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## ABSTRACT

The radiation chemistry of methane at  $260^{\circ}$  using 4.5 Mev electrons was studied in the absence and presence of mercury vapor. The mercury-sensitized photolysis of methane at  $260^{\circ}$  and the radiolysis of methane at  $25^{\circ}$  were studied for comparison. The condensation products were analyzed by mass spectrometry and the yields of  $H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_8$ , iso- $C_4H_{10}$ , n- $C_4H_{10}$ , iso- $C_5H_{12}$ , neo- $C_5H_{12}$ , and neo- $C_6H_{14}$  are reported in each case. The failure of mercury vapor to alter the product distribution by ion scavenging is taken as evidence for little contribution of ion-molecule reactions in methane radiolysis at  $260^{\circ}$ . The temperature coefficient of methane radiolysis was found too small to be accounted for in terms of thermal free radical reactions. A mechanism involving "hot" hydrogen atoms is proposed. A mechanism involving both ion-radicals and radicals is also consistent with the data.

THE MERCURY-SENSITIZED RADIOLYSIS AND PHOTOLYSIS OF METHANE<sup>1</sup>Gilbert J. Mains<sup>2</sup> and Amos S. NewtonLawrence Radiation Laboratory  
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## I. INTRODUCTION

The condensation of hydrocarbons using ionizing radiation has been studied from early times,<sup>3,4</sup> In 1926, S. C. Lind<sup>5</sup> reported the alpha particle radiolysis of methane to yield hydrogen and hydrocarbons as high as pentanes. Lind and Glockler<sup>6</sup> initiated a series of studies of the cathode ray radiolysis of methane in 1927 and reported the production of saturated hydrocarbon liquids. Honig and Sheppard<sup>7</sup> reported similar products using deuterons as ionizing radiation. In 1957, Lampe<sup>8</sup> studied the radiolysis of methane using 2 Mev electrons and determined the "G" yields for hydrogen, ethane, ethylene, propane, and butane.

A number of other studies concerning the mechanism of methane radiolysis have been made. Gevantman and Williams,<sup>9</sup> Meisels, Hamill, and Williams,<sup>10,11</sup> and Yang and Manno<sup>12</sup> report studies using iodine and nitric oxide as free radical scavengers. The use of inert gases to sensitize the radiolysis of methane has been described.<sup>10,11</sup>

The photolysis of methane in the vacuum ultraviolet region has been reported to yield hydrogen and acetylene as major products, with smaller yields of ethane, ethylene, and higher hydrocarbons.<sup>13</sup> The mercury-sensitized photolysis of methane was studied by Morikawa, Benedict, and Taylor<sup>14</sup> who, noting the formation of higher hydrocarbons, proposed free radical reactions for the formation of propane.

These previous radiation studies have generally been carried out at a single temperature. Some have been concerned with the use of free radical scavengers. In this paper we report the radiation chemistry of methane in the presence of mercury vapor which is expected to behave as an ion scavenger through reactions similar to reaction (1).



These asymmetric charge-transfer reactions<sup>15</sup> proceed with cross sections comparable to those for ion-molecule reactions<sup>16</sup> provided, of course, the ionization potential of RH exceeds 10.43 volts, the first ionization potential of mercury. The neutralization of  $\text{Hg}^+$  results in the formation of excited states of mercury,  $\text{Hg}^*$ , which would be expected to sensitize the free radical decomposition of methane by chemical quenching reactions,



as in the mercury-sensitized photolysis of methane. In order to directly compare the radiolysis experiments with photolysis results, the mercury-sensitized photolysis of methane was also studied. Inasmuch as Yang and Manno<sup>12</sup> reported that higher hydrocarbons arose from radical processes, the radiolysis of methane at 25° was studied so that temperature coefficients of the product formation could be ascertained. The present study is an attempt to evaluate the importance of ion-molecule reactions which have been recently emphasized by many authors.<sup>8,10,16</sup>

## II. EXPERIMENTAL

Phillips Research Grade methane was used without further purification. The principle impurity, ethane, constituted 0.13% of the total gas and a small amount of CO<sub>2</sub> was present. Instrument Grade mercury, Bethlehem Apparatus Company batch No. 290, was used without further purification.

