Radiolysis of Ethane-1,1,1-d 3

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fortunately, there is some uncertainty in making the comparison, i.e.,

$$\bar{S}_2^{E*}(p) = \bar{S}_2^{E*}(p') + \int_p^{p'} \left(\frac{\partial \bar{V}_2^*}{\partial T}\right)_p dp, \qquad (29)$$

where p' is 350 atm and p is the highest pressure at which experimental values of $\bar{V}_2^*$ are available. Because $\bar{V}_2^*$ was only measured to 150 atm, the evaluation of the integral in Eq. (29) involves an extrapolation of equations which are linear in $1/\bar{V}_2^*$.[6] This extrapolation

can be made with reasonable certainty at low temperatures where $(\partial \bar{V}_2^*/\partial T)_p$ is small, but the certainty gets less as the temperature is increased. Therefore, while the agreement between Eq. (28) and experiment in Table IV is probably meaningful up to 200°C, that at 230°C is fortuitous.

ACKNOWLEDGMENTS

Radiolysis of Ethane-1,1,1-d_3†

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The radiolysis of CH_3CD_3 has been investigated with particular emphasis on the effect of pressure, temperature, and addition of xenon on the molecular hydrogen formation. The hydrogen formed by molecular detachment was determined by irradiating CH_3CD_3 in the presence of C_2H_4, NO, O_2, or I_2. The formation of molecular hydrogen in the unimolecular decomposition of the parent ion and in the decomposition of the neutral excited ethane molecule are considered. Methane formed in the presence of scavengers may be attributed to an ion-molecule reaction or to an intramolecular process similar to that proposed in the direct photolysis of ethane. Evidence is presented for occurrence of a reaction producing ethylene in addition to the one in which molecular hydrogen accompanies the formation of ethylene.

INTRODUCTION

IN recent investigations[1,2] of the radiolysis of C_2H_6–C_2D_6 mixtures, it has been clearly demonstrated that nearly 50% of the hydrogen is formed by molecular-elimination processes. It was also shown in the course of these investigations that a considerable fraction of the methane is formed by molecular detachment from ethane.

Recently[3] similar processes have been observed in the short-wavelength photolysis of ethane. Of special interest are the results obtained in the photolysis of CH_3CD_3, which indicated that at 1470 A, hydrogen is mostly formed by elimination of a hydrogen molecule from a single carbon atom.

$$CD_3CH_3 + h\nu \rightarrow CD_3CH + H_2 \qquad (1)$$

$$\rightarrow CH_3CD + D_2. \qquad (2)$$
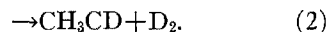
The present investigation was undertaken in order to determine (a) if similar processes occur in the

radiolysis of CH_3CD_3, (b) whether the distribution of the molecular hydrogen isotopes can be related to the mass spectral cracking pattern, (c) whether distribution of the isotopic methanes formed in the presence of radical scavengers is consistent with the results obtained in the C_2H_6–C_2D_6 system, and (d) whether the distribution of the isotopic ethylenes formed in the presence of scavengers is consistent with the distribution of the corresponding hydrogen isotopes.

EXPERIMENTAL

Materials

Ethane-1,1,1-d_3 was obtained from Merck and Company, Ltd. Small amounts of methane were removed by subjecting the ethane to successive cycles of freezing, pumping, and warming. The absence of ethylene in the CH_3CD_3 was checked by gas chromatographic analysis [Perkin–Elmer No. 154, silica gel (J) column, 35°]; as little as 0.001% ethylene would have been readily detected by this method. The isotopic purity of the CH_3CD_3 is discussed in the next section. Deuteroethane and ethane were obtained from Merck and Company, Ltd. and Union Carbide and Carbon Chemicals, respectively. Both were purified of noncondensables by a vacuum distillation procedure similar to that employed for CH_3CD_3. Ethylene was removed by gas chromatography (conditions as above),

[1] L. M. Dorfman, J. Phys. Chem. **60**, 826 (1956).
[2] L. M. Dorfman, J. Phys. Chem. **62**, 29 (1958).
[3] H. Okabe and J. R. McNesby, J. Chem. Phys. **34**, 668 (1961).

TABLE I. Mass spectral data for CH_3CD_3.

m/e	Ionizing voltage						
	75[a]	70[b]	70	25	18	14	12
12	1.19	10.07	4.8				
13	1.20	10.85	5.2				
14	3.42	22.7	11.8	0.17			
14.5	1.62	2.0	1.2				
15	6.19	24.4	15.2	3.63	1.06		
15.5	3.14	2.85	2.5				
16	4.77	14.4	11.8	1.15	0.29		
17	1.20	6.7	3.6	1.11	0.30		
18	2.5	13.0	13.3	4.38	1.31		
24	2.4	10.2	4.0				
25	5.2	20.4	7.8				
26	26.5	92.3	28.4	5.3	1.4		
27	61.2	150.7	75.4	24.2	5.7		
28	82.7	220.0	98.8	45.2	11.0	0.6	6.7
29	131.8	321.5	138.8	90.1	44.5	25.4	6.7
30	285.9	507.7	435.5	425.0	364.3	316.5	140.3
31	59.6	107.7	88.7	80.0	55.0	33.4	6.5
32	43.9	81.5	57.0	55.4	38.5	21.0	4.07
33	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] Reference 7.

