Chemical Reaction of Hydrocarbons in the Microwave

Discharge I: On the Mechanism of the Decomposition of Ethane and Ethylene

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Citation

Issue Date
1971-11-05

URL
http://hdl.handle.net/2433/76376

Type
Departmental Bulletin Paper
Chemical Reaction of Hydrocarbons in the Microwave Discharge

I. On the Mechanism of the Decomposition of Ethane and Ethylene

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Received June 14, 1971

The decomposition of acetylene, ethane, ethylene and methane in the microwave discharge (2450 MHz) has been investigated in the flow system at about 1 torr. The residence time of hydrocarbons in the discharge zone ranged from 1 msec to 10 msec. Hydrogen was the major gaseous product in every case. A variety of low molecular weight hydrocarbons were produced except for the case of acetylene where the gaseous products were hydrogen and diacetylene. The variation of the product distribution with the residence time was examined. The isotopic analyses of products in the discharge in C₂H₆+C₂D₄ mixtures and in C₆H₆+C₆D₆ mixtures have revealed the importance of molecular detachment process in the formation of dehydrogenated products. Infra-red analyses of the polymeric films formed on the wall of discharge zone indicated that they are almost identical to polyethylene except for the case of acetylene.

INTRODUCTION

The microwave discharge has been used successfully for the formation of atoms from diatomic gases, because this type of discharge can avoid contamination from the electrodes and catalytic action of them, and an efficient coupling of microwave power to the discharge can be achieved readily.1,2 On the other hand, recently the investigation of chemical reactions of organic compounds in electrical discharges has been attracting much attention since the electrical discharge is considered as an interesting and valuable tool for promoting a variety of chemical reactions. Particularly the microwave discharge would be desirable to generate the required active species at low gas temperature since the microwave discharge is regarded as a cold plasma—a high electron temperature and a low gas temperature.3-5

Only a little studies have been reported on the decomposition of hydrocarbons in the microwave discharge. McCarthy3 studied the decomposition of methane at 16–220 torr with the powers up to 1500 W, which yielded principally acetylene. Streitwieser and Ward7 passed toluene diluted with helium through a microwave discharge, and isolated benzene, ethylbenzene, styrene and phenylacetylene. They suggested the importance of a molecule anion as a reaction intermediate rather than free radicals and the tropylium cation from the consideration of product

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distribution. On the other hand, Coates$^8$ decomposed n-hexane under the flow system and stated the importance of free radicals in the product formation. Acetylene, benzene, ethane, ethylene, methane and naphthalene were studied in the microwave discharge under the static condition by Vastola and Wightman,$^9$ who concluded that the films and the observed gases could result from the interations of a basic hydrocarbon unit, perhaps CH. Wightman$^{10}$ also investigated the decomposition of methane and methyl chloride in the flow system at 0.15 torr.

Recently Kawahara$^{11}$ studied the effect of power on the decomposition of methane in the fast flow system at 10 torr using microwave discharge with incident power ranging from 200 to 500 W, and found out that the disappearance of methane followed first-order kinetics at a given incident power, and that the rate coefficient is an exponential function of the incident power. The decomposition of benzene in the radio-frequency discharge (27 MHz) and the microwave discharge (2450 MHz) was studied by Hiroaka et al.$^{12}$ and Taki$^{13}$ investigated the decomposition of toluene, xylene and methylcyclohexane in the radio-frequency discharge (10 MHz) and the microwave discharge (2450 MHz). Both of them used radical scavengers (NO, O$_2$, or I$_2$) and suggested the possibility of the contribution of ion-molecule reactions in the formation of some products. Besides, in the radio-frequency discharge there are some reports concerning the decomposition of aliphatic hydrocarbons$^{14}$ and aromatic hydrocarbons.$^{15}$ Among these studies, Albert-Pierre Bois d’Enghien et al.$^{14a}$ and Félix Le Goff et al.$^{14b}$ suggested the important roll of methylene radicals in the decomposition of methane.

In this paper, the mechanism of the decomposition of ethane and ethylene is discussed as the first step of the investigation of chemical reactions of hydrocarbons in the microwave discharge, and the result of the decomposition of acetylene and methane is also given in connection with the main course of the reactions.

**EXPERIMENTAL**

**Materials** Ethane (99.7%), ethylene (99.8%) and methane (99.9%) were obtained from Takachiho Chemical Industrial Company, and used without further purification. Acetylene (99.8%) was prepared by treating a cylinder gas with 10% NaHSO$_3$ solution and 5% KMnO$_4$ solution and then passing it through a liquid nitrogen trap. Ethylene-$d_4$ (99%) and ethane-$d_6$ (99%) were obtained from Merck, Sharpe and Dohme, Ltd., and used without further purification.

