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# Gas-Phase Photolysis and Radiolysis of Methane. Formation of Hydrogen and Ethylene\*

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The photolysis of CH<sub>4</sub> and of CH<sub>4</sub>-CD<sub>4</sub> mixtures has been investigated at 1236 Å (10.0 eV) and at 1048-67 Å (11.6-11.8 eV). The excited methane molecule dissociates to form H<sub>2</sub>, H, CH<sub>3</sub>, CH<sub>2</sub>, CH, and probably also C. The CH and CH<sub>2</sub> radicals insert into methane to form internally excited C<sub>2</sub>H<sub>5</sub>\* and C<sub>2</sub>H<sub>6</sub>\* species, respectively. Below one atmosphere, all  $C_2H_5$  radicals decompose to form  $C_2H_4$ , while the ethane molecules are partially stabilized. The relative quantum yield of CH increases about threefold when the wavelength is reduced from 1236 Å to 1048-67 Å. On the basis of an isotopic analysis of the hydrogen produced in the photolysis of CD<sub>4</sub>-H<sub>2</sub>S mixtures, it is concluded that at 1236 Å, D atoms constitute at least 65% of the "molecular" deuterium yield.

In the radiolysis, ethylene is largely, although not exclusively formed by the insertion of CH into methane. It is demonstrated that addition of small concentrations of an unsaturated hydrocarbon to methane profoundly affects the ion-molecule reaction mechanism and, therefore, does not lead to a dependable value of the "initial" ethylene yield as suggested in earlier studies. Upon application of an electrical field, the production of CH and CH2 is augmented in the saturation current region. The importance of the latter two radicals in the direct and rare-gas-sensitized radiolysis is examined briefly. The formation of hydrogen in the radiolysis will be discussed on the basis of new information derived from CD<sub>4</sub>-H<sub>2</sub>S experiments. The production of hydrogen in the radiolysis of Xe-CH-CD-NO mixtures has also been re-examined in view of a recent study in which it was asserted that all of the hydrogen in such a mixture is due to the unimolecular decomposition process

$$CH_4^* \rightarrow CH_2 + H_2$$

Our data disagree with this view and actually demonstrate that CH and CH<sub>2</sub> play a minor role in the xenon-sensitized radiolysis of methane.

#### INTRODUCTION

**O**NE of the least understood aspects of the photolysis and radiolysis of methane concerns the modes of formation of ethylene. In the first extensive study of the photolysis of methane at 1236 Å, which was carried out by Mahan and Mandel,<sup>1</sup> ethylene was not reported as a product. In two succeeding investigations<sup>2,3</sup> ethylene was observed in the photolysis of methane although in rather small yields. In the latter two studies it was tentatively suggested that ethylene was produced by the decomposition of the internally excited ethane molecule formed by the insertion of CH<sub>2</sub> into methane. That is:

$$C_2H_6^* \rightarrow C_2H_4 + H_2. \tag{2}$$

Such a mechanism was also proposed by Manton and Tickner<sup>4</sup> in order to account for the formation of ethylene in the decomposition of methane by lowenergy electrons. Such a mechanism does not, however, account for the fact that a 15-fold increase in pressure does not affect the yield of ethylene although the yield

 $CH_2+CH_4\rightarrow C_2H_6*$ 

of ethane formed in Reaction (1) followed by (3)

$$C_2H_6^* + M \rightarrow C_2H_6 + M \tag{3}$$

increases considerably.3 This observation was tentatively interpreted<sup>3</sup> by assuming that two distinct states of CH<sub>2</sub> are formed in the primary process. However, in a more recent study,<sup>5</sup> it was pointed out that CH, formed by decomposition of internally excited CH<sub>2</sub> and/or CH<sub>3</sub> radicals produced in a primary process at 1236 Å, could react to form ethylene:

$$CH+CH_4 \rightarrow C_2H_5^* \rightarrow C_2H_4+H.$$
(4)

In recent flash photolysis investigations<sup>6</sup> of methane, CH has been observed and evidence for Reaction (4) has been obtained. In the latter study it was, however, not possible to distinguish between the formation of CH through the dissociation of primary fragments or through the secondary photolysis of CH<sub>3</sub> and CH<sub>2</sub> radicals. In order to investigate further the formation of the CH radical and of the related ethylene, the methane photolysis has been investigated at lower wavelengths. An argon resonance lamp which emits at 1067 and 1048 Å (11.6-11.8 eV) was used for this purpose.

An investigation of the photolysis of methane at shorter wavelengths may also prove useful in the

(1)

<sup>\*</sup> This research was supported by the U.S. Atomic Energy Commission.

<sup>&</sup>lt;sup>1</sup> B. H. Mahan and R. Mandel, J. Chem. Phys. 37, 207 (1962).

<sup>&</sup>lt;sup>2</sup> E. M. Magee, J. Chem. Phys. **39**, 855 (1963). <sup>3</sup> P. Ausloos, R. Gorden, Jr., and S. G. Lias, J. Chem. Phys. **40**, 1854 (1964). <sup>4</sup> I. F. Manton and A. W. Tickner, Can. I. Chem. **38**, 858

J. E. Manton and A. W. Tickner, Can. J. Chem. 38, 858 (1960).

<sup>&</sup>lt;sup>5</sup> P. Ausloos, R. E. Rebbert, and S. G. Lias, J. Chem. Phys.

 <sup>42, 540 (1965).
 &</sup>lt;sup>6</sup> (a) W. Braun, J. R. McNesby, and A. M. Bass (unpublished data).
 (b) W. Braun, K. H. Welge, and J. R. McNesby, J. Chem. Phys. 45, 2650 (1966).

interpretation of the more complex reaction mechanism occurring in the radiolysis where neutral-excited methane molecules may be expected to be highly excited. The mode of formation of ethylene in the radiolysis is by no means clearly established as yet. It has on several occasions been suggested<sup>7,8</sup> that ethylene is formed by neutralization of an unreactive ion such as the  $C_2H_5^+$  ion;

$$C_2H_5^+ + e \rightarrow C_2H_4 + H. \tag{5}$$

This suggestion is, however, inconsistent with the fact that ethylene remains an important product even when the  $C_2H_5^+$  ions are effectively removed from the system by addition of a higher hydrocarbon to the methane.<sup>9</sup> It was, therefore, tentatively suggested<sup>3</sup> that ethylene might in part be formed by the same mechanism as the one responsible for the formation of ethylene in the photolysis. In the present paper, additional information concerning the modes of formation of ethylene is obtained by applying an electrical field during the radiolysis of methane. We also intend to examine the significance of values for the "initial" yields of ethylene in radiolysis which have been reported in the literature.<sup>10,11</sup>

The formation of hydrogen in the photolysis and radiolysis of methane is discussed. In particular, an attempt is described to arrive at a value of the hydrogen atom yield in these systems by using  $H_2S$  as a hydrogen atom interceptor.

## **EXPERIMENTAL**

#### Irradiation

The photochemical light sources were air-cooled electrodeless discharge lamps containing krypton or argon. The krypton resonance lamp was essentially an L-shaped Pyrex tube to which a CaF2 window, which transmits only the 1236-Å krypton line,12 was attached with an epoxy cement. One end of the lamp was cooled in liquid nitrogen during operation in order to remove water vapor.13 The argon resonance lamp was provided with a thin LiF window which was sealed onto the Pyrex with an epoxy cement. A titanium getter was used to remove trace impurities in the argon.14 There is a gradual decrease in the transmission of the LiF window during use at 1048 and 1067 Å, because of the formation of F centers. The window regains transparency when it is bleached with a medium pressure mercury arc.

The reaction vessels employed in the photolysis experiments, which have been described elsewhere,<sup>15</sup> were composed of two compartments, the first containing methane and the second, nitric oxide. Saturation currents measured between two parallel-plate electrodes made it possible to determine extinction coefficients of methane and to monitor the intensity of the resonance lamps.

