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Initiation Step of Methane Pyrolysis. Further Studies on Initiation Step of Methane Pyrolysis

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The pyrolysis of diluted mixture of equimolar CH_4 and CD_4 were performed in a shock tube between ~1500 K and ~1600 K, and pyrolysis products were quantitatively determined. A small amount of oxygen contaminating the sample gases had no influence on the results. The isotope exchange reactions in the equimolar lean mixture of H_2 and D_2 were also performed under the same conditions of methane pyrolysis. The results explained that the isotope exchange reaction between H_2 and D_2 had no influence on the hydrogen isotopic distribution produced by the CH_4–CD_4 pyrolysis. From the hydrogen isotopic distribution of the products of CH_4–CD_4 pyrolysis, methyl radical mechanism was confirmed as the initiation step of methane pyrolysis.

In the previous paper,[1] it was concluded that the initiation step of the methane pyrolysis was

$$CH_4 \longrightarrow CH_3 + H \tag{1}$$

but not be

$$CH_4 \longrightarrow CH_2 + H_2 . \tag{2}$$

This conclusion was derived from the predominant yield of HD molecule produced by the pyrolysis of an equimolar mixture of CH_4 and CD_4. If there is any side-reaction, however, and if it affects the isotopic distribution among hydrogen, the above-mentioned conclusion would become uncertain. It is desirable, therefore, to study the effects of the side-reactions on the hydrogen isotopic distribution. The following three exchange reactions, that is, (i) the reaction between reactant molecules, CH_4 and CD_4; (ii) the reaction between reactant methane and product hydrogen; and (iii) the reaction between product hydrogen

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[1] T. Yano and K. Kuratani, This Bulletin, **41**, 799 (1968).

molecules are examined. The effect of the small amounts of oxygen should be also taken into account, since Meyerson and Watt[2] have proved that the small amounts of oxygen accelerate the decomposition rate of hydrogen molecules significantly. If the considerable amounts of hydrogen atoms were formed by this reaction, the predominant yield of species HD would be obtained.

The exchange reaction between CH_4 and CD_4 behind a reflected shock wave was studied by Burcat and Lifshitz[3] in the temperature range from 1340 to 1745 K. When their rate equation is applied to the typical experimental runs reported in the previous paper, the extent of the exchange between CH_4 and CD_4 is calculated to be $(CD_3H)/(CD_4)=0.1$, *i.e.*, only 10% each of CH_4 and CD_4 may be converted to CH_3D and CD_3H, respectively. Then, if CH_3D and CD_3H are initially formed and then pyrolysis occurs, hydrogen molecules would be formed as follows by the methylene mechanism,

$$0.90\ CH_4 \rightarrow CH_2 + H_2$$

$$0.10\ CH_3D \rightarrow CH_2 + HD \text{ or } CHD + H_2 \text{ in equal amount}$$

$$0.10\ CD_3H \rightarrow CD_2 + HD \text{ or } CHD + D_2 \text{ in equal amount}$$

$$0.90\ CD_4 \rightarrow CD_2 + D_2 \qquad (3)$$

and the ratio of $(H_2) : (HD) : (D_2)$ would be 0.95 : 0.10 : 0.95. This clearly shows that the amount of HD produced by this scheme is much less than that obtained by the CH_4–CD_4 pyrolysis experiment. The effect of this side-reaction, (i), may be ignored.

The effect of the second reaction (ii) can be estimated by the results of Watt *et al.*[4] and the isotopic distribution ratio by the methylene mechanism proves

$$(H_2) : (HD) : (D_2) = 1.0 : 0.28 : 1.0\,. \qquad (4)$$

Therefore, the effect of the second side-reaction may also be neglected.