**Apparatus and Procedure** Experiments were almost carried out in the fast flow system shown schematically in Fig. 1. The microwave power source was a MR-1S type microwave generator from Ito Electro-Medical Instrument Mfg. Co. Ltd., (maximum output 200 W, 2450 MHz). The generator was connected to an air-cooled cavity (tapered rectangular$^{16}$) by a coaxial cable (characteristic impedance 75 Ω). Pressure in the discharge region was measured with a silicone oil manometer.

In Fig. 2, the relation is shown between pressure and minimum power input to the magnetron in order to maintain a stable discharge in the case of methane.
In Fig. 3, the relation between luminous zone length and power input to the magnetron is given. Since the definition of the reaction time in the microwave discharge has not been clearly given yet, we define the effective reaction time by the residence time of a reactant gas in the luminous zone. In order to reduce the residence time, we used the minimum power input so as to shorten the length of the luminous zone, in addition to the increase of flow rate of the reactant gas. Thus most experiments were carried out at pressures between 1 and 3 torr with power input ranging from 30 to 50 W. At the shortest residence time (≈1 msec), the extent of decomposition of reactant was estimated to be from 5 to 10 percent. On the other hand, in the cases of the isotopic mixtures, the residence time was longer than 5 msec because gas flow rate and pressure in the discharge zone were restricted to lower values due to the short of the available amount of raw materials used there, therefore the extent of decomposition must have been greater than 30 percent.

The product gas emerged from the discharge zone was collected into a 5l...
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glass holder by cutting off the steady state flow, introduced into a gas-burette using a Toepler pump and then analyzed by gas chromatography. C1 and C2 hydrocarbons and hydrogen were analyzed by using active carbon column, and a 30% squalane on C-22 column was used for C3 and C4 hydrocarbon analyses. In another flow system, T.O.F. mass spectrometer (Hokushin Electric Works Ltd.) was used for C4 hydrocarbon product analyses in the discharge in ethylene, where the electron accelerating voltage was set at 20 eV to reduce the fragmentation.

The isotope analyses of hydrogen, acetylene and ethylene were carried out with the T.O.F. mass spectrometer. Isotopic acetylenes and ethylenes in the products were separated from other products by active carbon column and were collected in the separate liquid nitrogen traps after emerging from the column. The calibration was performed for the relative sensitivities for hydrogen fractions, but not for other fractions. The elemental analyses and infra-red spectra of the polymeric films deposited on the wall of the discharge zone were examined for characterization.

RESULTS AND DISCUSSION

1. Discharges in the static system

The decomposition of ethane and methane was studied preliminarily in the usual static system in order to determine the optimum discharge time for the investigation of reaction mechanism in the discharge. The experimental conditions were: pressure about 1.5 torr and discharge time 5-100 sec. The results at 5 sec in Table 1 show that hydrogen was the main gaseous product. A small amounts of hydrocarbons of low molecular weight were also detected in the gaseous products. The H/C value of the gaseous products indicates the significant deposition of some species in the products on the wall of the discharge zone. In the case of ethane, about 80 percent of reacted ethane was lost from gas phase as a polymeric film having the H/C value of about 1.4. The variation of the product yield with the discharge time is shown in Fig. 4 for ethane, which indicates that the reaction already reached the final stage at about 30 sec.

These results are very similar to that reported by Vastola and Wightman. They concluded that the film and the observed gases could result from the interactions of a basic hydrocarbon unit, perhaps CH, on the basis of the findings

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Percentages of gaseous products</th>
<th>H/C of gaseous products</th>
<th>H/C of films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H2</td>
<td>CH4</td>
<td>C2H2</td>
</tr>
<tr>
<td>CH4</td>
<td>96.3</td>
<td>1.6</td>
<td>0.2</td>
</tr>
<tr>
<td>C2H6</td>
<td>91.3</td>
<td>5.2</td>
<td>2.4</td>
</tr>
<tr>
<td>C3H8</td>
<td>92.8</td>
<td>4.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Pressure 1.5 torr, discharge time 5 sec, power input 100 W.
that CH was a common species in the emission spectra of ethane, ethylene and methane, and that under their conditions the rearrangement of various hydrocarbons were similar. Furthermore, they stated that the presence and concentration of CH is independent of the type of chemical bonding in the parent molecule.