In the radiolysis experiments 10 mm of methane was loaded into a pyrex bombardment cell which had been previously cleaned, baked, and evacuated. If mercury was to be present in the experiment, about one ml of liquid mercury was added prior to evacuation and methane addition. The pyrex bombardment cell was a cylinder, 1-3/4-inch diameter and 3-inch long. One end of the cell was a thin concave window through which the electron beam was directed; the other was fitted with a glass break-seal to facilitate analysis of the gaseous products. The methane-containing bombardment cell was inserted into an oven made by boring a 4-inch diameter aluminum cylinder to an inside diameter slightly larger than the cell. This was heated by four 100 watt cartridge heating elements and was surrounded by a 5-liter heating mantle to minimize heat leaks. A Hallikainen resistance thermometer and control maintained the temperature of the aluminum oven to  $\pm 1^\circ$  at  $260^\circ$ . The oven-target cell system was positioned such that the electron beam from the accelerator snout would pass through a 0.001-inch aluminum foil window in the aluminum oven and through the thin glass window into the target cell. The entire assembly was electrically isolated for measurement of the electron current impinging on the cell. The electron source was a 4.5 Mev microwave linear accelerator which produced 50 ma square wave electron pulses of 5 microsecond duration at selected repetition rates of 7.5 to 30 pulses/second. After the bombardment the products were analyzed using a Consolidated Electrodynamics Corporation Model 21-103A mass spectrometer. The identity of all products from the butanes through the hexanes were checked by the mass spectra of the material collected in each of the respective peaks of a gas chromatographic separation of the condensable products. The  $25^\circ$  experiments were identical with the  $260^\circ$  experiments except the heating was omitted and an air jet cooled the aluminum cylinder during bombardment.

In the photolysis experiments 0.52 microliters of mercury were added to a quartz cell, 1-inch in diameter and 6-inch long. One end of the cell was fitted with a pyrex break-seal for removal of the products. After the addition of liquid mercury the cell was evacuated, 10 mm of methane added, and the cell sealed off. The methane-filled cell was inserted into an un-silvered quartz Dewar which was fitted internally with a 250 watt nichrome coil heating element. The same resistance thermometer used in the radiolysis experiments controlled the temperature of the cell to  $\pm 1^\circ$  at  $260^\circ$ . Six 4-watt low pressure mercury lamps, located about the quartz Dewar, were used to irradiate the heated photolysis cell.

Blanks were run using both the radiolysis and photolysis procedures to show that pyrolysis in both the sealing-off operation and the heating operation was negligible.

## III. RESULTS AND DISCUSSION

1. General - The results of the radiolysis experiments are given in Tables I, II, and III. The results of the photolysis experiments are given in Table IV. The yields of products are in agreement with those reported by other investigators<sup>8,11,12,17</sup> when dose rates are considered. However, we cannot confirm the large yield of n-butane reported by Manno and Yang.<sup>12</sup> Since most vapor chromatographic columns do not resolve n-butane and neopentane it is possible that the peak reported by these authors as n-butane was actually a mixture. The product identification and yields at 25° are in good agreement with those reported by Wolfgang<sup>17</sup> from recoil tritium with the exception of n-pentane which we did not observe. Although no dosimetry was performed, a reasonable approximation of the G yield of a product may be calculated by assuming  $G_{H_2} = 5.7$  as found by Lampe.<sup>8</sup> The data of Lampe<sup>8</sup> and others<sup>7</sup> indicate that the yield of hydrogen is essentially linearly dependent upon the total dose in the region of 0-18% H<sub>2</sub>. Although the microwave accelerator current drift during bombardment caused some error in estimating the total current passing through the sample, our data also indicate a linear dependence of hydrogen yield on total dose. Except for the fourth run in Table I and the third runs in Tables II and III, the yield of hydrogen varies linearly with the number of electron pulses to which the sample was exposed. It is significant that the yields of hydrogen observed in the high temperature experiments (Tables I, II, and IV) are less than the yields calculated by a material balance. In the room temperature experiments, Table III, the reverse is observed. The production of unobserved liquid products in small amounts could account for the failure to attain a material balance at room temperature. Traces of these liquid products being bombarded on the walls of the reaction vessel could account for the excess hydrogen. However, the lack of hydrogen in the high temperature runs is more difficult to explain. It would be tempting to attribute the loss of hydrogen to diffusion into the glass walls of the reaction cells since similar hydrogen losses are observed in hydrogen discharge lamps. It has also been shown by Wolfgang<sup>17</sup> that recoil hydrogen is driven into the walls of the reaction vessel and only partially recovered by heating. This explanation of the hydrogen balance is not very satisfying but alternatives seem more untenable.