The NBS 2000 Ci source was used for the radiolysis experiments which were carried out in the presence of an applied electrical field. A stainless steel vessel, described in an earlier paper<sup>16</sup> was used in these studies. Dosimetry was based on the current in the saturation region, which was 2  $\mu$ A at a methane pressure of 100 torr. The experiments listed in Table IV were carried out in a cylindrical Pyrex vessel of approximately the same dimensions (volume: 500 cc, height: 5 cm) as the stainless steel reaction cell. Dosimetry in the Pyrex vessels was performed by intercomparing experiments carried out at identical pressures in the different cells.

#### Analysis

The analytical procedure was essentially the same as described in previous studies from this laboratory.<sup>3,9</sup> After irradiation, an aliquot of the sample was expanded into a 25-cc loop attached to a gas chromatograph provided with a flame ionization detector. A 10-ft alumina column was used. Subsequently, hydrogen was distilled off after transferring the methane to a solid nitrogen trap immersed in a Dewar containing liquid nitrogen. 98% of the hydrogen could be removed in 15 min by an automatic Toepler pump. In some experiments, liquid hydrogen was used to retain the methane. The distilled fraction was further analyzed on a mass spectrometer. The irradiated mixture was passed through a spiral trap immersed in liquid nitrogen which retained the ethane and ethylene products, which were then introduced into a gas chromatograph provided with a silica gel column at the exit of which the different hydrocarbon products were trapped out separately, and introduced into the mass spectrometer after removal of the helium.

#### Materials

Methane- $d_4$  was obtained from Merck, Sharp and Dohme, Ltd. of Canada. Mass spectrometric analysis of the methane- $d_4$  indicated that it contained 5.0% CD<sub>3</sub>H and a variety of chemical impurities. Researchgrade methane was obtained from the Phillips Petro-

<sup>7</sup> G. G. Meisels, W. H. Hamill, and R. R. Williams, Jr., J. Phys. Chem. 61, 1456 (1957)

<sup>&</sup>lt;sup>8</sup>L. W. Sieck and R. H. Johnsen, J. Phys. Chem. 67, 2281 (1963). P. Ausloos, S. G. Lias, and R. Gorden, Jr., J. Chem. Phys.

<sup>&</sup>lt;sup>10</sup> R. W. Hummel, Discussions Faraday Soc. 36, 75 (1963).
<sup>10</sup> R. W. Hummel, Discussions Faraday Soc. 36, 75 (1963).
<sup>11</sup> W. P. Hauser, J. Phys. Chem. 68, 1576 (1964).
<sup>12</sup> A. H. Laufer, J. A. Pirog, and J. McNesby, J. Opt. Soc. Am.

<sup>55, 64 (1965).</sup> 

<sup>&</sup>lt;sup>13</sup> H. Okabe, J. Opt. Soc. Am. 54, 478 (1964).

<sup>&</sup>lt;sup>14</sup> The authors are greatly indebted to Ronald Royce for his assistance in the course of the preparation of the argon resonance lamps used in this study.

<sup>&</sup>lt;sup>15</sup> R. Gorden, Jr., R. D. Doepker, and P. Ausloos, J. Chem. Phys. **44**, 3733 (1966). <sup>16</sup> P. Ausloos and R. Gorden, Jr., J. Chem. Phys. **41**, 1278

<sup>(1964).</sup> 

4825

							Percent distributions									
	Pressure	Re	lative yields	3	Н	ydroge	ns			Ethylenes						
λ	torr	Hydrogen	Ethylene	Ethane	$D_2$	HD	$H_2$	$C_2D_4$	$C_2D_3H$	$C_2D_3H_2$	$C_2DH_3$	$C_2H_4$				
1236	3.4	100	2.0	n.d.	38.5	10.9	50.5									
	10	100	2.2	0.45	40.0	8.8	51.2									
	100	100	2.5	3.5	44.0	6.0	50.0	19.4	21.6	0.0	24.3	34.8				
1048-67	3.4	100	10.2	0.037	34.1	10.2	55.7									
	10.0	100	11.5	0.15	33.4	9.8	56.8	16.1	18.2	5.6	25.3	34.8				
	30.0	100	13.0	0.75	40.2	4.3	55.8	17.9	20.0	6.2	23.4	32.5				
	100	100	12.5	2.05	42.8	3.5	53.7									

TABLE I. Photolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO (1:1:0.04) mixtures.

leum Company. Both methanes were thoroughly purified by a repeated slow distillation through a sequence of traps maintained at  $-195^{\circ}$ C. Nitrogen, hydrogen, and oxygen were removed by continuous pumping during the distillation process. After the distillation process no impurities could be detected by gas chromatographic and mass spectrometric analyses indicating that the impurity level was below 0.002%.

The ethylene, propylene, and acetylene used in the study were purified by gas chromatography.

## RESULTS

#### Photolysis

The two-compartment cell<sup>15</sup> was used to derive values of the extinction coefficients of CH4 and CD4. By plotting the logarithm of the saturation currents measured in the second cell which contained NO, vs the pressure of methane contained in the first compartment, good straight lines were obtained. The slopes yield values of 855 and 866 atm<sup>-1</sup> cm<sup>-1</sup> for the extinction coefficients of CH<sub>4</sub> and CD<sub>4</sub>, respectively, at 1048-67 Å. Similar measurements, made at 1236 Å, gave values of 492 and 587 atm<sup>-1</sup> cm<sup>-1</sup> for the extinction coefficients of CH<sub>4</sub> and CD<sub>4</sub>. The latter values compare well with the extinction coefficient values of 420 and 604 atm<sup>-1</sup> cm<sup>-1</sup> reported by Laufer and McNesby.<sup>17</sup> Attempts were made to determine the quantum yield of hydrogen in the photolysis of CH<sub>4</sub>-NO (1:0.05) mixtures at 1236 Å by monitoring the saturation current due to ionization of the NO in this mixture. Using a value of 55 atm<sup>-1</sup> cm<sup>-1</sup> for the extinction coefficient of NO and a value of 0.833 for its ionization efficiency<sup>18</sup> at 1236 Å, a value of 1.4 was obtained for the quantum yield of H<sub>2</sub> at a CH<sub>4</sub> pressure of 10 torr.

Yields and isotopic compositions of the hydrogen and ethylene produced in the photolysis of CH4-CD4-NO (1:1:0.05) mixtures are given in Table I. In order to obtain a reliable isotopic analysis of ethylenes, about 0.1% of the methane had to be decomposed. The actual total product yields given in Table II were, however, obtained in experiments in which only about 0.02% of the methane was decomposed. It is of interest that at 1048–67 Å an increase in conversion from 0.02 to 0.1%resulted in an increase of the product ratio, ethane/ethylene of about 10%. The yield of acetylene relative to that of hydrogen did not vary over this conversion range. The isotopic composition of the ethane has not been given in Table I, but in all cases it consists almost exclusively of  $C_2D_6$ ,  $C_2D_4H_2$ ,  $C_2D_2H_4$ , and  $C_2H_6$ . Because the mass spectral cracking pattern of C<sub>2</sub>D<sub>4</sub>H<sub>2</sub> is not known with sufficient accuracy, the relative yields of C<sub>2</sub>D<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>DH<sub>5</sub>, and C<sub>2</sub>H<sub>6</sub> are not as reliable as those of C<sub>2</sub>D<sub>6</sub>, C<sub>2</sub>D<sub>5</sub>H, C<sub>2</sub>D<sub>4</sub>H<sub>2</sub>, and C<sub>2</sub>D<sub>3</sub>H<sub>3</sub>. As an example, the following calculated isotopic distribution of the ethane in the argon photolysis of a  $CD_4$ - $CH_4$ -NO (1:1:0.04) mixture at 300 torr is given:  $C_2D_6-20.4\%, C_2D_4H_2-22.1\%, C_2D_2H_4-22.6\%, C_2H_6-$ 34.9%. In order to arrive at these values a statistical correction had to be made for the presence of CD<sub>3</sub>H in the starting material. After correction, C<sub>2</sub>D<sub>5</sub>H, C<sub>2</sub>D<sub>3</sub>H<sub>3</sub>, and  $C_2DH_5$  were all less than 1% of the total ethane fraction. In the krypton photolysis experiments, each of the isotopically labeled ethylenes has been determined with an accuracy of better than 1%. The isotopic distribution obtained at 1236 Å and given in Table I is actually the average of four identical experiments. After correction for the presence of CD<sub>3</sub>H in the methane- $d_4$ , ethylene- $d_2$  was found to be entirely absent. The ethylenes produced in the argon photolysis experiments could not be calculated with such a high accuracy because of the relatively small amount of product formed, due to the short lifetime of such a lamp. These experiments were carried out in a 10-times smaller reaction vessel than the 1236-Å experiments and the actual amount of ethylene formed even at a conversion of 0.1% was, therefore, quite small. It can be estimated that the yield of any one of the isotopically labeled ethylenes produced at 1048–67 Å (Table I) is known within 10% of itself.