But, as mentioned above, the reaction was in the final stage under these conditions in our study, and the observed gases are considered to be the end products which were produced through various kinds of succeeding reactions, so that, it is not adequate to discuss the reaction mechanism on the basis of these results, and the investigation of the reaction at shorter discharge time is necessary.

2. Discharges in the flow system

The decomposition of acetylene, ethane, ethylene and methane was investigated in the flow system shown in Fig. 1. The composition of the gaseous pro-

![Graph](234)
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The major gaseous products are hydrogen and C₁, C₂ hydrocarbons except for the case of acetylene.

(2) The results of elemental analyses of the polymeric films give the H/C values ranging from 1.4 to 1.6 except for the case of acetylene.

(3) In the case of acetylene, the gaseous products are almost hydrogen and diacetylene, and the H/C value of the polymeric film is equal to unity.

In the discharge chemistry, the probability that molecules suffer from secondary interaction or that the products are attacked by exciting species, is very high. Thus, in the following discussions consideration will be given on the contribution of successive reactions.

Now, ion-molecule reactions may be able to contribute to the formation of the decomposition products in the discharge, but adopting the common concepts in the discharge chemistry and the experimental result, as given in the following, we are to neglect these possibilities for the present.

(i) Positive ion density is much smaller than molecule and radical densities in the weakly ionized gas such as in the present discharge.

(ii) The thresholds for excitation are lower than for ionization and the cross sections for excitation rise more rapidly with energy above the threshold than for ionization, therefore the tail of the electron energy distribution can be more effective in excitation than in ionization.

(iii) The presence of the tropylum ion as an intermediate in the discharge in the aromatic hydrocarbons is not shown by the product analysis.

(I) Ethylene

The main gaseous products were hydrogen and acetylene in the decomposition of ethylene, and as the minor products methane, ethane, propane and propylene were detected (see Table 2). It is of interest that only trace amount of n-butane was produced in the present case, while n-butane is one of the important products in the photolysis and radiolysis of ethylene where the formation of n-butane has been ascribed to the recombination of ethyl radicals produced by addition of hydrogen atom to ethylene. Furthermore, in the decomposition of ethylene in various types of discharges under pressures between 0.1 and 760 torr, n-butane is not significant, but none has yet referred to the cause of this discrepancy. The variation of relative composition of the main products is shown in Fig. 5.

Formation of acetylene and hydrogen

Excited ethylene molecule produced by the collision with electrons in the discharge can dissociate via the following reactions:

\[
\begin{align*}
\end{align*}
\]
Fig. 5. Variation of relative yield of products with the residence time in the discharge in C2H4 (pressure ~1 torr, power input 30 W).

(○ H2, ● C2H2, △ C2H6)

\[ \text{C}_2\text{H}_4^* \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 \] (1), \[ \text{C}_2\text{H}_4^* \rightarrow 2\text{C}_2\text{H}_2 + 2\text{H} \] (2), \[ \text{C}_2\text{H}_4^* \rightarrow \text{C}_2\text{H}_3 + \text{H} \] (3).

If stabilized vinyl radicals are formed by Reaction (3), butadiene should be produced as a product, but the failure of finding it in the product gas leads to the estimation that vinyl radicals would not have been produced to any significant extent, or that even if produced they would have decomposed further to hydrogen atom and acetylene immediately without undergoing stabilization. In the study of the flash photolysis of ethylene, Back et al.\textsuperscript{20} reported that the stabilization of vinyl radicals did not occur at pressures of 1 and 2 torr but appeared at 10 torr, as judged from the observation of propylene and 1-butene which were considered to be produced by the combination of vinyl with methyl and ethyl radicals. Thus Reaction (3) seems to be less important.

Next, the relative importance of Reactions (1) and (2) will be discussed, at shorter residence time where the effect of secondary reactions is less significant. If excited ethylene molecules decompose only through Reaction (1), the ratio of the initial yield of acetylene to that of hydrogen should be equal to unity. If Reaction (2) takes place in addition to Reaction (1) and if hydrogen atoms produced are thermalized, then this ratio will be larger than unity. These phenomena have been observed in the photolysis of ethylene.\textsuperscript{18,19,21,29}