Table I

Methane* Radiolysis at 260°				
Percentage yield of products				
Total electron pulses	3.6x10 <sup>4</sup>	7.2x10 <sup>4</sup>	21.6x10 <sup>4</sup>	21.6x10 <sup>4</sup>
H <sub>2</sub>	1.14	3.94	6.41	8.38
C <sub>2</sub> H <sub>6</sub>	.56	1.26	1.95	2.42
C <sub>3</sub> H <sub>8</sub>	.25	.41	.73	.86
n-C <sub>4</sub> H <sub>10</sub>	.03	.05	.10	.12
iso-C <sub>4</sub> H <sub>10</sub>	.11	.10	.24	.29
neo-C <sub>5</sub> H <sub>12</sub>	.05	.12	.26	.25
iso-C <sub>5</sub> H <sub>12</sub>	.03	.04	.07	.09
neohexane	.03	.03	.12	.09
diisopropyl	--	.01	--	.02
heptane	--	.01	.03	.03
ethylene	.19	.15	.21	.30
isobutene	.04	.03	.02	.08
isopentene	.02	.01	.02	.04
H <sub>2</sub> (calc.)	2.55	3.90	7.13	8.78

\* Initial pressure of methane was 10 mm at 25° in all experiments.

Table II

Methane-Mercury* Radiolysis at 260°					
Total electron pulses	Percentage yield of product				
	2.7x10 <sup>3</sup>	8.1x10 <sup>3</sup>	8.1x10 <sup>3</sup>	27x10 <sup>3</sup>	36x10 <sup>3</sup>
H <sub>2</sub>	1.28	4.37	6.00	11.00	16.46
C <sub>2</sub> H <sub>6</sub>	.81	2.10	2.65	3.64	5.07
C <sub>3</sub> H <sub>8</sub>	.22	.47	.54	1.03	1.41
n-C <sub>4</sub> H <sub>10</sub>	.04	.05	.06	.19	.22
iso-C <sub>4</sub> H <sub>10</sub>	.06	.14	.12	.46	.52
neo-C <sub>5</sub> H <sub>12</sub>	.02	.12	.22	.39	.59
iso-C <sub>5</sub> H <sub>12</sub>	.03	.03	.04	.05	.18
neohexane	.01	.04	.07	.20	.28
diisopropyl	.01	--	--	.09	--
heptane	<.01	.01	.02	.06	.11
ethylene	.06	.20	.06	.24	.25
isobutene	.02	.02	.04	.01	.19
isopentene	.02	.01	--	.03	--
H <sub>2</sub> (calc.)	2.15	5.00	6.08	11.89	16.55

\* Initial pressure of methane was 10 mm at 25° in all experiments. About one cc of liquid mercury was added in all experiments.

Table III

Methane* Radiolysis at 25°					
Percentage yield of product					
Total electron pulses	3.6x10 <sup>4</sup>	10.8x10 <sup>4</sup>	10.8x10 <sup>4</sup>	21.6x10 <sup>4</sup>	43.2x10 <sup>4</sup>
H <sub>2</sub>	1.00	3.22	4.49	7.63	16.29
C <sub>2</sub> H <sub>6</sub>	.46	1.25	1.62	2.53	4.98
C <sub>3</sub> H <sub>8</sub>	.09	.23	.31	.50	.94
n-C <sub>4</sub> H <sub>10</sub>	<.01	.05	.05	.06	.17
iso-C <sub>4</sub> H <sub>10</sub>	.02	.03	.05	.09	.17
neo-C <sub>5</sub> H <sub>12</sub>	<.01	.02	.03	.04	.06
iso-C <sub>5</sub> H <sub>12</sub>	--	.02	.03	.04	.11
neohexane	.01	.03	.05	.06	.12
diisopropyl	--	.04	--	.02	.13
heptane	--	.02	.01	.03	.08
ethylene	.02	.04	.04	.06	.10
isobutene	--	<.01	.03	.01	.04
isopentene	--	--	--	.03	.07
H <sub>2</sub> (calc.)	0.86	2.70	3.40	5.04	11.05

\* Initial pressure of methane was 10 mm at 25° in all experiments.