<sup>&</sup>lt;sup>17</sup> A. H. Laufer and J. R. McNesby, Can. J. Chem. 43, 3487 (1965)

<sup>&</sup>lt;sup>18</sup> K. Watanabe, Advan. Geophys. 5, 153 (1962).

			TABLE []	. Photolysis	of methane	pressure: 10	0 torr).				
λÅ	Additive	Hydrogen	Ethane	Ethylene	Acetylene	Propane	Propylene	Allene	n-Butane	Isobutane	Isobutene
1236		100	73.	1.6	0.23	7.6	0.034	0.010	0.60	0.10	
1236	NO (4%)	100	3.0	2.7	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	
1048-67	:	100	21.	15.	1.8	8.1	0.31	0.23	1.4	0.22	0.30
1048-67	Isobutene (1%)	100	34.	27.	7.0	1.7	2.1	26.	<0.05	29.	
1048-67	NO (4%)	100	2.0	13.	1.9	<0.05	n.d.ª	n.d.	n.d.	n.d.	n.d.
<sup>a</sup> n.dnot determ	ined.										

## Radiolysis

In Table III are given the total yields of the products produced in the radiolysis of a CH4-CD4-NO mixture in the absence and presence of an electrical field. The applied-field experiment was carried out at a field strength slightly lower than that needed to cause electron multiplication to occur. The isotopic composition of the ethane in the latter experiment was almost identical to that obtained in the absence of an applied field. It consisted, within experimental error exclusively of C<sub>2</sub>D<sub>6</sub>, C<sub>2</sub>D<sub>4</sub>H<sub>2</sub>, C<sub>2</sub>D<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. Similar isotopic compositions were obtained for the ethane produced in the rare-gas-sensitized radiolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO (1:1:0.04) mixtures (Table IV).

The accuracy with which the isotopic composition of the ethylene fraction produced in the radiolysis experiments could be calculated is approximately 10%. This rather large uncertainty is mainly due to the contribution of small amounts of oxygen to the mass spectrum of the ethylene fraction. When 3% of i-C<sub>4</sub>D<sub>10</sub> is added to a CH<sub>4</sub>-CD<sub>4</sub>-NO (1:1:0.02) mixture the ion pair yield of ethylene is reduced from 0.16 to 0.11. The isotopic composition of the ethylene in such a mixture is as follows: C<sub>2</sub>H<sub>4</sub>-27.0%, C<sub>2</sub>DH<sub>3</sub>-19.1%, C<sub>2</sub>D<sub>2</sub>H<sub>2</sub>-10.3%, C<sub>2</sub>D<sub>3</sub>H-18.7% and C<sub>2</sub>D<sub>4</sub>-24.9%.

#### DISCUSSION

## Formation of Ethylene

## Photolysis at 1236 Å

The fact that the ethylene fraction formed in the photolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO mixtures at 1236 Å does not contain any C<sub>2</sub>D<sub>2</sub>H<sub>2</sub> (Table I) is one of the most striking results obtained in the course of the present study. This result necessarily excludes Reaction (1) followed by Reaction (2) as a possible mode of formation of ethylene, since if such a mechanism were to occur, one would, on statistical grounds, expect  $C_2H_2D_2$ to be a major constituent of the ethylene fraction. The observed isotopic composition of the ethylene fraction can apparently best be accounted for by the insertion of CH and CD radicals into methane to form internally excited ethyl radicals which decompose to form ethylenes- $d_4$ ,  $d_3$ ,  $d_1$ , and  $d_0$ :

$$CH+CH_4\rightarrow CH_3CH_2^*\rightarrow CH_2CH_2+H,$$
 (6)

$$CH+CD_4\rightarrow CD_3CDH^*\rightarrow CD_2CDH+D,$$
 (7)

(8) $CD+CH_4\rightarrow CH_3CDH^*\rightarrow CH_2CDH+H$ ,

$$CD+CD_4\rightarrow CD_3CD_2^*\rightarrow CD_2CD_2+D.$$
 (9)

The ethylene distribution obtained at 1236 Å can be matched with the expected distribution from Reactions (6) through (9) if one assumes that CH is formed in somewhat larger yield than CD and that there is a

			Eff $M/N$ (	ect of electric molecules pe	al field r ion pair)	)			
	Hydrogen	Ethane	Ethylene	Acetylene	$C_2D_4$	$C_2D_3H$	$C_2D_2H_2$	$C_2 DH_8$	$C_2H_4$
3000 V	3.60	0.054	0.392	0.016	0.070	0.075	0.035	0.092	0.120
0 V	1.30	0.016	0.162	0.011	0.028	0.027	0.024	0.034	0.049
$\Delta M/N =$	2.30	0.038	0.230	0.005	0.042	0.048	0.011	0.058	0.071

TABLE III. Radiolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO (1:1:0.05) mixtures (pressure: 100 torr; saturation current: 2×10<sup>-6</sup> A).

slight isotopic effect favoring insertion into  $CH_4$  over insertion into  $CD_4$ . The first assumption is in qualitative agreement with the fact that  $H_2$  is formed in larger yield than  $D_2$  (Table I).

At 1236 Å, the over-all process leading to the formation of CH can be written as follows:

$$CH_4 \rightarrow CH + H_2 + H \qquad \Delta H = 9.1 \text{ eV}.$$
 (10)

It should be noted that even if the CH radical does not carry over any excess energy from the primary process, the ethyl radicals formed in Processes (6) through (9) may be expected to be very short-lived because they will have about 4-eV energy in excess of that required to break a C-H bond. It is thus not surprising that in the photolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO mixtures, the yield of ethylene was found<sup>3</sup> to be independent of pressure from 15 torr up to approximately 1000 torr, while the ethane which is formed in Reaction (1) followed by (3) shows a gradual increase with increase in pressure. One may conclude that at 1236 Å, at pressures below one atmosphere, the yield of ethylene formed in the scavenged photolysis of methane is equal or larger than that of CH.

To determine the "initial" yield of ethylene in pure methane is not an easy matter. At room temperature H atoms react very slowly with methane  $(k\sim 10^6 \text{ cc/mole\cdotsec})^{19}$  so that in a static system the product ethylene may be largely removed from the system by reaction with H atoms:

$$H + C_2 H_4 \rightleftharpoons C_2 H_5^* \tag{11}$$

$$C_2H_5^* + M \rightarrow C_2H_5 + M.$$
(12)

An approximate value for the relative initial yield of

TABLE IV. Rare-gas-sensitized radiolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO (1:1:0.04) mixtures (pressure of methane: 5 torr; pressure of rare gas: 100 torr).

(4).

			%			M/N (molecules/ion pair)		
Inert gas	$C_2H_4$	C <sub>2</sub> H <sub>3</sub> D	$C_2D_2H_2$	C2D3H	$C_2D_4$	Ethylene	Ethane <sup>a</sup>	
Xe	29.3	19.9	9.8	18.1	22.9	0.037	0.002	
Kr	28.7	19.8	13.3	18.4	19.8	0.120	0.020	
Ar	27.4	18.1	18.7	16.8	19.0	0.236	0.011	
None	30.2	21.2	14.8	16.5	17.3	0.162	0.016	

\* Ethane consists of  $C_2D_6$ ,  $C_2D_4H_2$ ,  $C_2D_2H_4$ , and  $C_2H_6$ .