[b] Reference 8. All other patterns were obtained using Consolidated model 21–101, trap current 50 μa; all relative intensities have been corrected for C_{13} abundance.

successively trapping and reintroducing the sample until the ethylene peak was reduced to less than 0.001% of the ethane. The oxygen, xenon, nitric oxide, and ethylene have been described previously.[4] Reagent-grade iodine was obtained from the Mallinckrodt Chemical Works and used without purification.

Irradiation Procedure

The 2000 curie cobalt-60 gamma-ray source at the National Bureau of Standards was used in this investigation. The procedure has been described previously.[5] The majority of the experiments in which scavengers were added were done at 0.2% conversion.

Analysis

The analytical system has been described.[2] The gases which are noncondensable at $-210°$ were removed by a Toepler pump, measured in a gas buret, and analyzed for isotopic hydrogen and methanes with a Consolidated model 21–101 mass spectrometer. The ethane was subjected to at least two successive warmup cycles to ensure complete removal of the methane. Only about half of the methane is removed by simply freezing and pumping. The distribution of the isotopic methanes was calculated from cracking patterns reported in the literature.[6]

The ethylene was determined by gas chromatography [Perkin–Elmer No. 154, silica gel (J) column, 25°]. Ethane was used as an internal reference. Analysis of known mixtures of ethane and ethylene, under conditions identical to those used for analysis of the irradiated

samples, showed that to within 5% the relationship between peak area and concentration was the same for both ethane and ethylene. The ethylene was trapped from the helium stream in a glass spiral trap immersed in liquid nitrogen. The helium was removed by pumping through a solid-nitrogen trap (to retain the ethylene) and the ethylene was then pumped from a Ward still at $-170°$. This sample was analyzed in the mass spectrometer for isotopic ethylenes. Patterns for all the isotopic ethylenes were obtained by running authentic samples (obtained from Merck and Company, Ltd.) in the same mass spectrometer.

RESULTS AND DISCUSSION

I. Mass Spectrum of CH_3CD_3

Before discussing the radiolysis results, it is essential to establish the isotopic purity of the ethane-1,1,1-d_3 used in this investigation.

A. High-Energy Electron Cracking Pattern

Taking into consideration the different types of mass spectrometers used, it can be seen (Table I) that there is fair agreement between the cracking pattern of the CH_3CD_3 used in this investigation and the one obtained by Schissler et al.[7] A sample of the CH_3CD_3 used in this investigation was also examined on a Nier-type instrument through the kindness of Dr. F. P. Lossing at the National Research Council of Canada. The cracking pattern obtained agreed within 5% of the one obtained by us. There is, however, considerable disagreement between the cracking pattern

[4] L. J. Stief and P. Ausloos, J. Phys. Chem. **65**, 1560 (1961).

[5] L. J. Stief and P. Ausloos, J. Phys. Chem. **65**, 877 (1961).

[6] F. L. Mohler, V. H. Dibeler, and E. Quinn, J. Research Natl. Bur. Standards **61**, 171 (1958).

[7] D. O. Schissler, S. O. Thompson, and J. Turkevich, Discussions Faraday Soc. Hydrocarbons, 46 (1951).

TABLE II. Radiolysis of ethane-1,1,1-d_3:Effect of scavengers.

	No scavenger	3% C₂H₄	0.4% O₂	3% NO	0.05% I₂	30% I₂
			cc(NTP)/min-mole×10⁸			
H₂	15.27	5.95[a]	7.09[b]	5.49	4.67	3.52
HD	17.93	10.42	13.07[b]	10.81	9.09	6.60
D₂	3.88	3.42	4.47[b]	3.65	3.10	2.28
CH₄	0.59	0.65	0.17	0.14	0.13	0.12
CH₃D	0.59	0.52	0.29	0.35	0.42	0.26
CH₂D₂	0.30	0.33	n.d.	0.13	0.16	0.03
CD₃H	1.17	1.14	0.68	0.71	n.d.	0.42
CD₄	0.32	0.12	0.26	0.13	n.d.	0.07
HD/D₂	4.62	3.05	2.92	2.96	2.93	2.90

Pressure of CH₃CD₃—250 mm at 25°.
Reaction temp.—16° (165° for 30% I₂ experiment).
Conversion—0.2% (0.05% for scavenger-free experiment).
n.d.—not determined.