In the present case, the ratio of acetylene to hydrogen is a little smaller than unity, probably due to the loss of acetylene through the polymerization reaction. The effect of polymerization of acetylene becomes appreciable at the residence time about 5 msec (see Fig. 5). Thus, in order to obtain the corrected ratio, \textit{i.e.}, the ratio of acetylene to hydrogen which would have been produced in the initial step of the decomposition in the discharge, we must take the effect of polymerization into account. When we regard the contribution of ethylene
and acetylene to the formation of the polymeric film as equivalent on the basis of the fact that the H/C value of the polymeric film is nearly equal to 1.5 (see Table 2), the value of 1.2 is derived as the corrected ratio of acetylene to hydrogen. This value suggests the possibility that when total scavenging of hydrogen atoms is assumed, excited ethylene molecule produced by the collision with electrons may decompose via Reaction (1) mainly, that is, Reaction (1)/Reaction (2) \(\frac{n'H_2}{(C_2H_2)_0-H_2}=5\), where \((C_2H_2)_0\) is the calculated initial yield of acetylene.

In order to obtain the more detailed information about the formation of acetylene and hydrogen, the decomposition of mixtures of \(C_2H_4\) and \(C_2D_4\) was examined, the results being shown in Table 3. As mentioned before, the condition of the discharge was limited by the amount of the raw materials and was appreciably severer than that in Table 2, that is, the decrease of pressure makes the electron temperature higher and the increase of residence time makes the contribution of secondary reactions more remarkable. Analyses of the isotopic fractions show the formation of a considerable amount of isotopically mixed products, \(i.e., HD\) and \(C_2HD\), under the present condition. But the yield of these products is supposed to be much lower at the shorter residence time, for these products must have been formed in the secondary reactions of isotopically unmixed primary products, occurrence of which is most likely as judged from the drastic condition performed here. Therefore, concerning the secondary reaction, the decomposition of acetylene was additionally studied.

Table 3. Isotopic Distribution of Hydrogen and Acetylene Produced in the Discharge in \(C_2H_4-C_2D_4\) Mixture.

<table>
<thead>
<tr>
<th>Reactant mixture</th>
<th>Reactant Pressure () (torr)</th>
<th>Reactant Residence time () (msec)</th>
<th>Hydrogen () (%)</th>
<th>Acetylene () (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(H_2)</td>
<td>(HD)</td>
</tr>
<tr>
<td>(C_2H_4-C_2D_4)</td>
<td>0.43</td>
<td>(~9.3)</td>
<td>44</td>
<td>28</td>
</tr>
<tr>
<td>((1: 0.90))</td>
<td>0.41</td>
<td>(~10.0)</td>
<td>42</td>
<td>25</td>
</tr>
</tbody>
</table>

Luminous zone \(3\sim4\) cm, power input 50 W.

Decomposition of acetylene The condition of the reaction was similar to that of mixtures of \(C_2H_4\) and \(C_2D_4\). The gaseous products were almost hydrogen and diacetylene as shown in Table 2. There were observed methane, propane, propylene and vinylacetylene, but even vinylacetylene which was the most abundant among these products, amounted to only a small percent of diacetylene. Benzene was not detected in gaseous products.

These facts suggest the formation of ethynyl radicals and hydrogen atoms. The ratio of diacetylene to hydrogen is nearly equal to \(1/6\), which indicates the loss of ethynyl radicals through the polymerization and/or the secondary decomposition, \(i.e., C_2H\) radicals produced in Reaction (4) either recombine to diacetylene (Reaction (5)), add to acetylene (Reaction (6)) or decompose to carbon and hydrogen atom (Reaction (7)).
M. TAKEUCHI and Y. TAKEZAKI

\[ \text{M} \text{(M)} \]
\[ \begin{align*}
C_2H_2^* & \rightarrow C_2H + H \quad (4), \\
2C_2H_2 & \rightarrow C_2H_2 \quad (5), \\
C_2H + C_2H_2 & \rightarrow (C_2H_3)^* \rightarrow C_4H_2 + H \quad (6), \\
C_2H_2 & \rightarrow C_2 + H \quad (7).
\end{align*} \]

On the other hand, hydrogen atoms can either recombine into hydrogen molecule (Reaction (8)) or abstract hydrogen atom from the parent molecule (Reaction (9)), but activated vinyl radicals formed by addition of hydrogen atom to acetylene must decompose immediately (Reaction (10)), because there existed only a trace amount of butadiene, vinylacetylene and ethylene among the reaction products in the discharge in acetylene.

\[ \begin{align*}
M & \rightarrow H + H \rightarrow H_2 \quad (8), \\
C_2H_2 + H & \rightarrow C_2H + H_2 \quad (9), \\
C_2H_2 + H & \rightarrow (C_2H_3)^* \rightarrow H + C_2H_2 \quad (10).
\end{align*} \]