As to the third side-reaction, (iii), circumstances are rather complicated. According to the rate law of Bauer,[5] an appreciable amount of HD is formed by the H_2–D_2 exchange reaction and it will be quite difficult to decide whether the initiation step of the methane pyrolysis will be eq. (1) or eq. (2). Later, however, Lifshitz[6] corrected the Bauer's result and when Lifshitz's result is adopted for the calculation the amount of HD is smaller than the value calculated from the Bauer's rate expression. The amount of HD calculated would be further small, if the H_2–D_2 exchange reaction occurs through the bimolecular process and the phenomenological expression given by Bauer can be used. Only a little influence on our previous conclusion is expected. These discrepancies are mainly due to the difference of the reaction order with respect to hydrogen. Accordingly, to know the effect of the third side-reaction to the methane pyrolysis, it is desirable to reinvestigate the exchange reaction of hydrogen molecules itself in the same low concentration as actually observed in the methane pyrolysis.

Experimental

High quality hydrogen (99.9999%), deuterium (99.5%) obtained from Takachiho Co. and high quality argon (99.999 %) supplied by Tomoe Co. were used without further purification.

For the study of the isotopic exchange between hydrogens, 1% of H_2 and 1% of D_2 were mixed with 98% of argon and after being kept over night, this mixture was further diluted tenfold by argon gas. The latter mixture was shock heated.

For the study of the effect of the trace amounts of oxygen on the methane pyrolysis, 99.5% perdeuteromethane (CD_4) from Matheson Co., pure methane (99.5%) and high quality argon were used.

Oxygen contents in CH_4 and CD_4 were analyzed by gas chromatography and were found to be 0.5% and 50 ppm, respectively. The gas chromatographic system was built into a vacuum line to avoid air contamination. For the removal of a small amount of oxygen from methanes, impure methane was passed through a freshly reduced copper column at 160 °C. By this process, the oxygen content in the original CD_4 and CH_4 was reduced from 5000 to 50 and from 50 to 7 ppm, respectively. The oxygen content in the high quality argon gas, was also analyzed in a similar manner after being passed through the copper column at 160 °C, and it was confirmed to be less than 1 ppm. Then, two gas mixtures of 6% each of CH_4 and CD_4 in high quality argon gas were prepared. In the mixture A, purified CH_4 and CD_4 were diluted in argon and in the mixture B, unpurified CH_4 and CD_4 were used. Consequently the oxygen levels of mixture A and B were about 3 and 300 ppm, respectively.

In addition to the careful preparation of sample gases, the contamination during the storage and the gas handling was also examined. Gas mixtures were kept for at least 15 hours in a gas holder to accomplish complete mixing. Then, a part of the sample gas was analyzed by gas chromatography before shock heating and it was confirmed that the oxygen contamination during the storage was negligible. The gas leak of the driven section of the shock tube, however, was about 6×10^{-5}Torr/min and the air contamination from this was to be estimated. High quality argon was introduced into the driven section to the level of 65 Torr and was kept for two days. After that, the gas was analyzed by gas chromatography. Oxygen contamination was about 300 ppm after 48 hr at the total pressure of 65 Torr. That is, about 0.5 ppm of oxygen was mixed into the sample gas since it took 5 min to handle the sample gas in the driven section before shock firing.

The shock tube used in this study was the same that Tsuda and Kuratani[7] used, but the volume of a damp tank of driver gas was changed from 20 l to 80 l to decrease the amount of driver gas mixing into the sample gas after reaction. As soon as the shock was fired and the reaction was over, the reaction mixture behind the reflected shock wave was withdrawn into an evacuated vessel and its composition was determined by the gas chromatograph Shimadzu GC–1C. Isotopic hydrogen molecules were separated by an alumina column coated with $MnCl_2$ of 2 m length at 77 K. After the separation of H_2, HD and D_2, the gas flow, using He

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[2] A. L. Meyerson and W. S. Watt, *J. Chem. Phys.*, **49**, 425 (1968).

[3] A. Burcat and A. Lifshitz, *ibid.*, **52**, 3613 (1970).