<sup>19</sup> E. R. W. Steacie, Atomic and Free Radical Reactions (Reinhold Publ. Corp., New York, 1954), 2nd ed., Vol. II, p. 511.

(13)

ethylene can, however, be calculated from a product

distribution such as that given in the first row of

Table II. It has been shown before<sup>3</sup> that propane is

almost entirely produced by the recombination reaction:

 $C_2H_5+CH_3\rightarrow C_3H_8$ ,

where  $C_2H_5$  is produced by H atom addition to ethylene. Furthermore, if one ascribes the formation of n-C<sub>4</sub>H<sub>10</sub>

to a combination of two ethyl radicals and accepts that

only a minor fraction of the C<sub>2</sub>H<sub>5</sub> radicals are removed

by combination with an H atom, it can be estimated

that the initial ethylene yield is roughly 10% of the

hydrogen yield. This estimate is considerably higher

than the yield of ethylene observed in the photolysis

of a CH<sub>4</sub>-NO mixture at 1236 Å. (Table II) No

obvious explanation can be given for this discrepancy.

Although partial scavenging of CH by NO could ac-

count for the low ethylene yield in this experiment, it

should be noted that the rate of reaction of CH with

CH<sub>4</sub> is quite high. According to Braun et al.,<sup>6</sup> the

probability of a reactive collision for Reaction (4) is

approximately 10<sup>-2</sup>. It is of interest to note that

 $C_2D_2H_2$  was reported to be formed in the unscavenged

photolysis of a  $CH_4$ - $CD_4$  mixture at 1236 Å, but is not

formed in the presence of a scavenger (Table I). This

can in part be accounted for by the fact that in the

absence of NO, ethylene molecules can be regenerated

by decomposition of the internally excited ethyl radical formed in Reaction (11). We can, however, not exclude the possibility that in the absence of NO there may be another mode of formation of ethylene besides Reaction

# Photolysis at 1048-67 Å

The product distribution obtained at this wavelength (see Table II) differs rather drastically from that measured at 1236 Å. The major difference is the much higher relative yield of  $C_2H_4$  at 1048–67 Å than at 1236 Å. From the products formed in pure CH<sub>4</sub>, it can be estimated that the "initial" yield of C<sub>2</sub>H<sub>4</sub> is approximately 26% of that of the hydrogen. This value was confirmed by photolyzing a CH<sub>4</sub>-*i*-C<sub>4</sub>D<sub>8</sub> mixture, (see Table II). The ethylene and hydrogen formed in this experiment contained, respectively, 92% C<sub>2</sub>H<sub>4</sub> and 90% H<sub>2</sub>. It may thus be concluded that any photolysis of the C<sub>4</sub>D<sub>8</sub> which might have occurred in the mixture did not greatly contribute to the formation of ethylene. The yield of C<sub>2</sub>H<sub>4</sub> in this experiment is approximately one fourth of the hydrogen in good agreement with that calculated from the product distribution observed in pure methane. It can also be noted that in the NO containing mixtures, (Table I) the relative yield of ethylene at 1048–67 Å is considerably higher than at 1236 Å, although lower than that estimated from the product distribution in the photolysis of pure  $CH_4$  (Table II). The isotopic composition of the ethylene formed in the photolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO mixtures at 1048-67 Å (Table I) indicates that Reactions (6) and (9) may largely account for the formation of this product. The formation of up to 6.2% CH<sub>2</sub>CD<sub>2</sub> can, however, not be neglected and may be indicative of an additional mode of formation of ethylene, such as the originally proposed insertion Reaction (1) followed by decomposition Reaction (2). At 1048–67 Å the methylene radical can be formed with as much as 8 eV. Insertion into methane could thus lead to the formation of an electronically excited ethane which would mainly decompose by the loss of a hydrogen molecule.20

Of interest is the observation that at 1048-67 Å an increase in pressure from 3.4 to 100 torr has little effect on the yield of ethylene relative to that of hydrogen.

The ethane formed in the photolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO mixtures, is, according to its isotopic composition (see Results), entirely formed by insertion of methylene into methane. The sharp increase of the yield of this product (see Table I) relative to that of hydrogen or ethylene demonstrates once more that collisional stabilization of the insertion product does occur, although with somewhat lower efficiency than in the photolysis at 1236 Å.

The modes of formation of various minor products such as acetylene, propylene and allene (Table II) remains to be explained. At 1048-67 Å production of C atom could lead to the formation of acetylene by a reaction mechanism such as the one proposed by

Dubrin et al.<sup>21</sup> If one acetylene molecule is produced for each C atom, we must conclude, however, that at 1048-67 Å, C atoms account for not more than 2% of the decomposition fragments.

$$C + CH_4 \rightarrow C_2H_4^* \rightarrow C_2H_2 + H_2.$$
(14)

A much lower value prevails at 1236 Å. Because acetylene reacts more slowly with H atoms than ethylene<sup>22</sup> it is not surprising to note that the relative yield of the acetylene is not augmented upon addition of NO as a free-radical scavenger. Stabilization of the C<sub>2</sub>H<sub>4</sub>\* which would be formed as an intermediate in Process (14), would raise our evaluation of the C atom yield. However, according to the results given in Table I,  $C_2D_4$  is smaller than  $C_2D_3H$ . Therefore, insertion of a C atom into CD4 cannot contribute heavily to the ethylene fraction.

Propylene is probably formed by combination of methyl radicals with vinyl radicals which could originate from decomposition of excited species such as  $C_2H_4^*$  formed in Process (14). Isobutane can be formed as a result of the addition of an H atom to propylene. This would yield primarily a sec-C<sub>3</sub>H<sub>7</sub> radical which by combination with a methyl radical would form the observed isobutane.

It is obvious that the present results do not enable us to decide if the CH radical is formed by decomposition of an internally excited CH3 or CH2 radical formed, respectively, in the primary fragmentation processes

 $CH_4* \rightarrow CH_3 + H$ 

$$CH_4^* \rightarrow CH_2 + H_2.$$
 (16)

(15)

Actually, it has thus far not been clearly established whether Process (15) occurs in the gas phase photolysis at 1236 Å. Methyl radicals are obviously formed, but isotopic labeling experiments do not distinguish between those formed by Process (15) and those formed in Reaction (1) followed by unimolecular decomposition

$$C_2H_6^* \longrightarrow 2CH_3. \tag{17}$$

In the solid-phase photolysis of methane, the internally excited product C<sub>2</sub>H<sub>6</sub>\* molecules are, however, collisionally stabilized. The formation of CH<sub>3</sub>CD<sub>3</sub> in the photolysis of solid CH<sub>4</sub>-CD<sub>4</sub>-Ar mixtures, therefore, constitutes evidence for the formation of CH<sub>3</sub> radicals by the primary Process (15). It may be anticipated that such a process will also occur in the gas phase. The obvious way to evaluate the relative quantum yield of such a process would consist in determining the yield of H atoms relative to that of "molecular" hydrogen in the photolysis of methane. This will be considered in detail later in the Discussion.

In view of the presence of CH radicals in the low-<sup>21</sup> J. Dubrin, C. Mackay, and R. Wolfgang, J. Am. Chem. Soc.
 86, 959 (1964).
 <sup>22</sup> G. G. Volpi and F. Zocchi, J. Chem. Phys. 44, 4010 (1966).

and

<sup>&</sup>lt;sup>20</sup> J. R. McNesby, "Vacuum-Ultraviolet Photolysis of Parafin Hydrocarbons," in *Actions Chimiques et Biologiques des Radia-tions*, M. Haissinsky, Ed. (Masson Cie, Paris, 1966), Vol. 9.

intensity photolysis, it may be concluded that a considerable fraction of the CH radicals observed in the flash photolysis of methane<sup>6</sup> may be formed as a result of the primary dissociative process, rather than by secondary photolysis of  $CH_2$  or  $CH_3$ . The present data do, however, not throw any additional light on the reaction mechanism occurring in the flash photolysis. Possible interaction between CH, CH<sub>2</sub>, and CH<sub>3</sub> radicals in the flash photolysis render any comparison with the low-intensity photolysis system particularly difficult.