Table IV

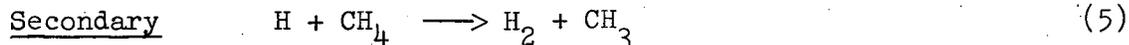
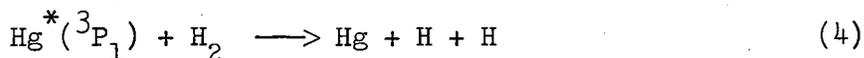
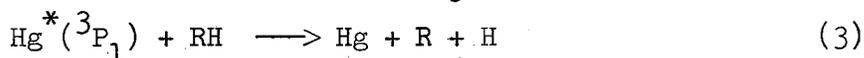
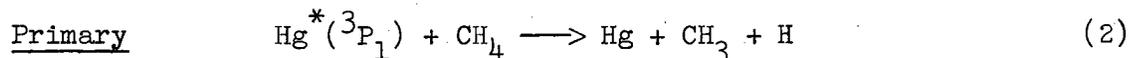
Methane-Mercury* Photolysis at 260°					
Irradiation time (lamp-minutes)	Percentage yield of product				
	3	12	12	24	90
H <sub>2</sub>	2.08	4.83	7.30	10.61	16.83
C <sub>2</sub> H <sub>6</sub>	1.17	1.48	1.79	1.53	1.59
C <sub>3</sub> H <sub>8</sub>	.18	.27	.32	.18	.26
n-C <sub>4</sub> H <sub>10</sub>	.02	.02	.02	.02	--
iso-C <sub>4</sub> H <sub>10</sub>	.04	.13	.20	.20	.52
neo-C <sub>5</sub> H <sub>12</sub>	.10	.58	.84	1.90	3.32
iso-C <sub>5</sub> H <sub>12</sub>	<.01	.02	.02	.02	.06
neohexane	.02	.09	.11	.27	.40
heptane	<.01	.02	.02	.03	.07
ethylene	.06	.07	--	--	.08
isobutene	<.01	.01	.02	--	--
isopentene	<.01	.01	.02	--	-.05
H <sub>2</sub> (calc.)	2.38	5.68	7.36	11.76	19.83

\* Initial pressure of methane was 10 mm at 25° in all experiments. 0.52 micro-liters of liquid mercury was added in each experiment.

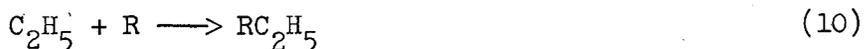
2. Comparison of Radiolysis and Photolysis at 260° - A very striking feature of the data is that the radiolysis of methane and the mercury-sensitized photolysis of methane yield identical products. Indeed, as was noted previously,<sup>18</sup> the nature and distribution of the products for these two different types of radiation were nearly identical. A more complete study indicates that the dose dependence of the products resulting from radiolysis differs significantly from the dose dependence of the products resulting from photolysis. It is evident from a consideration of Table IV that a steady state is apparently attained in the photolysis experiments and the concentrations of the lower hydrocarbon products are independent of the extent of decomposition after a few percent hydrogen is formed. The net effect of extended photolysis is to build up only higher hydrocarbon products. It is further evident from Tables I and II that a steady state is not attained in the radiolysis experiments and extended radiolysis continues to build up all condensation products. Significantly, no difference in the nature of the products of photolysis and radiolysis was observed in the range of decompositions studied.