[a] Corrected for contribution from C₂H₄ decomposition.
[b] These yields may be too high because of the uncertainty in measuring small amounts of noncondensibles in the presence of a large quantity of oxygen.

reported by Quinn and Mohler[8] and the one obtained by us, although the mass spectrometers used were of a very similar design. This difference is even more surprising if one considers the fact that the spectra of C₂H₆ and C₂D₆ obtained by us agreed closely with the ones reported by Quinn and Mohler. It was stated by these authors that there is a wide variation in the abundances of the parent-molecule ions of the different ethanes. By making the sums of the ions in each ethane cracking pattern equal, relative intensities, 22.1, 13.0, and 18.7 were reported for the parent ions C₂H₆⁺, CH₃CD₃⁺, and C₂D₆⁺, respectively. It was thus concluded that highly asymmetrical ions gave low values for the abundance of parent-molecule ion. However, if we use the cracking pattern of CH₃CD₃ obtained by us, the distribution is as follows: 22.1, 20.0, 18.7. Because the latter distribution seems more reasonable[9] than the one presented by Quinn and Mohler, we are led to believe that the sample used by these authors must have contained impurities contributing to the abundance of the peaks in the mass region 24–32.

B. The Low-Energy Electron Cracking Pattern

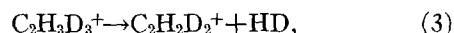The following two conclusions may be drawn from the cracking pattern obtained at 12 v[10]:

(1) The maximum amount of C₂H₄D₂ is about 4%.
(2) The abundance of the fragment ion correspond-

ing to mass 30 is more than 20 times that of any other fragment ion. This clearly demonstrates the importance of the reaction

$$C_2H_3D_3^+ \rightarrow C_2H_2D_2^+ + HD, \qquad (3)$$

which in turn indicates that CH₃CD₃ is the major isotopic component of the C₂H₃D₃ used in this investigation.

It may be noted that after making a correction[11] for the contribution of the C₂H₃D₂⁺ ion to mass 31, the amounts of hydrogen (H₂: HD: D₂) removed at 14 v are in the relation 0.058: 0.872: 0.07. Assuming there is 4% of CHD₂CH₃ in the ethane sample, these probabilities become[12] 0.065: 0.886: 0.049. Incidentally, these distributions differ considerably from the one which Schissler et al. deduced from their 13-v cracking pattern. Their probabilities for removal of H₂: HD: D₂ are 0.04: 0.71: 0.25 which lead to the unlikely conclusion that the removal of D₂ is strongly favored over the removal of H₂ from the CH₃CD₃ ion.

In view of the presence of possible traces of isotopic impurities and the difficulty of obtaining accurate cracking patterns below 12 v, it is not possible to decide whether or not the 29 and 31 peaks can be attributed to a reaction such as

$$CH_3CD_3^+ \rightarrow CH_2DCD_2H^+, \qquad (4)$$

followed by a loss of hydrogen molecule from two adjacent carbon atoms.[13] The distribution obtained at 12 v indicates, however, that reshuffling of hydrogen atoms is not an important process at low electron

[8] E. I. Quinn and F. L. Mohler, J. Research Natl. Bur. Standards 65A, 93 (1961).

[9] A similar distribution can be deduced from the data of Schissler et al. Also, for other hydrocarbons, only gradual variations in the abundance of the parent ions with varying degrees of deuteration, have been reported in the literature. For instance, in the case of ethylene [V. H. Dibeler, F. L. Mohler, and M. de Hemptrime, J. Research Natl. Bur. Standards 53, 107 (1954)] the cracking pattern of the asymmetrical CH₂CD₂ and the symmetrical CHDCHD are very similar and the abundances of the parent ions of these two isomers lie in between those of C₂H₄, and C₂D₄.

[10] The values of the electron voltages given in this paper are only nominal values, which are accurate within 0.5 v.

[11] A weighting factor of 1.67, as deduced by Quinn and Mohler from the cracking pattern of C₂D₅H at 70 v was used for estimating probabilities of removal of an H and a D atom from the parent ion.

[12] It was approximated by a statistical argument that the probability for the loss of HD from CHD₂CH₃ is twice that for the loss of H₂.

[13] M. Krauss, A. L. Wahrhaftig, and H. Eyring, Ann. Rev. Nuclear Sci. 5, 256 (1955).

energies. At high energies, on the other hand, the presence of ions of mass 17 shows that a process such as (4) may precede the split of the ethane-molecule ion along the carbon–carbon axis. The decrease in the ratio of the relative intensities of masses 17 and 18 with decrease in electron energy may be related to the diminishing importance of reaction (4) at lower electron energies.