[4] W. S. Watt, P. Borrell, D. Lewis and S. H. Bauer, *ibid.*, **45**, 444 (1966).

[5] S. H. Bauer and E. Occa, *ibid.*, **45**, 434 (1966).

[6] A. Burcat and A. Lifshitz, *ibid.*, **47**, 3079 (1967).

[7] M. Tsuda and K. Kuratani, This Bulletin, **41** 53 (1968).

as a carrier gas, was introduced into the heated column of CuO to oxidize these components to water vapors and was detected by a cathetometer. The analysis of the hydrocarbons were also made by the gas chromaotgraphy with a charcoal column of 1 m length and a hydrogen flame ionization detector.

Results

H_2–D_2 Exchange Reaction. Reaction times behind the reflected shock wave were assumed to be the same as the residence time observed by a pressure transducer at an end plate and were nearly 1 ms. The temperature range was 1135~1940 K. Reaction rates observed, $\Delta(\mathrm{HD})/\Delta t$, are compared with those calculated by Bauer's rate law in Table 1. It is obvious that the isotope exchange rate is about one hundredth of the rate calculated from the equation obtained by Bauer at high concentration of hydrogen molecules and that the reaction orders with respect to H_2 and D_2, given by Bauer, is not accurate at least at the low concentration ranges of hydrogen. For the accurate estimation of the partial reaction order with respect to H_2 and D_2, it is necessary to study in the concentration range as wide as possible. Bauer carried out the study in a relatively high concentration, while the present work was studied in a relatively low concentration, and when two experiments are combined, the sum of the partial orders can be estimated more accurately.

Since the argon concentration in above two experiments is alike, the difference of the reaction rate due to the argon concentration may be ignored. Therefore, the empirical power-rate expression was deduced to

$$\Delta(\mathrm{HD})/\Delta t = k(\mathrm{H_2})^y(\mathrm{D_2})^x \qquad (5)$$

in which k includes the contribution of argon. When the mixtures were restricted to the equimolar ones, the sum of the partial reaction orders, or $n=x+y$, and the activation energy, E, could be determined by the least-squares method (Fig. 1). From the figure, the values of E and n were determined to be 41.2 kcal/mol and 1.80 respectively.

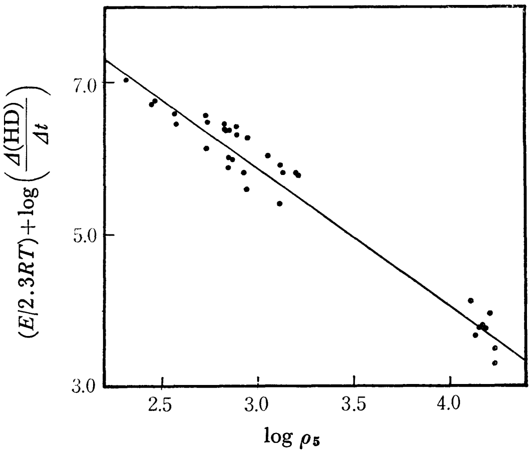

Fig. 1. The determination of reaction order n by the relation derived from Eq. (5) with $E=41.2$ kcal/mol at the least standard deviation. ($n=1.80$ from the slope)
ρ_5: The total density of sample gas mixture behind the reflected shock wave.
Bauer: ●, Yano: ◐

CH_4–CD_4 Pyrolysis. *Mixture A*: Reaction times behind the reflected shock wave were about 1 ms and the temperature range was 1501~1678 K. For all of the experimental runs, $(\mathrm{H_2}):(\mathrm{HD}):(\mathrm{D_2})$ ratios were examined and for some, hydrocarbons were also analyzed as shown in Table 2. The average ratios $(\mathrm{HD})/(\mathrm{H_2})$ and $(\mathrm{D_2})/(\mathrm{H_2})$ were 1.56±0.05 and 0.50±0.05, respectively. These values are slightly different from those in the previous paper[1] (1.7 and 0.6 respectively). Because of the improved separation between gas chromatographic peaks, the ratios obtained in the present work are more accurate than those in the previous paper.