**Formation of the isotopically mixed products** Since acetylene and hydrogen are the major products in the decomposition of ethylene and the extent of decomposition of ethylene in the discharge in mixtures of C_2H_4 and C_2D_4 is estimated to be larger than 30 percent, the occurrence of the succeeding reactions is necessarily expected. Table 4 shows the relative peak heights of C_4 species to that of reactant ethylene in the mass spectra of the product gas taken from the discharge in ethylene in another flow system (electron accelerating voltage 20 eV). Although the experimental conditions are a little different, the rapid increase of m/e 50, mostly ascribed to diacetylene, indicates the formation of diacetylene due to the secondary decomposition of acetylene. Thus Reaction (10) and the reverse of Reaction (4) must contribute remarkably to the observed isotopic mixing of acetylene fractions in the discharge in mixtures of C_2H_4 and C_2D_4. Reactions (8) and (9) can also contribute the formation of HD in these experiments. Furthermore, the yield of HD will become higher by the isotopic exchange due to the secondary decomposition of H_2 and D_2 produced by Reaction (1) and also by the

<table>
<thead>
<tr>
<th>Decomposition (%)</th>
<th>[\frac{\text{(m/e X)}}{\text{(m/e 28)}_0}] × 100 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td>4.3</td>
<td>0</td>
</tr>
<tr>
<td>14.5</td>
<td>0.11</td>
</tr>
<tr>
<td>29.9</td>
<td>0.96</td>
</tr>
<tr>
<td>35.0</td>
<td>1.46</td>
</tr>
<tr>
<td>40.2</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Electron accelerating voltage 20 eV.
Pressure in the discharge zone ~2 torr.

\[\text{(m/e X)}: \text{peak height of C}_4 \text{ species.}\]

\[\text{(m/e 28)}_0: \text{peak height of raw material ethylene.}\]
recombination between H and D atoms produced by Reaction (2).

The fact that a lot of HD were produced in the presence of ethylene in the present case while ethylene is considered to be a good scavenger for thermalized hydrogen atom at higher pressure, indicates that a lot of hydrogen atoms were not scavenged effectively. This suggests that hot hydrogen atoms may exist and/or the scavenging of thermalized hydrogen atoms by ethylene may be inefficient, both of which seem natural in our system as clarified in the following discussion.

In the former case, hydrogen atom abstracts the other hydrogen atom from ethylene molecule so that vinyl radical and hydrogen molecule (H₂, HD and D₂ in the case of C₂H₄+C₂D₄) are produced (Reaction (11)). This vinyl radical will recombine into butadiene (Reaction (12)).

\[ \text{H(hot)} + \text{C}_2\text{H}_4 \rightarrow \text{H}_2 + \text{C}_2\text{H}_3 \quad (11) \]
\[ 2\text{C}_2\text{H}_3 \rightarrow \text{C}_4\text{H}_6 \quad (12) \]

The increase of m/e 54—mostly ascribed to butadiene—in the mass spectra is considered to indicate the increase of hot hydrogen atom concentration with the extent of decomposition.

On the other hand, in the latter case, activated ethyl radicals produced by addition of thermalized hydrogen atom to ethylene appreciably either redissociate to ethylene and hydrogen atom without undergoing stabilization, or contribute to the catalytic recombination of hydrogen atoms. Ishihara et al. studied the reaction of hydrogen atom with ethylene under the similar condition to the present authors, and found out the ratio of the rate constant of the stabilization \(k_1\) to that of the redissociation \(k_2\) of activated ethyl radicals produced in Reaction (13) to be 6 x 10⁻², which indicates an inefficient stabilization of activated ethyl radicals under these conditions.

\[ \text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5^* \quad (13) \]
\[ \text{C}_2\text{H}_5^* \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad (14) \]

Besides, Knox et al. suggested that about 40 percent of the initially formed ethyl radicals would redissociate in their system at 300°K and 2 torr. They also reported that the alkyl radicals which are considered to be thermally unequilibrated have higher ratios of the rate constant of abstraction to that of combination between hydrogen atoms and alkyl radicals, that is, Reaction (15) contributes to the catalytic recombination of hydrogen atoms appreciably.

\[ \text{C}_2\text{H}_5 + \text{H} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad (15) \]

From the similarities of experimental conditions used by them and by us, it seems reasonable to conclude that a large amount of hydrogen atoms were not scavenged by ethylene, prevented by the occurrence of Reactions (11), (13) and (15).