II. Hydrogen Formation in Radiolysis of Ethane

A. Experimental Observations

The radiolysis of an equimolar mixture of C_2H_6 and C_2D_6 in presence of iodine at 16° gave the following distribution of the hydrogens, H_2, HD, D_2: 50.8, 6.8, 42.4. The latter distribution is in good agreement with the one obtained by Dorfman[2] in experiments using C_2H_4 as a radical scavenger, and thus confirms Dorfman's conclusion that most of the hydrogen not removed by the ethylene is formed in a molecular detach-

TABLE III. Radiolysis of ethane-1,1,1,-d_3: effect of pressure.

Pressure (mm Hg)	3.0	50.0	150.0	250.0
	cc. (NTP)/min.-mol×10³			
H_2	5.40	5.93	5.46	5.96
HD	10.44	11.29	9.91	10.42
D_2	3.10	3.51	3.20	3.42
CH_4	0.64	0.25	0.55	0.65
CH_3D	0.42	0.47	0.53	0.52
CH_2D_2	0.20	0.28	0.31	0.33
CD_3H	1.17	0.90	1.00	1.14
CD_4	0.18	0.20	0.13	0.12
HD/D_2	3.37	3.27	3.09	3.05
HD/H_2	1.94	1.91	1.82	1.75

Reaction temp.—16°.
All experiments performed in presence of 3% C_2H_4.
H_2 yields corrected for contribution from C_2H_4 decomposition.

ment not involving free hydrogen atoms. It may thus be safely stated that the hydrogens produced in the radiolysis of CH_3CD_3 should arise from a similar process.

The scavenger experiments (Table II) indicate that in the radiolysis of CH_3CD_3, molecular H_2, DH and D_2 are eliminated from the ethane molecule. The distribution H_2:HD:D_2 is, within experimental error, 1.7:3.0:1.0 for all scavengers.[14] It is interesting to note that although addition of iodine up to 30% does reduce the total hydrogen yield, it does not significantly affect the distribution of the three hydrogens.

The results of Table III show that, within experimental error, the total yield of molecular hydrogen is independent of pressure. The relative yield of HD as

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[14] The ratio HD/D_2 given in the last row of Table II is a good measure of the constancy of the hydrogen distribution. It has been shown before[4] that some H_2 may be produced from the walls of the reaction vessel, and may cause small fluctuations in the ratio H_2/HD.

TABLE IV. Radiolysis of ethane-1,1,1-d_3: effect of temperature.

	16°[a]	155°[a]	221°[a]	314°[a]	320°	394°
	cc(NTP)/min-mol×10³					
H_2	4.60	4.93	5.12	8.85	23.10	23.04
HD	8.16	8.82	8.96	12.27	19.51	25.84
D_2	2.71	2.85	2.90	3.70	4.88	7.37
CH_4	0.41	0.74	0.93	n.d.	3.21	7.34
CH_3D	0.30	0.52	0.71	n.d.	2.14	6.33
CH_2D_2	0.36	0.30	0.38	n.d.	1.56	4.74
CD_3H	0.85	1.01	1.37	n.d.	3.37	9.67
CD_4	0.19	0.11	0.33	n.d.	0.96	2.99
HD/D_2	3.01	3.09	3.09	3.32	4.00	3.51

Pressure of CH_3CD_3—250 mm at 25°.
n.d.—not determined.
Conversion—0.2%.

[a] 3% C_2H_4 added; H_2 corrected for contribution from C_2H_4 decomposition.

compared to the yields of H_2 and D_2 does undergo a slight but definite increase with decrease in pressure.

An increase in temperature from 16° to 221° (Table IV) has apparently no effect on the total yield or on the distribution of the molecular hydrogen isotopes. The increase in the yield of hydrogen at 314° can be ascribed to the inefficiency of ethylene in trapping hydrogen atoms at this temperature.

It may finally be seen (Table V) that addition of xenon considerably increases the total yield[11] of molecular hydrogen, but does not affect the relative yields of isotopic hydrogens.

B. Discussion

The unimolecular decomposition of the parent ion and that of the neutral excited ethane molecule are probably the two principal sources for the formation of molecular hydrogen. As pointed out before,[2] the formation of molecular hydrogen by an ion–molecule reaction may be tentatively excluded because, as yet, no efficient reaction leading to the formation of molecular hydrogen has been observed in mass spectrometric studies of ethane.

a. Decomposition of the ethane ion. If we assume that the decomposition of an ion in the radiolysis system can be deduced from its mass spectral cracking pattern, it can be concluded that a large fraction of the ethane

TABLE V. Radiolysis of ethane-1,1,1-d_3: effect of xenon.