#### Radiolysis

The formation of neutral-excited methane molecules in the gas-phase radiolysis is well established. It has been, for instance, demonstrated that CH<sub>2</sub> radicals originating from the decomposition of methane are definitely produced in the radiolysis of methane. Because the ionization efficiency of methane approaches unity only at about 15 eV,23 it is clear that dissociation of superexcited molecules, that is molecules possessing energy in excess to the ionization energy  $(12.7 \text{ eV})^{24}$ has to be considered.<sup>25</sup> The formation of very highly excited methane molecules in the radiolysis is supported by the results of Sieck and Johnsen<sup>9</sup> who observed the system of CH corresponding to 3144 Å (3.94 eV) which is about 1 eV above the maximum amount of energy which the CH can carry over from Process (10) at the argon resonance lines. Therefore, although the vacuum ultraviolet photochemical observations discussed above provide useful qualitative information about the processes which the neutral-excited molecules produced in the radiolysis will undergo, the relative importance of different processes may differ considerably. We in particular expect that CH radicals and highly excited  $CH_2$  radicals will be of importance. Because in the radiolysis, excitation occurs by electron impact, we first investigated the effect of an applied electrical field in the gas-phase radiolysis. As noted in earlier studies,<sup>26</sup> application of an electrical field in the saturation current region will cause increased excitation by collision between the accelerated electrons and the hydrocarbon molecules. In Table III are given the increments which can be ascribed to such excitation processes in the ion pair yield of some of the major products. Because the field strength was chosen at the point where electron multiplication starts to occur it can be assumed that the mean energy transferred to the methane by electron impact lies somewhat below the ionization energy of methane, that is 12.7 eV. Of special importance is the observation that the isotopic composition of the ethylene which can be ascribed to additional excitation is comparable to that observed in the photolysis at 11.6-11.8 eV. The relatively low yield of C<sub>2</sub>D<sub>2</sub>H<sub>2</sub> definitely indicates that a large fraction of the ethylene must be formed by insertion of the methyne radical into methane. Also of interest is the fact that the vield of ethane is entirely formed by insertion of methylene into methane.

Although these results indicate that the excited methane molecule formed by electron impact undergoes fragmentation to yield the same radicals as those formed by photon absorption, the applied-field experiment does not provide us with information about the behavior of neutral-excited molecules in the absence of an applied field. The yield as well as the isotopic composition of the ethylene formed in the radiolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO mixtures may give some clues about the fragmentation of the methane molecules formed in the direct radiolysis.

It should first be realized that a fraction of the ethylene observed in the radiolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO mixtures may be produced by an ionic reaction mechanism. Reaction (18) followed by (19)

$$CH_2^+ + CH_4 \rightarrow C_2H_4^+ + H_2 \tag{18}$$

$$C_2H_4^+ + NO \rightarrow C_2H_4 + NO^+$$
(19)

or loss of a proton by a  $C_2H_5^+$  ion may be suggested as plausible modes of formation of ethylene. In order to remove the possible contribution to the ethylene fraction of these ions, isobutane was added to a CH<sub>4</sub>-CD<sub>4</sub>-NO mixture (see Results). It is known<sup>9,27</sup> that isobutane reacts efficiently with C2H4+, C2H5+, and  $C_3H_7^+$ . Removal of these ions may, therefore, account for the drop in M(ethylene)/N from 0.16 to 0.11 upon addition of isobutane (see Results). Of interest is the fact that the isotopic composition of the residual ethylene compares well with that derived from the increments ascribed to excitation by electron impact in the applied-electrical-field experiments (Table III). The larger contribution of  $C_2D_2H_2$  in the normal radiolysis may tentatively be ascribed to a greater importance of reactions such as (1) and (2).

# Rare-Gas-Sensitized Radiolysis

There are rather wide variations in the ion pair yield as well as in the isotopic composition of the ethylene fractions formed in the rare-gas-sensitized radiolysis of CH<sub>4</sub>-CD<sub>4</sub>-NO (1:1:0.04) mixtures. The gradual increase of the M(ethylene)/N with the recombination energy of rare-gas ion is paired with an increase of the percentage of  $C_2D_2H_2$  in the ethylene fraction. The most logical explanation would be that ion molecule reactions contribute more heavily to the formation of ethylene when more energy is transferred to the methane ion.

 <sup>&</sup>lt;sup>23</sup> R. L. Platzman, Vortex 23, 1 (1962).
 <sup>24</sup> V. H. Dibeler, M. Krauss, R. M. Reese, and F. N. Harlee, J. Chem. Phys. 42, 3791 (1965).

<sup>&</sup>lt;sup>25</sup> R. L. Platzman, Radiation Res. 17, 419 (1962).
<sup>26</sup> P. Ausloos and S. G. Lias, "Gas Phase Radiolysis of Hydro-carbons," in *Actions Chimiques et Biologiques des Radiations*, M. Haissinsky, Ed. (Masson Cie, Paris, 1967), Vol. 11.

<sup>&</sup>lt;sup>27</sup> M. S. B. Munson, J. L. Franklin, and F. H. Field, J. Phys. Chem. 68, 3097 (1964)

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		TAB	LE V. Radioly	sis of methane i	n the presence	of unsaturate	d hydrocarbons	(pressure: 1(	0 torr). <sup>a</sup>			
	Additive	C2D4	C <sub>3</sub> D <sub>3</sub> H	$C_{2}D_{2}H_{2}$	C <sub>2</sub> DH <sub>8</sub>	C2H4	Ethylene	Acetylene	Ethane	Propane	Propylene	Butane
CH4	NO (4%)					0.162	0.162	0.011	0.016			
	$C_{2}D_{2}$ (1%)	<0.01	0.09	0.109	0.008	0.124	0.341	÷	0.278	0.037	0.121	0.110
	C2D2 (3%)	0.015	0.08	0.107	0.012	0.120	0.334					
	C2D4 (0.5%)	:	0.04	<0.02	0.015	0.145	:	0.011	0.49	0.53	0.048	0.477
	C <sub>3</sub> D <sub>6</sub> (1%)	<0.01	0.015	0.025	0.046	0.271	0.35	0.030	0.32	0.26	:	0.350
CD4	NO (1%)	0.167					0.167		0.020			
	C <sub>2</sub> H <sub>4</sub> (0.5%)	0.149	0.015	0.026	0.294	:	÷	0.012	0.44	0.55	0.028	0.389
	H <sub>2</sub> S (0.7%)	0.270					0.280					
a All prod	Icts expressed as $M/N$ .		-									

On the basis of charge-transfer spectra obtained in the mass spectrometer the relative fraction of CH2+ and CH<sub>3</sub><sup>+</sup> ions is higher in the Ar-CH<sub>4</sub> mixtures<sup>28</sup> than in Kr-CH<sub>4</sub> mixtures. Larger yields of C<sub>2</sub>H<sub>4</sub><sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup> ions could thus account for the rather high value of M(ethylene)/N obtained in the argon-sensitized radiolysis.

On the other hand, changes in the ion-pair yield of neutral excited molecules and the degree of excitation thereof will also effect the ethylene yield. For instance, the fact that the ethylene as well as the ethane which is formed by the insertion Reaction (1) (see Results) does diminish when krypton is replaced by xenon as the sensitizer indicates that the ion-pair yields of CH and CH<sub>2</sub> radicals are quite low in the xenon-sensitized radiolysis. This is not surprising in view of the recent findings of von Bunau and Schindler<sup>29</sup> who noted that in the xenon-sensitized photolysis of methane, there is no evidence for the formation of CH<sub>2</sub> radicals.

That ethane is highest in the krypton-sensitized radiolysis is also to be expected in view of the fact that the dissociative process (15) is most important at the krypton resonance lines. Finally, the drop in M(ethane)/N in replacing krypton by argon is not inconsistent with the photolysis data which indicated that at higher energies CH becomes a more important species while CH<sub>2</sub> will be more highly excited. It is clear, however, that more information will be needed before a more definitive interpretation can be obtained concerning the role of neutral excited molecules in the rare-gas-sensitized radiolysis.