Thus, considering the contribution of secondary reactions of acetylene and hydrogen produced primarily, we may say qualitatively that at the shorter residence time excited ethylene molecule will decompose mainly through Reaction (1).
Formation of the minor products

The reaction of hydrogen atom with ethylene probably give the minor products such as methane, ethane and propane. Ishihara et al. reported the formation of ethane, methane and propane in decreasing order of importance, and the absence of n-butane. This reaction was re-examined in our study, in which ethylene was added downstream the pure hydrogen flow suffered from the microwave discharge. The ratio of reactants, hydrogen to ethylene, was nearly equal to unity and the result is given in Table 5 together with Ishihara's. The last line in Table 5 shows the result of the discharge in ethylene under the similar condition.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>CH₄</th>
<th>C₂H₂</th>
<th>C₂H₆</th>
<th>C₃H₆</th>
<th>n-C₄H₁₀</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>H + C₂H₄</td>
<td>1</td>
<td>0</td>
<td>2.9</td>
<td>0</td>
<td>0.33</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>H + C₂H₄</td>
<td>1</td>
<td></td>
<td>2.5~4.3</td>
<td>0.26~</td>
<td>0.38</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30 b</td>
</tr>
<tr>
<td>C₂H₄ discharge</td>
<td>1</td>
<td></td>
<td>2.4</td>
<td>1.2</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>this work</td>
</tr>
</tbody>
</table>

The nature of products and the coincidence of the ratio of ethane to methane in these three different experiments suggest that, the reactions such as (16) to (20) may play an important role in the formation of ethane, methane and a part of propane in succession to Reactions (13) and (14), in the same way as mentioned by Ishihara et al., though Knox et al. reported that all the ethane molecules produced in Reaction (16) decompose effectively to methyl radicals (Reaction (18)) in their system.

\[
\begin{align*}
H + C₂H₄ \rightarrow & C₂H₄* \quad (16), \quad \text{(M)} \\
\quad \quad & \quad C₂H₄* \rightarrow C₂H₆ \quad (17), \\
\quad \quad & \quad 2CH₃ \quad (18), \\
H + CH₃ \rightarrow & CH₄ \quad (19), \quad \text{(M)} \\
\quad \quad & \quad CH₃ + C₂H₅ \rightarrow C₂H₈ \quad (20).
\end{align*}
\]

The mechanism of the formation of propylene and most of propane is not clear, but the precursors must be propyl radicals because preliminary examination of the effect of addition of hydrogen molecules showed the increase of propane formation which probably had come from the abstraction of hydrogen atoms by propyl radicals.

Now again we consider the relative importance between Reactions (1) and (2) at the shorter residence time on the basis of the result shown in Table 2. If we assume that ethane, methane and propane are all produced through Reactions (13) to (20) excepting Reaction (15), and that all the hydrogen atoms are scavenged, the relative importance can be obtained approximately by summing the products, that is, the value of \( \frac{H₂/(CH₄+C₂H₆+C₃H₈)}{H₂} \), which is essentially equivalent to that of \( \frac{1-(C₂H₅)}{H₂} \) as mentioned before, gives the approximate ratio of Reaction (1) to Reaction (2), and this ratio is equal to about 5.5. In reality, the efficiency of deactivation of the excited ethyl radical must be taken

\[ (240) \]
into account, but since it is unknown in our system, it is difficult to determine the exact relative importance between Reactions (1) and (2). However, if we assume that 50 percent of the excited ethyl radicals are deactivated, on the basis of the report by Knox et al. as quoted in the preceding discussion, the ratio of about 4.5 is obtained. Since the latter assumption seems more reasonable as judged from the similarity of our experimental condition to that of Knox, the value of 4.5 would be the more plausible ratio of Reaction (1) to Reaction (2). Furthermore, the resemblance of the ratio in these two cases, i.e., the total scavenging and the half scavenging, indicates that in any case ethylene must be decomposed mainly by Reaction (1) under our condition.

(II) Ethane

The major gaseous products were hydrogen, ethylene, acetylene, methane and propane, and also a small quantity of propylene and n-butane were produced (see Table 2). The result is similar to that in the photolysis of ethane at 1067 Å where n-butane is absent as a product. This indicates the formation of only a small amount of ethyl radical in the present reaction system. The relative yield of hydrocarbon products with residence time is given in Fig. 6.

![Graph](image)

Fig. 6. Variation of relative yield of hydrocarbon products with the residence time in the discharge in C2H6 (pressure ~1 torr, power input 30 W).