Xe/CH_3CD_3	0[a]	1[a]	2[a]	4[a]	1[b]
	cc(NTP)/min-mol×10³				
H_2	5.96	23.77	32.26	72.98	19.04
HD	10.42	37.20	52.88	105.70	33.18
D_2	3.42	12.66	17.69	35.17	10.61
HD/D_2	3.05	2.94	2.99	3.00	3.13

Reaction temperature—16°.

[a] 3% C_2H_4 added; H_2 yield corrected for contribution from C_2H_4 decomposition.
[b] 1% NO added.

ions produced in the radiolysis decompose according to process (5)

$$CH_3CD_3^+ \rightarrow C_2H_2D_2^+ + HD. \qquad (5)$$
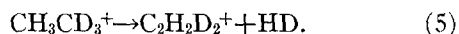
At 70 v, the relative intensity of the peak corresponding to mass 30 is about equal to the combined relative intensities of all other fragment ions, while at 12 v about 90% of the ethane ions break down according to reaction (5). In order to obtain a more accurate estimate of the distribution of the molecular hydrogens formed in the fragmentation of $CH_3CD_3^+$ at 70 v, the following decomposition steps will have to be considered:

(1) From the contribution to mass 31, it can be deduced[11] that

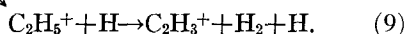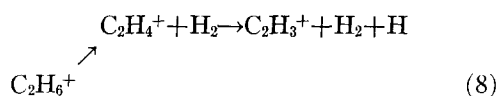$$CH_3CD_3^+ \rightarrow C_2D_3H^+ + H_2 \qquad (6)$$
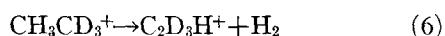
may occur with a probability which is at most one-tenth that of process (5). If one accepts the existence of an isotope effect, it may be estimated that the analogous process
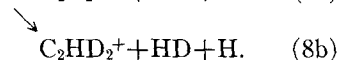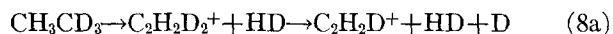
$$CH_3CD_3^+ \rightarrow C_2H_3D^+ + D_2 \qquad (7)$$
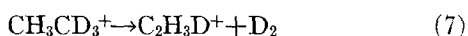
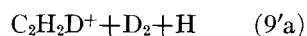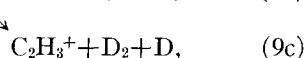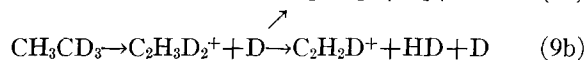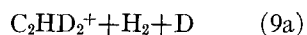will only be about half as important as process (6).

(2) $C_2H_3^+$, which is a relatively important fragment ion in the C_2H_6 spectrum, can be formed in two alternative ways which are both thermodynamically possible.[15]

$$C_2H_6^+ \begin{array}{l} \nearrow C_2H_4^+ + H_2 \rightarrow C_2H_3^+ + H_2 + H \\[1em] \searrow C_2H_5^+ + H \rightarrow C_2H_3^+ + H_2 + H. \end{array} \qquad \begin{array}{l} (8) \\[1em] (9) \end{array}$$

In view of the fact that in the case of CH_3CD_3 the ethylene ion is largely formed by the loss of a hydrogen molecule from two adjacent carbon atoms, process (8) may be written as follows:
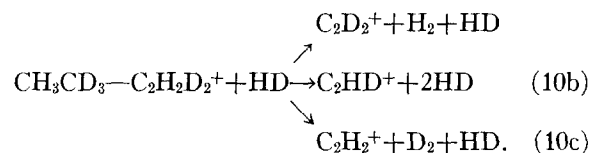
$$CH_3CD_3 \rightarrow C_2H_2D_2^+ + HD \begin{array}{l} \rightarrow C_2H_2D^+ + HD + D \\[1em] \searrow C_2HD_2^+ + HD + H. \end{array} \qquad \begin{array}{l} (8a) \\[1em] (8b) \end{array}$$

The analog of reaction (9) for CH_3CD_3 consists of six different reaction steps.

$$CH_3CD_3 \rightarrow C_2H_3D_2^+ + D \begin{array}{l} \nearrow C_2HD_2^+ + H_2 + D \\[1em] \rightarrow C_2H_2D^+ + HD + D \\[1em] \searrow C_2H_3^+ + D_2 + D, \end{array} \qquad \begin{array}{l} (9a) \\[1em] (9b) \\[1em] (9c) \end{array}$$

$$CH_3CD_3 \rightarrow C_2H_2D_3^+ + H \begin{array}{l} \nearrow C_2H_2D^+ + D_2 + H \\[1em] \rightarrow C_2HD_2^+ + HD + H \\[1em] \searrow C_2D_3^+ + H_2 + H. \end{array} \qquad \begin{array}{l} (9'a) \\[1em] (9'b) \\[1em] (9'c) \end{array}$$
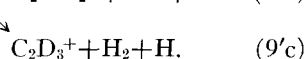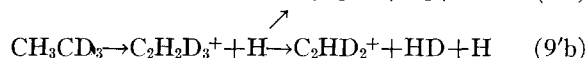
If one accepts that randomization of the hydrogen atoms in the ethyl ion is rapid,[16] and neglects the isotope effect, it can be readily seen that reactions (a), (b), (c) correspond to a calculated distribution of: 0.3, 0.6, 0.1.