Mixture B: Temperature range was 1470~1608 K. The average ratios $(\mathrm{HD})/(\mathrm{H_2})$ and $(\mathrm{D_2})/(\mathrm{H_2})$ were

TABLE 1. OBSERVED H_2–D_2 EXCHANGE REACTION RATE AND THE ONE CALCULATED BY BAUER'S EQUATION

T_5K	ρ_5 ×10^3	τ ms	$(\rho_5)_{\mathrm{HD}}$ ×10^6	$(\mathrm{HD})/(\mathrm{H_2})$	$\Delta(\mathrm{HD})/\Delta t$	
					Obsd ×10^3	Calcd ×10^1
1135	2.83	0.964	nil	—	—	0.001
1183	2.73	1.00	nil	—	—	0.003
1255	3.04	0.828	0.008	0.0025	0.0971	0.101
1395	3.84	0.934	3.30	0.092	3.53	0.891
1417	3.07	0.861	0.928	0.029	1.07	0.711
1497	3.24	0.952	4.10	0.14	4.31	1.91
1540	3.18	0.861	8.41	0.29	9.77	2.61
1555	3.43	0.783	6.24	0.21	7.97	3.61
1556	3.62	0.843	5.03	0.15	5.97	3.81
1610	3.44	0.813	10.21	0.36	12.5	5.91
1670	2.67	1.08	18.1	0.79	16.61	6.91

ρ_5: Total density of the sample gas behind a reflected shock wave, expressed in mol/l.
$(\rho_5)_{\mathrm{HD}}$: ρ_5 multiplied by mole fraction of product HD.

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8) The contribution from argon to the rate was taken into account, as proposed by Bauer, the values of E and n were calculated to be 41.2 kcal/mol and 1.84, respectively.

Table 2. Products distribution of methane pyrolysis
(Product yields are represented in mol% of sample gas)

	Mixt. A					Mixt. B					
T_5K	1501	1517	1519	1578	1600	1470	1530	1532	1552	1580	1608
Run	1	3	4	2	5	6	7	9	10	8	11
H_2 %	0.0056	0.0052	0.0077	0.0279	0.0416	0.0029	0.0175	0.0155	0.0227	0.0368	0.0670
HD %	0.0088	0.0100	0.0115	0.0403	0.0580	0.0058	0.0265	0.0236	0.0336	0.0549	0.1070
D_2 %	0.0026	0.0030	0.0030	0.0135	0.0167	0.0007	0.0105	0.0090	0.0113	0.0202	0.0416
$\sum H$ %	0.0170	0.0182	0.0222	0.0817	0.1163	0.0094	0.0545	0.0481	0.0676	0.1119	0.2156
C_2H_6 %	0.0078	0.0106	0.0112	0.0230	0.0228	—[a]	—[a]	0.0197	0.0233	0.0282	0.0337
C_2H_4 %	0.0017	0.0035	0.0041	0.0179	0.0240	—[a]	—[a]	0.0107	0.0148	0.0218	0.0427
C_2H_2 %	nil	0.0002	0.0002	0.0025	0.0029	—[a]	—[a]	0.0001	0.0004	0.0011	0.0036
$\sum' C_2$ %	0.0112	0.0182	0.0200	0.0663	0.0795	—	—	0.041	0.053	0.075	0.13
HD/H_2	1.57	1.92	1.49	1.44	1.39	1.97	1.51	1.52	1.48	1.49	1.63
D_2/H_2	0.46	0.58	0.39	0.48	0.40	0.24	0.60	0.58	0.50	0.55	0.64
$\sum C_2/\sum H$	0.56	0.79	0.70	0.53	0.43						

a) Not studied.