# Determination of the "Initial" Ethylene Yield in Radiolysis

Recently a few attempts have been made<sup>10,11</sup> to determine the "initial" yield of ethylene, that is, the yield of ethylene formed in the radiolysis of methane under conditions where it is not consumed by secondary reactions and is not produced by reaction of less reactive ions or radicals with accumulated products or purposely added compounds. Lowering the conversion until a constant yield of ethylene is obtained is obviously the most dependable means of assessing the initial yield of ethylene. This, however, requires extremely pure methane, and raises analytical problems which are not easy to solve. Instead, it was attempted<sup>10</sup> to obtain values for the "initial" yield of ethylene by adding small amounts of unsaturated hydrocarbons or radical scavengers such as O<sub>2</sub> or NO to methane in the expectation that this would protect the ethylene from further attack (mainly by H atoms) and thus produce a yield of ethylene which might be considered to be the initial ethylene yield in the radiolysis of pure methane. The

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 <sup>&</sup>lt;sup>28</sup> (a) G. V. Karachevtsev, M. I. Markin, and V. L. Tal'rose, Kinetika i Kataliz 5, 377 (1964); (b) F. H. Field, H. N. Head, and J. L. Franklin, J. Am. Chem. Soc. 84, 118 (1962).
 <sup>29</sup> G. von Bunau and R. N. Schindler, J. Chem. Phys. 44, 420 (1966)

<sup>(1966).</sup> 

drawback of this method is that addition of trace amounts of foreign compounds to methane will also profoundly affect the ionic reaction mechanism<sup>9</sup> and thus eventually lead to an ion-pair yield of ethylene which is unrelated to that of pure methane. This is best demonstrated by the experiments listed in Table V. For instance, in  $CH_4$ - $C_2D_2$  mixtures, ethylene is produced with an ion-pair yield of 0.34 in reasonable agreement with the value of 0.4 reported by Hummel<sup>10</sup> for  $M(C_2H_4)/N$  in the radiolysis of a  $CH_4$ - $C_2H_2(1:0.01)$ mixtures. In that study it was suggested that the C<sub>2</sub>H<sub>4</sub> formed in the CH<sub>4</sub>-C<sub>2</sub>H<sub>2</sub> mixture was essentially equal to the initial yield of ethylene in pure methane but the results given in Table V indicate that this is not the case. It can actually be seen that  $C_2H_4$  accounts for only 40% of the total ethylene yield, independent of the percentage of  $C_2D_2$  in the reaction mixture. Although no mechanism can be offered for the formation of the partially deuterated ethylenes, it can be surmised that they are produced by reactions of ions which react slowly with methane itself. Similarly, Hummel<sup>10</sup> obtained a value of 0.38 for the ion-pair yield of ethylene formed in the radiolysis of CH4-C3H6 mixtures and concluded that this is the most reliable value for the initial yield of ethylene because the direct radiolysis of propylene yields a negligible amount of ethylene and because, furthermore, a tenfold change in the concentration of  $C_3H_6$  does not alter the value of  $M(C_2H_4)/N$ . Again, the ion-pair yield of 0.35 for the total amount of ethylene formed in the radiolysis of CH<sub>4</sub>-C<sub>3</sub>D<sub>6</sub> mixtures (Table V) is in good agreement with the value reported by Hummel. However, only 77.5% of this ethylene is  $C_2H_4[M(C_2H_4)/N=0.27]$ . Furthermore, it has been demonstrated<sup>30</sup> before that in the radiolysis of C<sub>3</sub>H<sub>8</sub>- $C_3D_6$  mixtures,  $C_2H_4$  is produced also by the protontransfer reaction

$$C_2H_5^++C_3D_6 \rightarrow C_2H_4+C_3D_6H^+.$$
(20)

At a methane pressure of 100 torr,  $M(C_2H_5^+)/N$  has been estimated<sup>3</sup> at about 0.30. When as much as 1% propylene is added to CH<sub>4</sub>, all C<sub>2</sub>H<sub>5</sub><sup>+</sup> will react with propylene, but only about 50% will react by Reaction (20) to form ethylene the other 50% will undergo hydride transfer and condensation reactions.<sup>30</sup> Therefore, of the C<sub>2</sub>H<sub>4</sub> formed in the radiolysis of CH<sub>4</sub>-C<sub>3</sub>D<sub>6</sub> mixtures, only a fraction, corresponding to an ion-pair yield of 0.12, could originate from reactions occurring in pure CH<sub>4</sub>. The latter value, is in good, although perhaps fortuitous, agreement with the value obtained in the radiolysis of the CH<sub>4</sub>-C<sub>2</sub>D<sub>2</sub> and CH<sub>4</sub>-*i*-C<sub>4</sub>D<sub>10</sub>-NO mixtures. It should be noted that in the CH<sub>4</sub>-C<sub>2</sub>D<sub>2</sub> mixtures, C<sub>2</sub>H<sub>4</sub> will not be formed by the protontransfer reaction

$$C_2H_5^+ + C_2D_2 \rightarrow C_2D_2H^+ + C_2H_4 \tag{21}$$

because such a reaction is endothermic by about 16 kcal.

<sup>30</sup> P. Ausloos and S. G. Lias, Discussions Faraday Soc. 39, 36 (1965).

When  $H_2S$  is added to  $CD_4$  as a D-atom interceptor, the ion-pair yield of  $C_2D_4$  formed in the mixture is 0.28, a yield well above that of ethylene formed in  $CD_4$ -NO mixtures (Table V). Again, a considerable fraction of this ethylene can be ascribed to a deuteron-transfer reaction between the ethyl ion and the additive:

$$C_2D_5^+ + H_2S \rightarrow C_2D_4 + H_2DS^+.$$
(22)

It has been shown in a recent study<sup>28</sup> that about one third of ethyl ions which undergo a reactive collision with H<sub>2</sub>S will form ethylene. If the ion-pair yield of  $C_2D_4$  is, therefore, corrected for this contribution, a residual yield of 0.17 is obtained, which is only in fair agreement with the yields derived from the other experiments discussed above. It is of interest to note that the ion-pair yield of  $C_2D_4$  is approximately independent of the concentration of H<sub>2</sub>S up to 10% (see Table VII). At higher percentages of H<sub>2</sub>S, there is, however, a definite decrease of the ion-pair yield of this product which can be ascribed to a reaction of the precursor ion of  $C_2D_5^+$ , namely  $CD_3^+$ , with H<sub>2</sub>S.

Hauser<sup>11</sup> recently attempted to determine the "initial" yield of ethylene by irradiating C  $^{14}H_4$  in the presence of 0.02 to 0.17% C<sub>2</sub> <sup>12</sup>H<sub>4</sub>. On the basis of the measured yield of C<sub>2</sub><sup>14</sup>H<sub>4</sub>, a value of 0.3 to 0.35 was ascribed to the "initial" yield of ethylene. Analogous experiments involving the determination of the yields of C2D4 and C<sub>2</sub>H<sub>4</sub> formed in the radiolysis of CD<sub>4</sub>-C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub>- $C_2D_4$  mixtures, respectively, were carried out in the course of this investigation. The results of these experiments, given in Table V show ion-pair yields of C2H4 and  $C_2D_4$  are considerably lower than that of  $C_2$  <sup>14</sup> $H_4$ reported by Hauser. No explanation can be given for the discrepancies between the two studies, except for the fact that the dosimetry is rather poorly defined in the study by Hauser. It is of incidental interest to note that the value of  $M(C_2H_4)/N$  obtained in the radiolysis of CH<sub>4</sub>-C<sub>2</sub>D<sub>4</sub> mixtures is again rather close to the value obtained in the radiolysis of CH<sub>4</sub>-C<sub>2</sub>D<sub>2</sub> mixtures.