A free radical mechanism has been proposed<sup>14</sup> for the formation of ethane and propane in the mercury-sensitized photolysis of methane. It seems reasonable to generalize this mechanism to account for higher hydrocarbon products:

Free Radical Formation in Photolysis



Product Formation in Photolysis



The relative rates of reactions (2), (3), and (4) may be estimated from the cross-sections for chemical quenching.<sup>19</sup> Because the cross-section for reaction (4) is about a factor of one hundred larger than the cross-section for reaction (2), it is clear that reaction (4) will be more important than reaction (2) after one percent hydrogen has been formed. Reaction (3) also becomes competitive with reaction (2) in these studies because, in some cases, sufficient products are built up for this to occur. Since the secondary reactions (5), (6), and (7), totally or partially involve activation energies of the order of 8 to 10 kcal/mole whereas the chemical quenching reactions involve little or no activation energy, reaction (3) initially must be faster than reaction (6).<sup>20</sup> This is especially true in the experiments reported here because of the very high relative concentration of  $^3P_1$  Hg atoms near the walls of the reaction vessel. However, because the quantum yield of methane decomposition exceeds unity<sup>14</sup> at 260° it is clear that reaction (5) must become important very rapidly. The steady state concentrations of ethane, propane, and n-butane is therefore expected to depend upon both the concentration of hydrogen atoms and upon the concentration of excited mercury atoms. The conclusion that reaction (6) is appreciable compared to reaction (3) requires that the rapid build up of neopentane must be ascribed to a low cross-section for hydrogen abstraction from neopentane as well as a low cross-section for chemical quenching by neopentane. Inasmuch as neither cross-section are known absolutely with accuracy, it is impossible to decide whether reaction (3) or reaction (6) predominates in these experiments. Steady state calculations assuming reaction (3) to predominate indicate the ratio of ethyl radicals to methyl radicals to be 0.16, a value which is consistent with the steady state concentration of ethane, propane and n-butane.

From the nature and distribution of the photolysis products we conclude that the mechanism of product build-up must proceed primarily by one carbon additions. However, the presence of n-butane and isopentane may be evidence for a two carbon branching step at the ethane, with possible branching at propane or isobutane. An over-all mechanism could be represented as follows:



3. Mercury-Sensitized Radiolysis at 260° - A comparison of Tables I and II indicates that the presence of excess mercury vapor (~100 mm at 260°) did not alter the distribution of products in the radiolysis of methane. That the mercury transferred its absorbed energy to the methane is obvious from a comparison of the first column of Table I with the last column of Table II. In both experiments the reaction vessels were subjected to approximately the same amount of radiation. In the absence of mercury only 1.14% hydrogen was obtained; in the presence of mercury 16.46% hydrogen was obtained. Inasmuch as the ionization potential of mercury is considerably less than the ionization potential of methane (and higher hydrocarbon products up to isobutane), the mechanism of energy transfer cannot involve charge transfer. Multiply-charged mercury ions,  $\text{Hg}^{+2}$ ,  $\text{Hg}^{+3}$ , etc., and excited ions,  $(\text{Hg}^+)^*$ , are expected to be removed by collision with unexcited mercury atoms. Therefore, it would appear that reactions (2), (3), and (4), and possibly analogous reactions involving higher excited states of atomic mercury, are the mechanism of energy transfer from the mercury to the methane.

Because of the low ionization potential of mercury and because the ratio of mercury to methane was over five in these experiments, it is reasonable to conclude that the mercury vapor would effectively scavenge  $\text{H}_2^+$ ,  $\text{H}^+$ ,  $\text{CH}_4^+$ ,  $\text{C}_3\text{H}_8^+$ , and  $\text{C}_4\text{H}_{10}^+$  formed in the system. Rudolph and Melton<sup>23</sup> have shown that energy alone is an insufficient criterion for charge transfer reactions in competition with ion-molecule reactions. However in the systems studied by Rudolph and Melton both charge transfer and ion-molecule reactions could occur as the result of the collision. In the systems reported here an ion must survive an average of five collisions with mercury atoms before the possibility of an ion-molecule reaction with methane presents itself. Inasmuch as the probable removal of these ions does not alter the nature or distribution of radiolysis products it would appear that these intermediates are either unimportant in the radiolysis of methane at 260°, or that they undergo reactions very similar to free radical reactions. The latter alternative has found recent support in the studies of Martin and Melton.<sup>24</sup> If the principal reaction of  $\text{CH}_4^+$  in these systems is