(3) The acetylene ion, which is the only important ion still to be considered, may be expected to be formed in the following reaction sequence

$$CH_3CD_3 - C_2H_2D_2^+ + HD \begin{array}{l} \nearrow C_2D_2^+ + H_2 + HD \\[1em] \rightarrow C_2HD^+ + 2HD \\[1em] \searrow C_2H_2^+ + D_2 + HD. \end{array} \qquad \begin{array}{l} \\[1em] (10b) \\[1em] (10c) \end{array}$$

From the cracking patterns of CHDCHD and CH_2CD_2 it can be deduced[17] that the ethylene-d_2 ion in reaction (10) eliminates H_2, HD, D_2 with the probabilities: 0.23, 0.65, 0.12.

Using the reactions discussed above, it can be calculated from the cracking pattern that the molecular hydrogen produced in the fragmentation of CH_3CD_3 at 70 v consists of 78 to 88% HD,[18] at low electron energies, the percentage of molecular HD will be considerably higher.

b. Decomposition of neutral CH_3CD_3. As mentioned in the introduction, photochemical studies on CH_3CD_3 have clearly demonstrated[3] that the elimination of a hydrogen molecule from one carbon atom [Eq. (1) and (2)] is a relatively important process. At 1470 Å, processes (1) and (2) account for more than 80% of the total hydrogen yield. Although the effect of wavelength on the relative importance of primary processes (1), (2), and (11) is not known,

$$CH_3CD_3 + h\nu \rightarrow CH_2CD_2 + HD, \qquad (11)$$

there are indications[19] that the distribution of the molecular hydrogens at 1237 Å is not greatly different from that observed at 1470 Å. A similar independence of wavelength on the molecular hydrogen distribution has been observed in the photolysis of CH_2CD_2.[20]

c. Hydrogen formation in the radiolysis of CH_3CD_3. From the foregoing discussion we may conclude that the average molecular hydrogen distribution: 0.30, 0.52, 0.18 observed in the radiolysis of CH_3CD_3 cannot

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[15] A. Kropf, Ph.D. thesis, University of Utah (1954).

[16] A. Kropf, E. M. Eyring, A. L. Wahrhaftig, and H. Eyring, J. Chem. Phys. **32**, 149 (1960). Experimental evidence for an efficient rearrangement of the hydrogen atoms in $CH_3CD_2^+$ has been obtained recently [P. Ausloos and S. Lias, J. Chem. Phys. (to be published)].

[17] P. Ausloos and R. Gorden, Jr., J. Chem. Phys. **36**, 5 (1962).

[18] The lower value has been obtained by assuming that reaction (9) accounts for the $C_2H_3^+$ contribution in the spectral pattern of C_2H_6, while the higher value is based on the occurrence of reaction (8). Although the values for the lower and upper limits are only approximate, it can be estimated that they are reliable within 5%.

[19] The increased importance of H- and D-atom production at the shorter wavelengths (1237 Å) complicates the interpretation of the observed hydrogen distribution. (H. Okabe, unpublished results.)

[20] H. Okabe and J. McNesby, J. Chem. Phys. (to be published).

be adequately explained by either a decomposition of the ion or of the neutral excited molecule. A combination of the two modes of decomposition may, however, fit the data. A similar conclusion had to be drawn from the results obtained in the radiolysis of ethylene-d_2.[17]

It is obvious that an accurate estimate of the relative importance of molecule-ion decomposition and neutral molecule decomposition cannot be obtained from the information available at present. Needed are: (a) a complete analysis of the cracking patterns, as well as the energy distribution of the ions produced in the radiolysis, (b) quantum yields of the molecular elimination processes in the photolysis of ethane as a function of wavelength, and (c) the degree of excitation of the neutral ethane molecules in the radiolysis system.

In view of the disagreement between the molecular hydrogen distribution calculated from the mass spectral pattern of CH_3CD_3 and the one observed in the radiolysis, we may conclude that any correspondence[21-23] between the G value for molecules H_2 calculated from the cracking pattern of C_2H_6 and the experimentally determined G values, does not necessarily mean that ion decompositions are solely responsible for the radiolysis products.

