (2) and (6),

$$\begin{aligned} &H_2 : HD : D_2 \\ &= (1-R)a/[2(a+b)] + Ra(3a+b)/ \\ &\quad [2(3a^2+2ab+3b^2)] : \\ &\quad (1-R)(a+b)/[2(a+b)] + \\ &\quad R(3a^2+2ab+3b^2)/[2(3a^2+2ab+3b^2)] : \\ &\quad (1-R)b/[2(a+b)] + Rb(a+3b)/ \\ &\quad [2(3a^2+2ab+3b^2)] \\ &= (1-R)a/[2(a+b)] + Ra(3a+b)/ \\ &\quad [2(3a^2+2ab+3b^2)] : \\ &\quad 1/2 : \\ &\quad (1-R)b/[2(a+b)] + Rb(a+3b)/ \\ &\quad [2(3a^2+2ab+3b^2)]. \end{aligned}$$

The experimental results shown in Table 2 are interpreted by these equations and the values of $a : b$ are determined as nearly equal to 1 : 0.6—0.7 in both cases. If we assume that the ratio of the isotopic rate constants k_H/k_D of the initiation step is expressed by the zero-point energy difference of the reaction coordinates of this process,

$$a/b = k_H/k_D = \exp\left[-(h\nu_D - h\nu_H)/2\boldsymbol{k}T\right]$$

and take the values of $\nu_H=3000\ \mathrm{cm}^{-1}$, $\nu_D=2200\ \mathrm{cm}^{-1}$, the ratio of a/b at 1560°K is calculated as 1/0.69, and agrees with the observed values. However, this calculation is an approximate one, and we are planning to obtain the more accurate ratio taking into account the differences in partition functions. The result will be reported in near future.