The above discussion confirms that initial ethylene yields cannot be determined by addition of foreign compounds to methane. It may, however, be said that addition of these various hydrocarbons to methane lead to a fairly consistent value for ion-pair yields of ethylene which cannot be accounted for by ion-molecule reactions which can in the absence of additional information be ascribed to reactions of CH and  $CH_2$  with methane.

Unexplained remain the high yields of ethylene  $[M(C_2H_4)/N=0.8 \text{ at 1 torr}]$  obtained by Hummel in the radiolysis of pure CH<sub>4</sub> at 0.04% conversion. At the very high dose rates  $(10^{21} \text{ eV min}^{-1} \text{ g}^{-1})$  and low pressures at which these values are obtained neutralization of relatively unreactive ions such as  $C_2H_5^+$  and  $C_3H_7^+$  may effectively enter into competition with reactions of these ions with accumulated products. Such ions would, however, be removed from the system by the olefins.

		Hydr	ogen distrib	oution
Pressure torr	$\%\mathrm{H_2S}$	$D_2$	HD	$H_2$
20	1.3	1.00	0.57	0.35
20	4.5	1.00	0.67	0.75
20	11.4	1.00	0.67	1.39
20	11.9ª	1,00	0.65	
100	10.0	1.00	0.74	2.21
20	24.2	1.00	0.94	1.93

TABLE VI. Krypton photolysis of CD<sub>4</sub>-H<sub>2</sub>S mixtures.

 $^{a}$  Intensity: 1014 quanta/sec. In all other experiments, intensity is  $5 \times 10^{14}$  quanta/sec.

#### Formation of Hydrogen

#### **Photolysis**

The isotopic composition of the hydrogen fractions formed in the photolysis of  $CH_4$ - $CD_4$ -NO mixtures at 1236 and 1048–67 Å indicates that the hydrogen is mainly, although not exclusively, formed by a molecular detachment process. The gradual decrease of HD with an increase in pressure (Table I) may in part be due to the increased effectiveness of NO as a free-radical scavenger at higher pressure. Collisional stabilization of HNO and DNO formed in the combination reaction enhances the scavenging action of NO.

It is difficult to estimate the actual contribution of bimolecular processes to the formation of hydrogen. Secondary reactions may exhibit rather pronounced isotope effects which would favor the formation of  $H_2$ . This is to some extent corroborated by the observation that an increase in pressure lowers the ratio  $H_2/D_2$  as well as the percentage HD (Table I). However, even at 100 torr does one find  $H_2 > D_2$ , although the percentage HD is quite small. This is rather surprising in view of the fact that the extinction coefficient of CH<sub>4</sub> is lower than that of  $CD_4$  (see Results). As noted before, the isotopic composition of the ethylene formed in an equimolar CH<sub>4</sub>-CD<sub>4</sub> mixture at 1236 Å indicates that CH>CD. It may be surmised that secondary fragmentation of excited methyl or methylene exhibits an isotope effect.

On the basis of the isotopic composition of the hydrogen (Table I) it may be surmised that at a pressure of 10 torr at least 20% of the hydrogen is formed by bimolecular processes. If one accepts a value of 1.4 for the quantum yield of hydrogen at 1236 Å (see Results)<sup>31</sup> one is forced to conclude that H atoms are produced in rather high yields. At 1236 Å, usually one "molecular" hydrogen entity will be produced per photon. As noted before in the Discussion a process such as

$$CH_4^* \rightarrow C + 2H_2$$
 (23)

is not important at 1236 Å, while Reaction (2), which would be an additional source of hydrogen, does not also seem to be of importance at this wavelength. However, Process (10) does yield an H atom for each  $H_2$  molecule. Furthermore, reaction of the CH radical leads to the production of an additional H atom. H atoms may, of course, also be produced by primary process (15) but these will not raise the quantum yield of hydrogen, assuming that the rather highly excited methyl radicals formed in this process do not take part in any different reactions from those which thermal methyl radicals are known to undergo. Isotopic scrambling of methyl radicals formed as a result of the decomposition of ethane formed in Reaction (1) renders the determination of the quantum yield of Process (15) quite difficult. Therefore, the isotopic composition of the hydrogen produced in the photolysis of various CD<sub>4</sub>-H<sub>2</sub>S mixtures (Table VI) was determined in the expectation that this would provide a fairly direct estimate of the abundance of Process (15). The D atoms should react predominantly with H<sub>2</sub>S to form HD [Reaction (24)], while H atoms formed by photolysis of H<sub>2</sub>S would yield mainly H<sub>2</sub>.<sup>32</sup>

$$D+H_2S\rightarrow HD+HS.$$
 (24)

The results of Table VI show that the product ratio:  $HD/D_2$  is fairly constant over a tenfold increase of the percentage of  $H_2S$ , as well as over a fivefold variation in intensity or pressure. When the H<sub>2</sub>S percentage is increased from 11 to 24.2% a definite increase is seen in the ratio:  $HD/D_2$ . However, at this point, extensive photolysis of H<sub>2</sub>S must occur, probably leading to the formation of hot H atoms which may abstract from  $CD_4$  to form HD. If we make the reasonable assumption that at relatively low percentages of H<sub>2</sub>S, the CD radicals do react exclusively with CD4, two D atoms and one  $D_2$  molecule will be formed for each CD radical produced. If we further accept that on the basis of the previous discussion, approximately one methyne radical is formed for every 10 hydrogen molecules, we arrive at a rough estimate of five stable methyl radicals formed by Process (15) for every 10 hydrogen molecules. This value is not inconsistent with the observation<sup>5</sup> that in the argon matrix experiments, approximately 30% of the ethane was formed by a combination of methyl radicals formed in Process (15), the remainder being formed by insertion of methylene into methane.

#### Radiolysis

The results of Table VII show that a 20-fold increase in the percentage  $H_2S$  in  $H_2S-CD_4$  mixtures results in only a 6% increase in the product ratio  $HD/D_2$ . It may, therefore, be concluded even at the lowest  $H_2S$  concentration the large majority of the D atoms react with

 $<sup>^{</sup>a1}$  The quantum yield will be lower than 1.4, if the ionization efficiency of NO at 1236 Å is less than the value of 0.833 given in Ref. 18.

<sup>&</sup>lt;sup>32</sup> P. Ausloos and S. G. Lias, J. Chem. Phys. 44, 521 (1966).

					$M/N_{{ m CD4}}$			
			Hydrogen		Eth	ylene	Eth	ane
$\%~{ m H_2S}$	$\mathrm{HD}/\mathrm{D}_{2}$	$D_2$	HD	$H_2$	$C_2D_4$	$C_2D_3H$	$\overline{C_2D_6}$	C₂D₅H
0.7 4.5 15.5 37.6	1.73 1.77 1.83 2.13	0.691 0.667 0.554	1.20 1.08 1.18	0.236 0.370 1.85	$\begin{array}{c} 0.270 \\ 0.262 \\ 0.259 \\ 0.194 \end{array}$	0.012 0.017 0.020 0.024	$\begin{array}{c} 0.012 \\ 0.011 \\ 0.0065 \\ 0.0030 \end{array}$	0.006 0.006 0.0027 0.0020
NO (6%)		0.705	0.026	0.033	0.160	0.021	0.011	0.0020

TABLE VII. Radiolysis of CD<sub>4</sub>-H<sub>2</sub>S mixtures (pressure of CD<sub>4</sub>: 40 torr).

H<sub>2</sub>S to form HD as a product. The fact that in the latter experiment the value for  $M(D_2)/N$  is within experimental error equal to that observed in the radiolysis of a CD<sub>4</sub>-NO mixture, indicates that while 0.7% H<sub>2</sub>S removes the D atoms it does not affect the processes which lead to the formation of nonscavengable hydrogen. On the other hand the decrease of  $M(D_2)/N$  at higher H<sub>2</sub>S percentages is probably<sup>33</sup> due to reaction of H<sub>2</sub>S with CD<sub>3</sub><sup>+</sup>, the latter ion being responsible for the production of "molecular" hydrogen by Reaction (25).

$$CD_3^+ + CD_4 \rightarrow C_2D_5^+ + D_2. \tag{25}$$

The corresponding drop in  $M(C_2D_4)/N$  must be in part ascribed to the lowering in yield of the  $C_2D_5^+$  ions, which participate in part in the deuteron transfer reaction (22).