The gradual decrease of the ratios HD/D_2 and HD/H_2 with increase in pressure (Table III) indicates that the higher the pressure, the more the distribution of the molecular hydrogens approaches the photochemically observed distribution. A very similar effect of pressure can be deduced from the isotopic hydrogens formed in the radiolysis of CH_2CD_2.[17] This effect may be due to a variation of the energy distribution of the secondary electrons with pressure. An alternative explanation could be based on a competition between reaction and decomposition of the ethane ion.[24]

Addition of xenon (Table V) does lead to an augmentation of the total yield of molecular hydrogen which approximates the expected increase based on the absorption characteristics. The fact that in the xenon experiments the isotopic distributions of the hydrogens are very similar to those obtained in the pure ethane runs indicates that the relative importance of ion to neutral molecule decomposition is approximately the same for both cases. In contrast to this behavior, it may be pointed out that the distributions of molecular products observed in the radiolyses of CH_2CD_2[17] and $CH_3CD_2CH_3$[25] differ considerably from those found in mixtures containing xenon.

### III. The Formation of Methane

The relative concentrations of the methanes produced in the radiolysis of an equimolar mixture of C_2H_6 and

C_2D_6 in the presence of iodine are as follows:

CH_4	CH_3D	CD_2H_2	CD_3H	CD_4
100	16.2	16.2	30.2	86.0.

This distribution is in close agreement with that obtained by Dorfman[2] in the radiolysis of C_2H_6–C_2D_6–C_2H_4 mixtures. The scavenger experiments thus clearly indicate that a considerable fraction of the methanes is formed in a molecular-detachment process.[2] Consequently, the methanes produced in the radiolysis of CH_3CD_3-scavenger mixtures should consist largely of CH_3D and CD_3H. The results of Table II indicate that in the presence of NO, I_2, and O_2 this is indeed the case. It can also be seen that the ratio CD_3H/CH_3D is roughly equal to 2, indicating the existence of a considerable isotope effect.[26]

In order to explain the formation of molecular methane in the radiolysis of ethane the following reaction has been proposed[4]:
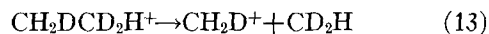
$$C_2H_3^+ + C_2H_6 \rightarrow C_3H_5^+ + CH_4. \qquad (10)$$
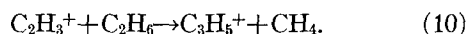
However, in view of the fact that recent photolysis studies of C_2H_6–C_2D_2 mixtures have shown that excited ethane molecules may decompose in part according to the process

$$CH_3CH_3 + h\nu \rightarrow CH_4 + CH_2, \qquad (11)$$
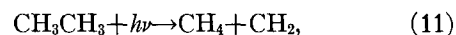
reaction (10) should not be considered as the only possible mode of molecular methane formation in the ethane radiolysis.

The results of Table IV show that an increase in temperature leads to an increase in the yields of all the methanes. This may be explained by abstraction of a hydrogen atom by a methyl radical from ethane. No obvious explanation can be given for the formation of CH_2D_2. The facts that its yield can be reduced by scavengers (Table II) and increased with temperature (Table IV) suggest that CH_2D_2 is partly formed in a radical reaction. A sequence of reactions such as:

$$CH_3CD_3^+ \rightarrow CH_2DCD_2H^+, \qquad (12)$$

$$CH_2DCD_2H^+ \rightarrow CH_2D^+ + CD_2H \qquad (13)$$

$$\rightarrow CH_2D + CD_2H^+, \qquad (14)$$

followed by abstraction reactions involving the radicals CH_2D and CD_2H would be consistent with the results on CH_3CD_3, but would not explain the formation of CH_2D_2 in the radiolysis of C_2H_6–C_2D_6 mixtures.[2]

[21] R. A. Back, J. Phys. Chem. **64**, 124 (1960).
[22] L. M. Dorfman and M. C. Sauer, Jr., J. Chem. Phys. **32**, 1886 (1961).
[23] K. Yang and P. L. Gant, J. Phys. Chem. **65**, 1861 (1961).
[24] D. P. Stevenson, Radiation Research **10**, 610 (1959).
[25] S. Lias and P. Ausloos, J. Chem. Phys. (to be published).

[26] In view of the presence of CD_4, CH_2D_2, CH_4 among the methanes, it may be expected that a fraction of the total CH_3D and CD_3H is formed in bimolecular reactions. If one makes the reasonable assumption that the yields of CH_3D and CD_3H produced by these reactions are, respectively, equal to the yields of CD_4 and CH_4, the isotope effect reaches a value of 3. The latter value depends strongly on the accuracy by which CH_4 can be determined.

TABLE VI. Radiolysis of ethane-1,1,1-d_3: ethylene formation.