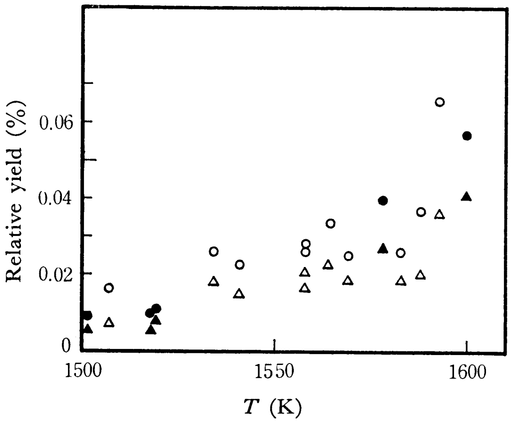

Fig. 2. The effect of oxygen on the relative yields of products at various temperature.
Mixture A ●: (HD) ▲: (H_2)
Mixture B ○: (HD) △: (H_2)

found to be 1.53±0.05 and 0.60±0.05, respectively (see Table 2, Mixt. B). These values are in good agreement with those obtained for the mixture A. As shown in Fig. 2, the effect of the trace amounts of oxygen (less than 300 ppm) is negligible. This conclusion is consistent with the calculation[9] after Meyerson.

As described in the previous paper, methane is converted into ethane in the early reaction stage and the latter is further transformed into ethylene, acetylene and higher hydrocarbons. When the products of the methane pyrolysis are assumed to be only C_2 hydrocarbons, the total hydrogen produced by the pyrolysis, $\sum H$ $(=(H_2)+(HD)+(D_2))$, should be equivalent to the sum $\sum' C_2 (=(C_2H_6)+2(C_2H_4)+3(C_2H_2))$. $\sum H$ is, however, always larger than $\sum' C_2$ in both the present and the previous works, and the ratio $\sum' C_2/\sum H$ decreases as the temperature increases as shown in Fig. 3. In order to confirm this, product analysis was made for three runs shock heated at higher temperature with a mixture of 12% CH_4 in argon. From Table 3, it is clear that at higher temperatures the ratio $\sum' C_2/\sum H$ decreased remarkably. This inclination may be explained by the formation of higher hydrocarbons during the pyrolysis of methane. Actually, a small amount of propylene was detected in the experimental runs 8 and 11 (see Table 2, Mixt. B).

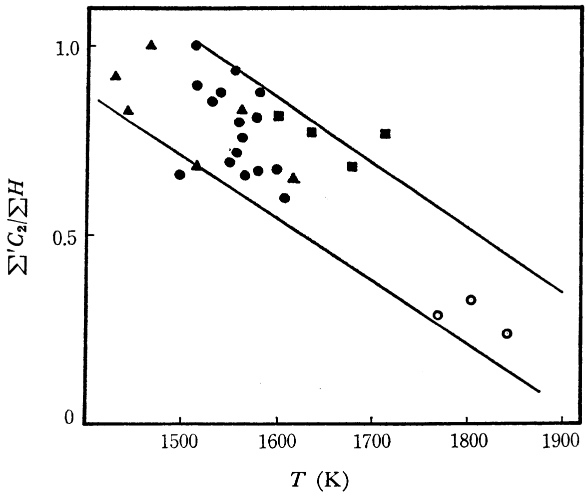

Fig. 3. The temperature dependence of $\sum' C_2/\sum H$.
Yano ●: CH_4-CD_4-Ar(6—6—88%) $\tau=1$ ms
○: CH_4-Ar(12—88%) $\tau=1$ ms
Skinner ▲: CH_4-Ar(12—88%) $\tau=1$ ms
■: CH_4-Ar(12—88%) $\tau=10$ ms