(○ C2H4, ● C2H6, △ CH4, □ C3H8, × C3H6)

Formation of ethylene and acetylene Since ethylene and acetylene are the important products in the present case, and only both of them showed remarkable change with the residence time as shown in Fig. 6, the mechanism of formation of these two products will be discussed with attention to the relation between them. The change of the ratio of acetylene to ethylene with residence time is presented in Fig. 7. This ratio does not pass through the origin at zero residence time, and
the intercept is 0.35-0.40, which shows the primary formation of acetylene. The similar phenomenon has been observed in the photolysis of ethane,33a) where the increase of this ratio with conversion is ascribed to the loss of ethylene consumed in scavenging of hydrogen atoms.

Meanwhile, in the present case, many other secondary reactions will be able to occur with the increase of the residence time, principally the decomposition of ethylene to acetylene or the polymerization of ethylene and acetylene produced primarily. The H/C value of the polymeric film was equal to about 1.5 as in the case of ethylene. When we again regard this as being resulted from the equivalent contribution from ethylene and acetylene to the formation of the polymeric film, and refer to the discussion on the decomposition of ethylene in the former section, then an estimation can be deduced that, under these conditions the principal secondary reaction with the increase of the residence time will be the decomposition of produced ethylene to acetylene, which is observed as the increase of the ratio of acetylene to ethylene as shown in Fig. 7.

In the photolysis of ethane,33) it has been confirmed that the ratio of acetylene to ethylene at high temperature or very low conversion, where the internal scavenging of hydrogen atoms does not occur, shows the pressure dependence and the intercept at zero pressure is equal to 0.6-0.7 at 1470 Å and 1577 Å. This pressure dependence has been interpreted as the evidence of the existence of the intermediate excited ethylene molecule in the formation of acetylene. For example, Akimoto et al.33b) proposed the following reaction scheme:

\[
\begin{align*}
\text{C}_2\text{H}_6^* & \rightarrow \text{H}_2 + \text{C}_2\text{H}_4'' \rightarrow \text{H}_2 + \text{C}_2\text{H}_2 \\
& \left(\text{M}\right) \\
\text{H}_2 + \text{C}_2\text{H}_4' & \rightarrow \text{C}_2\text{H}_4 \\
\text{C}_2\text{H}_6^* & \rightarrow 2\text{H} + \text{C}_2\text{H}_4
\end{align*}
\]

In the present case, though very speculative since the pressure effect on the
ratio extrapolated to zero time is not examined, the resemblance of the value of our intercept at about 1 torr to that at zero pressure in the photolysis of ethane would suggest the possibility of the existence of the intermediate excited ethylene molecule in the decomposition of ethane in this system, too.

Next, as to the formation of ethylene, acetylene and hydrogen, the decomposition of mixtures of C2H6 and C2D6 was examined as shown in Table 6. The experimental condition was similar to that in the case of C2H4 and C2D4. Isotopic distribution in ethylene and acetylene fractions indicates that they are produced by the molecular detachment processes predominantly. The isotopic mixing observed in each fraction must be mainly due to the secondary reactions as mentioned before. For example, Reactions (13) and (15) must have made an important contribution to the formation of the isotopically mixed ethylenes, and Reaction (10) and the reverse of Reaction (4) to the isotopic mixing in acetylene fractions. The formation of HD in high yield must have resulted from Reactions (8) and (15) mainly. From these limited data, however, we can not touch on the relative importance between Reactions (21) and (22).

<table>
<thead>
<tr>
<th>Reactant mixture</th>
<th>Pressure (torr)</th>
<th>Residence time (msec)</th>
<th>Hydrogen (%)</th>
<th>Ethylene (%)</th>
<th>Acetylene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C2H6-C2D6</td>
<td></td>
<td>C2H2</td>
<td>C2HD</td>
<td>C2D2</td>
</tr>
<tr>
<td>0.59-1.09</td>
<td>0.59-1.00</td>
<td>7</td>
<td>49</td>
<td>29</td>
<td>22</td>
</tr>
<tr>
<td>0.48-1.00</td>
<td>0.48-1.00</td>
<td>10</td>
<td>42</td>
<td>31</td>
<td>27</td>
</tr>
</tbody>
</table>

Luminous zone ~5 cm, power input 50 W.