Scavenger pressure	I_2 0.3 mm	NO 7.5 mm	O_2 7.5 mm
	Relative concentrations		
C_2HD_3	30.0	22.1	38.5
$C_2H_2D_2$[a]	127.5	92.4	120.0
C_2H_3D	14.7	11.5	18.3
H_2	50.0	50.8	54.2
HD	100.0	100.0	100.0
D_2	32.0	33.8	34.0

[a] $C_2H_2D_2$ consists of more than 85% CH_2CD_2. Pressure of CH_3CD_3: 250 mm at 25°C.

On the other hand, a reaction sequence such as[27]

$$D+CH_3 \rightarrow CH_3D^*, \tag{12}$$

$$CH_3D^* \rightarrow CH_2D+H, \tag{13}$$
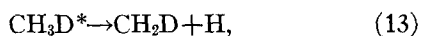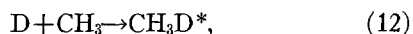
followed by an abstraction or disproportionation reaction, would explain the formation of scavengable CH_2D_2. It is reasonable to assume that the CH_2D_2 observed in the $C_2H_6-C_2D_6-I_2$ system is formed by the reactions

$$C_2H_3^+ + C_2D_6 \rightarrow CH_2D_2 + C_3D_4H^+, \tag{14}$$

$$C_2D_3^+ + C_2H_6 \rightarrow CH_2D_2 + C_3H_4D^+. \tag{15}$$
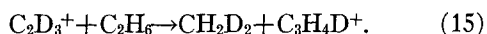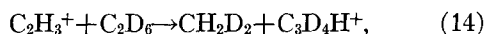
It may be pointed out that although the formation of CH_3D and CD_3H in the radiolysis of $C_2H_6-C_2D_6-I_2$ can be partly due to a hot radical effect, the production of CH_2D_2 cannot be explained this way.

IV. The Formation of Ethylene

The composition of the ethylene produced in the radiolysis of an equimolar mixture of C_2H_6 and C_2D_6 in the presence of iodine is as follows:

| C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2D_3H	C_2D_4
41.1	7.5	0.1	8.9	42.5

[27] See for instance: R. A. Marcus, J. Chem. Phys. **20**, 352 (1952).

These results indicate that a large fraction of the ethylene may be formed by a decomposition of the ethane molecule. The data of Table VI show that in the radiolysis of CH_3CD_3, ethylene-d_2 is the principal ethylene formed. The fact that the ethylene-d_2 is mainly CH_2CD_2 indicates that randomization of the hydrogen atoms in the ethane molecule or ethyl fragment, prior to decomposition, is not important.

The decomposition of neutral excited CH_3CD_3 according to reactions (16) and (17) probably accounts for a large fraction of the CH_2CD_2. If, as

$$CH_3CD_3 \rightarrow CH_2CD_2 + HD, \tag{16}$$

$$CH_3CD_3 \rightarrow CH_2CD_2 + H + D, \tag{17}$$
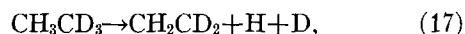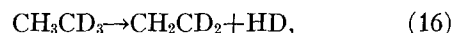
mentioned before, HD is mostly formed in the decomposition of the ethane ion, it may be concluded that process (17) is the major source of CH_2CD_2.[28] The latter reaction may eventually be written as a sequence of two stages

$$CH_3CD_3 \rightarrow CH_2CD_3^* + H, \tag{17a}$$

$$CH_2CD_3^* \rightarrow CH_2CD_2 + D, \tag{17b}$$
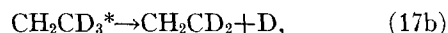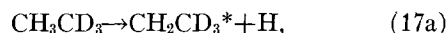
where $CH_2CD_3^*$ denote a vibrationally excited ethyl radical. Evidence for a process analogous to 17 has recently been obtained in the photolysis of ethylene,[29] and has recently been confirmed independently.[20]

Since, under all conditions $H_2 > C_2D_3H$ and $D_2 > C_2H_3D$, we conclude that the ethylidene di-radicals, if formed, do not all rearrange to form ethylene. The extent of bimolecular mixing evidenced in the $C_2H_6-C_2D_6-I_2$ system is enough to account for a large portion of the C_2D_3H and C_2H_3D formed from CH_3CD_3.

[28] $C_2H_2D_2^+$ produced in the decomposition of $CH_3CD_3^+$, will not lead to the formation of a stable CH_2CD_2 molecule. Neutralization of $C_2H_2D_2^+$ will always result in the formation of a highly excited species which will undergo decomposition into smaller fragments. There is also evidence[17] which indicates that the hydrogen atoms in the ethylene ion rearrange rapidly.

[29] M. C. Sauer, Jr. and L. M. Dorfman, J. Chem. Phys. **35**, 497 (1961).