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[9] Even if hydrogen molecules are produced by the methane pyrolysis *via* methylene mechanism and dissociated into hydrogen atoms, at the rate given by Meyerson and Watt under the presence of 1000 ppm oxygen, and if H and D atoms from this process may be converted into HD molecules by the abstraction reaction with CH_4 and CD_4, *i. e.*,

$$\left.\begin{array}{l} H+CD_4 \rightarrow HD+CD_3 \\ D+CH_4 \rightarrow HD+CH_3 \end{array}\right\} \quad k_1=1.5\times10^{11}\exp(-14000/RT) \quad (\mathrm{mol^{-1}\cdot l\cdot s^{-1}}) \qquad \text{(A)},$$

the amount of HD molecules obtained through these processes will be only 1.4% of total hydrogen molecules initially produced. The reactions

$$\left.\begin{array}{l} H+D_2 \rightarrow HD+D \\ D+H_2 \rightarrow HD+H \end{array}\right\} \quad k_2=5\times10^{10}\exp(-7500/RT) \quad (\mathrm{mol^{-1}\cdot l\cdot s^{-1}}) \qquad \text{(B)}$$

are ignored since the processes (A) are faster than (B).

This small value with respect to HD molecules, obtained on above assumptions, contradicts with the experimental results.

TABLE 3. $\sum' C_2/H_2$ AT RELATIVELY HIGH TEMPERATURE IN CH_4 (12% IN Ar) PYROLYSIS

	C_2H_6 %	C_2H_4 %	C_2H_2 %	$\sum' C_2$ %	H_2 %	$\sum' C_2/H_2$	T_5K
Run 1	0.0135	0.0700	0.0775	0.386	1.9	0.203	1848
Run 2	0.0286	0.1439	0.0955	0.603	2.11	0.286	1770
Run 3	0.0300	0.1512	0.1026	0.640	1.99	0.325	1805

Discussion

The yield of HD molecules in products has great significance in judging the validity of a methyl mechanism, proposed by Skinner,[10] compared with a methylene mechanism by Kevorkian.[11] In the previous paper, the formation of only C_2 hydrocarbons was taken into consideration, and the product hydrogen was divided into two parts, the primary and the secondary hydrogen. That is, the primary hydrogen was produced from the process

$$2\,CH_4 \longrightarrow C_2H_6 + H_2\,, \tag{6}$$

and the secondary one was produced from the dehydrogenation process,

$$\begin{array}{l} C_2H_6 \longrightarrow C_2H_4 + H_2 \\ \qquad\qquad \llcorner\!\!\longrightarrow C_2H_2 + H_2\,. \end{array} \tag{7}$$

Then, the formation of one mole of ethane corresponded to one mole of the primary hydrogen. And one mole of ethylene in the products corresponded to one mole each of the primary and the secondary hydrogens. In the similar way, the formation of one mole acetylene is equivalent to one mole primary and two moles secondary hydrogens. According to a methylene mechanism, small amount of HD would be formed in the primary process, while in the secondary process HD would be appreciably formed. Yet, the previous experimental results have been inconsistent with methylene mechanism as far as only C_2 hydrocarbons are concerned, even if the equilibrium distribution of hydrogen isotopes among the secondary hydrogens is assumed.

As shown in Fig. 3, however, the formation of considerable amounts of higher hydrocarbons is revealed. Therefore, the contribution from the higher hydrocarbons must be considered in addition to C_2 hydrocarbons, and the problem should be discussed more precisely. The ratio of the primary hydrogen to total hydrogen $\sum H$, A, is now expressed,

$$A = (\sum C_2 + \sum F_n(C_n))/\sum H \qquad (n \gtrsim 3) \tag{8}$$

where $\sum C_2$ gives the sum of C_2 hydrocarbons, *i.e.*, $\sum C_2 = (C_2H_6)+(C_2H_4)+(C_2H_2)$, and $F_n(C_n)$ means the sum of the primary hydrogen corresponding to C_n hydrocarbons. When the concentration of the hydrocarbon C_nH_m is expressed by C_n,

$$F_n(C_n) = n\cdot C_n/2\,. \tag{9}$$

To simplify the notation, A is divided into two parts, A' and A'', or

$$A = (\sum C_2 + \sum nC_n/2)\sum H = \sum C_2/\sum H + \sum nC_n/2\sum H = A' + A''\,. \tag{10}$$