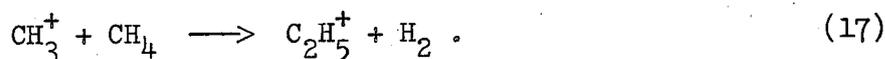


and this reaction is chemically similar to the analogous free radical reaction (7), then the small effect of mercury on the product distribution is understandable. The net effect of mercury vapor would be the suppression of reaction (14) and the acceleration of reaction (7). Since these two reactions are presumably chemically similar, the product distribution would be expected to show only small changes owing to the increased dose rate in the presence of mercury.

It must be noted that  $\text{CH}_3^+$ , an important ion in the mass spectrum of methane, would not be scavenged by mercury. However, this ion is presumably derived in whole or in part from the unimolecular dissociation of  $\text{CH}_4^+$  in the mass spectrometer ionization chamber. Since the ion collection time in a mass spectrometer is about  $10^{-6}$  seconds while the calculated lifetime of  $\text{CH}_4^+$  in the experiments reported here is about  $10^{-9}$  seconds, it seems reasonable to conclude that  $\text{CH}_3^+$  is less abundant than  $\text{CH}_4^+$ . Should  $\text{CH}_3^+$  survive neutralization for an average of five collisions it would be expected to undergo an ion-molecule reaction of the type depicted as reaction (17), *vide infra*, as suggested by Meisels, Hamill, and Williams.<sup>11</sup> Inasmuch as  $\text{C}_2\text{H}_5^+$  would also not be scavenged by mercury vapor, the possibility of further ion-molecule reactions involving  $\text{C}_2\text{H}_5^+$  cannot be ruled out. In view of the probable reduced importance of  $\text{CH}_3^+$  in these experiments and the ten-fold acceleration of the free radical reaction by the mercury vapor without altering the product distribution, it seems probable that ion-molecule reactions do not significantly contribute to the radiolysis of methane at  $260^\circ\text{C}$ . Manno and Yang<sup>12</sup> estimate that 15% of the ethane and propane and none of the higher products arise by non-free radical processes. If the free radical mechanism is characterized by a temperature coefficient of 8 kcal/mole (a typical activation energy for hydrogen abstraction) and no temperature coefficient is ascribed to the non-free radical mechanism, the latter, would be expected to constitute less than 0.1% to the reaction at  $260^\circ$ . If such a calculation and its assumptions are accepted, the conclusions of this section are in accord with the results of Manno and Yang.

4. Radiolysis at 25° - The radiolysis yields of propane and higher hydrocarbons are markedly less in the 25° runs given in Table III than in comparable runs at 260° in Table I. The yields of propane and butanes are reduced by about a factor of two or three at 25°. The yield of neopentane is reduced by a factor of about five. These temperature coefficients are too small to be attributed to a thermal radical mechanism involving hydrogen abstractions such as reactions (5), (6), and (7). It appears necessary to postulate that all or part of the radiolysis of methane must proceed via a mechanism with a temperature coefficient corresponding to an activation energy of two kcal/mole or less. As the results of this investigation and the results of Manno and Yang<sup>12</sup> indicate that a significant fraction of the radiolysis reaction proceeds via a thermal free radical path, it seems reasonable to propose that two radiolysis mechanisms, a thermal radical mechanism and a temperature-independent mechanism, are in competition. The former dominates at 260°; the latter becoming significant only at lower temperatures.

One possible temperature-independent mechanism which requires consideration is the ion-molecule mechanism, via,



There are several reasons for questioning the importance of this mechanism. No reactions analogous to reaction (17) have been found which yield hydrocarbon products as high as the pentanes yet such reactions are required to explain the low temperature coefficients of these higher products. Furthermore, both Meisels, Hamill, and Williams<sup>11</sup> and Manno and Yang<sup>12</sup> reject an ion-molecule mechanism for these higher hydrocarbon products. If  $\text{CH}_3^+$  arises by unimolecular thermal decomposition of  $\text{CH}_4^+$ , this mechanism should also exhibit a temperature coefficient. Melton and Rudolph<sup>25</sup> have shown that the relative abundance of  $\text{CH}_3^+$  in the mass spectrum of methane is reduced by a factor of two when 5.1 Mev alpha particles are used to ionize methane at room temperature. While reactions

(15), (16), and (17) cannot be ruled out as contributing to the production of ethane in the radiolysis of methane, similar ion-molecule sequences cannot account for higher hydrocarbon products.