The actual significance of the measured yield of HD is, however, not obvious. Although M(HD)/N can probably be equaled to M(D)/N, it should be realized that the latter value has been obtained with H<sub>2</sub>S in the system. Because C<sub>2</sub>D<sub>5</sub><sup>+</sup> ions, and probably others as well definitely react with H<sub>2</sub>S, the formation of hydrogen atoms which in pure methane may come from neutralization of these slow reacting secondary or higher-order ions would be suppressed. The inter-



FIG. 1. The effect of conversion on the product  $HD/D_2$  ratio obtained in the radiolysis of Xe-CH<sub>4</sub>-CD<sub>4</sub>-NO mixtures. The open circles denote the results of this work while the closed circles represent the data of Aquilanti.

<sup>33</sup> F. H. Field and F. W. Lampe, J. Am. Chem. Soc. 80, 5583 (1958).

pretation of the measured yield of HD in terms of the hydrogen atom production in pure methane will, therefore, have to await additional quantitative information on the reactions of the major ions with  $H_2S$ .

The  $CD_4$ -H<sub>2</sub>S experiments indicate that  $C_2D_3$  and  $C_2D_5$  radicals play a relatively minor role in these mixtures. Because 0.7% H<sub>2</sub>S is not expected to compete efficiently with CD<sub>4</sub> for the CD radicals formed, it may be concluded that as indicated by the pressure independence of ethylene in the photolysis experiments, very few of the C<sub>2</sub>D<sub>5</sub> radicals which would be formed by Reaction (9) are collisionally stabilized. The  $C_2D_6$ , which according to the CH<sub>4</sub>-CD<sub>4</sub> experiments is formed by insertion of CD<sub>2</sub> into CD<sub>4</sub>, decreases gradually with an increase in the percentage of H<sub>2</sub>S. It may, therefore, be surmised that the  $CD_2$  radicals react with  $H_2S$ . However, because the ion-pair yield of C<sub>2</sub>D<sub>6</sub> in the radiolysis of a CD<sub>4</sub>-NO mixture is approximately equal to that observed in a CD<sub>4</sub>-H<sub>2</sub>S mixtures containing up to 4.5% H<sub>2</sub>S it follows that the CD<sub>2</sub> radicals react mainly with CD<sub>4</sub> at low H<sub>2</sub>S concentrations.

## Rare-Gas-Sensitized Radiolysis

In a recent study, Aquilanti<sup>34</sup> suggested that the major process in the xenon-sensitized radiolysis of  $CH_4$  can be written as follows:

$$Xe^* + CH_4 \rightarrow Xe + CH_2 + H_2. \tag{26}$$

This conclusion was based on the apparent observation that in the radiolysis of a Xe–CD<sub>4</sub>–CH<sub>4</sub> (100:5.38:2.43) mixture in the presence of NO the ratio HD/D<sub>2</sub> approaches zero provided the percent conversion is sufficiently low (see Fig. 1). Because the latter results could not be brought into agreement with an earlier study of the xenon-sensitized radiolysis of CH<sub>4</sub>–CD<sub>4</sub> mixtures,<sup>35</sup> we re-examined the effect of conversion on the ratio HD/D<sub>2</sub> in the radiolysis of a mixture identical to that used by Aquilanti. The data obtained have been included in Fig. 1. They show that the HD/D<sub>2</sub> ratio does not, within experimental error, vary with conversion and also does not go through the origin, although the percent conversion in our study was considerably

<sup>&</sup>lt;sup>34</sup> V. Aquilanti, J. Phys. Chem. 69, 3434 (1965)

<sup>&</sup>lt;sup>35</sup> P. Ausloos and S. G. Lias, J. Chem. Phys. 38, 2207 (1963).

lower than in the investigation of Aquilanti. It would thus seem that Process (26) is not as important as suggested by Aquilanti. This is consistent with the low ethylene and ethane yields formed in the xenonsensitized radiolysis of  $CH_4$ - $CD_4$ -NO mixtures (Table IV) which as noted earlier in the Discussion indicate a low yield of methyne and methylene radicals.

We also irradiated a Ar-CH<sub>4</sub>-CD<sub>4</sub> (100:4.96:2.59) mixtures in the presence of NO and obtained a value of 0.365 for HD/D<sub>2</sub> independent of conversion from 0.01 to 0.2%. The latter value is again considerably higher than the extrapolated value of 0.1 reported by Aquilanti for an identical mixture. The actual mechanism of the formation of hydrogen in the xenon- and argon-sensitized radiolysis remains to be explored. As noted before<sup>35</sup> ion-molecule reactions as well as the decomposition of neutral excited molecules contribute to the formation

of nonscavengable hydrogen in the radiolysis of methane.

We suggest that the decrease of  $HD/D_2$  with diminishing conversion, reported by Aquilanti may be an experimental artifact. In the present study, the hydrogen was distilled from the bulk methane and analyzed separately. In the study of Aquilanti the hydrogen was analyzed in the presence of the methane. It seems likely that in the latter study the contribution to mass 4 from fragmentation of  $CD_4^+$  was not correctly taken into account in the calculation of the  $D_2$  yield from the mass spectrum of the irradiated mixture. If this correction is underestimated the ratio  $HD/D_2$  would seemingly go through the origin at sufficiently low conversion. By the same token it is believed that the extrapolated values of  $HD/D_2$  reported for the argonand krypton-sensitized radiolyses are too low.

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# Crossed Molecular Beam Reactions of Tritium Bromide\*

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A radioisotope detection method was successfully employed to determine the product distribution in crossed molecular beam experiments. Angular distributions of the atomic tritium product were measured for the reactions  $K+TBr\rightarrow KBr+T$  and  $Cs+TBr\rightarrow CsBr+T$ . The measured distributions correspond to "backward" scattering ( $\chi \simeq \pi$ ) of the potassium bromide relative to incoming potassium in the center-of-mass coordinate system for both reactions, i.e., the reactions are *rebound* reactions.

## INTRODUCTION

THE interpretation of crossed molecular beam experiments in terms of differential cross sections in the center-of-mass coordinate system is well understood.<sup>1</sup> However, unfavorable kinematic factors and limitations on experimental resolution frequently make it difficult to resolve clearly even the qualitative behavior of some parameters in chemical reactions. One of the reactions most thoroughly studied, K+HBr→KBr+H, is particularly intractable to detailed examination of the angular and velocity distribution of products. The easily observed product, KBr, is so much heavier than its partner that it is kinematically restricted to very slight motion relative to the center of mass. Resolution

† Present address: Department of Chemistry, California Institute of Technology, Pasadena, Calif. † Alfred P. Shan Research Fellow of the KBr motion from that of the center of mass becomes very difficult in this case. The masses of the reactants, however, are more nearly equal, so that there is no such difficulty in measuring reactant angular distributions. Indeed, the nonreactive scattering of K by HBr has been one of the most thoroughly investigated systems in molecular beam experiments.<sup>2</sup>

Because of the detailed information available from the elastic-scattering work about the reactants, our study was undertaken to provide complementary information about the products by measurement of their center-of-mass angular distribution. In order to operate on the favorable end of the disproportionate velocity distribution a new method of detection was developed for observing the lighter product. This was accomplished by choosing to study a slightly different reaction,  $K+TBr\rightarrow KBr+T$ , in which a radioactive product was formed. The radioactive decay of the atomic tritium product selectively absorbed on molybdenum trioxide

<sup>2</sup> (a) D. Beck, J. Chem. Phys. **37**, 2884 (1962); (b) D. Beck, E. F. Greene, and J. Ross, J. Chem. Phys. **37**, 2895 (1962).

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<sup>&</sup>lt;sup>‡</sup> Alfred P. Sloan Research Fellow. <sup>1</sup> S. Datz, D. R. Herschbach, and E. H. Taylor, J. Chem. Phys. **37**, 2895 (1962).