A' can be directly obtained from experimental data but A'' cannot because nC_n is unknown. The minimum value of A'', however, can be estimated from the extreme case where the n-carbons skeleton is taking the place of C_n-hydrocarbons. That is, all of the hydrogen atoms, attached to the carbon atom of the reactant methane molecule, are converted into hydrogen molecules. When $g(C_n)$ gives the amount of the total hydrogen released through the formation of C_n-skeleton, following two equations are obtained,

$$g_n(C_n) = 2n\cdot C_n \tag{11}$$

$$\sum_{n \geq 3} g_n(C_n) = \sum H - \sum' C_2\,. \tag{12}$$

Since $\sum' C_2$ has a value between $0.60\sum H$ and $0.92\sum H$ (Table 2), $\sum nC_n$ comes between $0.20\sum H$ and$0.04\sum H$, therefore, the minimum value of A'' is given by,

$$A'' = \sum nC_n/2\sum H = 0.1\sim 0.02\,. \tag{13}$$

The value of A' has proved to be between 0.43 and 0.79 (see Table 2, Mixt. A) and so, A is estimated to be between 0.53 and 0.81.[12] Therefore, from this A and eq. (4), $(H_2)_{\rm prim}$ and the upper limit of $({\rm HD})_{\rm prim}$ are expected to be,

$$(H_2)_{\rm prim} = (1.0/2.28)(\sum H)_{\rm prim} = (1.0/2.28)(\sum H)A \tag{14}$$

$$({\rm HD})_{\rm prim} = (0.28/2.28)(\sum H)_{\rm prim} = (0.28/2.28)(\sum H)A\,. \tag{15}$$

while, the isotopic distribution in the secondary hydrogen is assumed to be in equilibrium state. The amount of $(H_2)_{\rm sec}$ and $({\rm HD})_{\rm sec}$ are given as,

$$(H_2)_{\rm sec} = (1-A)(\sum H)/4 \tag{16}$$

$$({\rm HD})_{\rm sce} = (1-A)(\sum H)(2/4)\,. \tag{17}$$

The ratio of HD to H_2 is now expressed as,

$$\begin{aligned} ({\rm HD})/(H_2) &= \{({\rm HD})_{\rm prim} + ({\rm HD})_{\rm sec}\}/\{(H_2)_{\rm prim} + (H_2)_{\rm sec}\} \\ &= \{4(0.28/2.28)A + 2(1-A)\}/\{4(1.0/2.28)A + (1-A)\} \\ &= 0.86\sim 0.48\,. \end{aligned} \tag{18}$$

Thus, even if the most favorable cases for the methylene mechanism are assumed, it cannot explain the observed high ratio of 1.53 for $({\rm HD})/(H_2)$.

Since no carbon-soot was detected but actually propylene and also other hydrocarbons are expected, the value of calculated A'' should be higher and the ratio $({\rm HD})/(H_2)$ should be lower than those calculated above for carbon skeletons.

The author wishes to thank Professor Kenji Kuratani for his helpful discussions and encouragement.

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[10] G. B. Skinner and R. A. Ruehrwein, *J. Phys. Chem.*, **63**, 1736 (1959).

[11] V. Kevorkian, G. E. Hearth and M. Boudart, *ibid.*, **64**, 964 (1960).

[12] There is a positive correlation between $\sum' C_2/\sum H$ and $\sum C_2/\sum H$ in the present experimental conditions. That is, A' values of 0.43 and 0.79 correspond to $\sum' C_2/\sum H$ values of 0.69 and 0.92, respectively. So, the range of A value is 0.53∼0.81.