Formation of methane and propane  Methane and propane are the other important products in the decomposition of ethane. The propane yield increased with pressure in the discharge zone as shown in Fig. 8, obtained at the constant residence time of about 2 msec. The pressure effect like this was observed in the photolysis at 1236 Å and the radiolysis of ethane, where the cause of it was ascribed to the collisional deactivation of the excited propane produced through Reactions (23) and (24)

\[
\text{C}_2\text{H}_6 \rightarrow \text{CH}_2 + \text{CH}_4 \quad (23),
\]

\[
\text{CH}_4 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_8 \quad (24),
\]

In the present case, the excited propane must be produced, but the formation of it does not always come only from Reaction (24), for the excited propane can be produced by Reactions (20) as well. Meanwhile in the formation of methane Reactions (19) and (23) are able to contribute. From the present results we cannot conclude which reaction is predominant in the formation of methane and propane.
(III) Methane

The products in the decomposition of methane are shown in Table 2. The major gaseous products were hydrogen, ethane, ethylene and acetylene, and in the minor products propylene and propane were found. The variation of the major gaseous products with the residence time is given in Fig. 9. These results are very similar to those obtained by Kawahara\textsuperscript{14} in the microwave discharge and Albert-Pierre Bois d’Enghien et al.\textsuperscript{14a} in the radio-frequency discharge, the
latter authors reporting that methylene radical is the most important species in the decomposition of methane. The most remarkable feature in these studies including ours, is the formation of only a small amount of propane which is one of the important products in the photolysis of methane at 1236 Å and 1048 Å. Since the formation of propane has been ascribed to the recombination of methyl and ethyl radicals, low yield of propane may indicate the lack of ethyl radicals, which was estimated in the case of ethylene and ethane as mentioned before. Figure 9 suggests that most of acetylene would be produced in the secondary reaction, probably due to the decomposition of ethane and ethylene, and that ethane and ethylene would be produced in some reactions including methyl, methylene or methyne radicals.

(IV) Polymeric film

As mentioned above, the deposition of polymeric film was observed on the wall of discharge zone in all cases. Wightman et al. characterized the films formed from various hydrocarbons under their conditions, using elemental analyses, infra-red analyses, e.s.r. measurements and X-ray and electron diffractions. The results of elemental analyses of the polymeric films in our experiments are given in Table 2 together with the composition of product gases. The H/C values of the films were equal to 1.4-1.6 in the cases of ethane, ethylene and methane, while it was 1.0 in the case of acetylene, very consistent with the results of Wightman et al.

The infra-red spectra of the films were determined in potassium bromide discs, and those obtained from ethane, ethylene and methane were very similar. The spectrum of the film in the case of methane is shown in Fig. 10. This is also consistent with those obtained by Wightman et al. and Coates, the former authors reporting that the film produced from methane is comprised mainly of highly branched saturated carbon chains and that it assumes the behavior similar to polyethylene in the thermogravimetric analysis. From the consideration that ethylene and acetylene must be the precursors in the polymerization in
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the discharge, it becomes natural to obtain the similar films in the decomposition of ethane, ethylene and methane in our system, because ethylene and acetylene were always the principal products in the decomposition of these reactants. Furthermore, the extraordinary similarity between the film produced from n-hexane⁸ and that shown in Fig. 10 is understandable from the fact that ethane, ethylene and methane were the main products in the decomposition of n-hexane.

CONCLUSION

The major gaseous products in the decomposition of C₁ and C₂ hydrocarbons in the microwave discharge under the fast flow system are hydrogen and C₁ and C₂ hydrocarbons. In the decomposition of ethane and ethylene, the dehydrogenated products are the major hydrocarbon products which seem to be produced predominantly by molecular detachment processes from the parent molecules. In the case of ethane, there is a possibility that the intermediate excited ethylene molecule is involved in the formation of acetylene as proposed in the photolysis of ethane.

The most remarkable difference from the results in the photolyses of C₁ and C₂ hydrocarbons is the formation of a small amount of products which are estimated to be produced through the contribution of ethyl radicals, which must be due to the inefficacy of the collisional deactivation of the activated ethyl radicals produced by the internal scavenging of hydrogen atoms at lower pressure in this study.

The main overall paths of the transformation of C₁ and C₂ hydrocarbons in the microwave discharge are shown by:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{C}_2\text{H}_4 \\
\text{C}_2\text{H}_6 & \rightarrow \text{C}_2\text{H}_2 \\
\text{polymer (H/C} & \approx 1.5) 
\end{align*}
\]

ACKNOWLEDGMENTS

The authors would like to thank Mr. S. Mori and Mr. T. Ibuki for their kind supports and discussions.

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Chemical Reaction of Hydrocarbons in the Microwave Discharge

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