Another temperature-independent mechanism, proposed by Gevantman and Williams<sup>9</sup> and recently supported by Davison,<sup>26</sup> involves translationally "hot" hydrogen atoms. Thus the sequence of hydrogen abstraction reactions, (5) and (6), can be replaced by their "hot" analogs, viz,



The evidence for "hot" hydrogen atoms in systems subjected to ionizing radiation is manifold. The doppler broadening of atomic hydrogen spectra in hydrogen discharge lamps is well known.<sup>27</sup> The distortion of the mass one peak in the mass spectra of hydrocarbons may be interpreted as evidence for "hot" ions and by inference for "hot" neutral species. "Hot" hydrogen atoms would be expected from the dissociative neutralization of hydrocarbon ions, viz,



especially in methane where little of the 8.5 ev liberated could be accommodated in vibrational degrees of freedom. Yang and Gant<sup>28</sup> have postulated that "hot" tritium atoms occur in the  $\beta$ -induced tritium labeling of ethylene and in the recoil labeling of ethylene by neutralization of hydrogen molecule ions. Probably some "hot" hydrogen atoms also arise from direct action of ionizing radiation on the hydrocarbon molecule. Estrup and Wolfgang<sup>29</sup> have shown that translationally hot tritium atoms are responsible for the labeling of methane in the presence of scavengers,  $\text{I}_2$ ,  $\text{Br}_2$  and  $\text{NO}$ . The series of inert gases, He, Ne, Ar, Xe were shown to moderate the hot tritium atoms in the order given.

A "hot" hydrogen atom mechanism seems reasonable based upon the similarities between the radiolysis and photolysis results already discussed. If, for example, 50% of the hydrogen atoms in the room temperature radiolysis are translationally "hot", the failure of Manno and Yang to scavenge them with  $\text{NO}$  is understood. These "hot" atoms are poorly moderated by  $\text{H}_2$ , methane, and

ethane<sup>30</sup> and would not be expected to thermalize rapidly by elastic collisions. If only 10% of these "hot" hydrogen atoms abstract hydrogen from methane, the production of ethane in the presence of NO can be explained. Hamill and Magee<sup>31</sup> have compared "hot" and thermal hydrogen atom abstraction reactions and deduced a "probability factor" of .04 and .16 for the hydrogen abstraction reaction from methane and ethane, respectively, by an .8 ev deuterium atom. The equations developed by these authors indicate that a much larger "probability factor" is to be expected for hydrogen atoms arising from reaction (18). Since reactions (5') and (6') could effectively occur at almost every collision, the rapid build up of higher hydrocarbon products at room temperature is readily understood. Recently Williams<sup>32</sup> described the radiolysis of methane by electrons of energy near or below the ionization potential of methane. The distribution of products found was similar to that reported here. While Williams did not propose a mechanism, the "hot" hydrogen atom mechanism suggested here is in accordance with his results.

It should be noted that the experiments described here do not eliminate reactions of radical molecule ions such as reaction (14) as possible free radical precursors. Similarly the neutralization of  $\text{CH}_5^+$  must result in either a methyl radical and hydrogen, a methyl radical and two hydrogen atoms, or methane and a hydrogen atom. The addition of mercury as an ion scavenger may simply transfer the role of radical precursor from the molecule ion to the excited mercury atom through reactions (1) and (2). A mechanism involving molecule ions as radical precursors can be used to explain the reduction of methane radiolysis in the presence of xenon scavenger<sup>29</sup> and the reduction in higher products by the addition of NO or iodine.<sup>9,10,11</sup> One can also use reaction (14) to explain the acceleration of methane radiolysis in the presence of argon or krypton.<sup>10,11</sup>

It is clear that further experiments will be necessary to uniquely establish the role of reaction (14) in the radiolysis of methane.

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