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H₂S as a Free-Radical Interceptor in the Gas-Phase Radiolysis and Photolysis of Propane*

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The gas-phase photolysis (1236 Å) and the γ -ray radiolysis of C₈D₈ has been investigated in the presence of varying concentrations of H_2S . When 10% or more H_2S is added to C_8D_8 , the majority of the D, CD_8 , C2D3, and C2D5 radicals abstract an H atom from H2S to form HD, CD3H, C2D3H, and C2D5H, respectively. The fully deuterated molecules formed in these mixtures result from the unimolecular elimination of a stable molecule from C₈D₈ or C₈D₈⁺ and from fast bimolecular processes such as ion-molecule reactions

The mechanisms of the radiolysis and the photolysis proposed in earlier studies have been re-examined in the light of the information derived from the C₈D₈-H₂S experiments and of some additional photolysis experiments on CD₃CH₂CD₃-NO mixtures. The results indicate that the modes of decomposition of the neutral excited propane molecule are as follows:

> $C_3D_8^* \rightarrow C_2D_6 + CD_2$ $\rightarrow CD_4 + C_2D_4$ $\rightarrow D_2 + C_8 D_6$ $\rightarrow CD_3 + C_2D_5$ $\rightarrow D + C_3 D_7$.

The internally excited C2D4, C2D5, C3D6, and C3D7 species formed in these primary processes decompose to form D, CD₃, C₂D₂, C₂D₃, and C₂D₄ unless they are collisionally stabilized.

In the radiolysis of C₈D₈-H₂S mixtures, yields of the free radicals can be adequately accounted for by taking into account the modes of fragmentation of the parent ion and of the excited propane. The $C_2D_5^+$ ions are shown to react with H₂S in part by the deuteron-transfer reaction

$$C_2D_5^++H_2S\rightarrow C_2D_4+DH_2S^+.$$

The effect of pressure and the effectiveness of HI as a free-radical interceptor in the radiolysis have been examined.

INTRODUCTION

'N studies of the gas-phase radiolysis and photolysis I of alkanes, one of the more difficult problems is obtaining quantitative information concerning the production of free radicals. In the photolysis, such information is usually derived from the yields of the hydrogen and the hydrocarbon products formed when the pure alkane is photolyzed.¹ The reliability of such a derivation necessarily depends, however, on the validity of the free-radical reaction mechanism, which has been assumed to take place in the photolytic system. Although such a diagnostic analysis of the products may, in some cases, yield correct answers, especially if judicious use has been made of isotopically labeled materials, the method is rather tedious, because it should be supported by a detailed examination of changes in parameters, such as pressure, intensity, temperature, and percent conversion.

In the gas-phase radiolysis of alkanes, free radicals have, on a few occasions, been determined more directly by adding iodine²⁻⁴ to the system and measuring the alkyl iodides produced, assuming that all alkyl iodides are formed by the fast reaction

$$R \cdot + I_2 \rightarrow RI + I,$$
 (1)

where $R \cdot$ is an alkyl radical. The major drawback of this technique is that it does not provide dependable information on the production of H atoms in the radiolysis because of the difficulties involved in recovering HI as a product after radiolysis. In one study⁴ HI was added to a radiolytic system as a free-radical interceptor. The present study also includes a brief exploration of the use of HI as a free-radical interceptor in the radiolysis. Meisels et al.4 pointed out, however, that the presence of HI, as well as of I_2 , in a radiolytic system may have a profound effect on the neutralization mechanism because of the high electron-capture cross section of these additives. In view of these possible complications, and because of the difficulties involved in using either HI or I2 as free-radical scavengers in the vacuum-ultraviolet photolysis, it was decided to examine the usefulness of H2S as a free-radical interceptor. It is well known⁵⁻⁷ that H atoms and CH₃ radicals abstract a hydrogen atom from H₂S with low activation energies. Accordingly, C₃D₈ has been

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¹ J. R. McNesby and H. Okabe, Advan. Photochem. 3, 157 (1964).

² L. H. Gevantman and R. R. Williams, J. Phys. Chem. 56, 569 (1952)

⁸ W. H. T. Davison, Symposium on Reactions of Free Radicals in the Gas Phase (The Chemical Society, London, 1957), p. 151. ⁴ G. G. Meisels, W. H. Hamill, and R. R. Williams, Jr., J. Phys. Chem. 61, 1456 (1957).

⁶ B. de B. Darwent and R. Roberts, Discussions Faraday Soc. 14, 55 (1953). ⁶ N. Imai and O. Toyama, Bull. Chem. Soc. Japan 33, 652

^{(1960).} ⁷ N. Imai and O. Tayma, Bull. Chem. Soc. Japan 33, 1120 (1960).

C ₃ D ₈ Pressure (Torr)	H ₂ S %	CD4	CD₃H	C_2D_4	C ₂ D ₃ H	C_2D_6	C₂D₅H	Acety- lene	Isobu- tane	<i>n</i> - Butane	D_2	HD	${ m H}_2$
28.7ª 29.9 29.4	4.0 12.9	1.00 1.00 1.00	0.00 1.24 1.96	1.75 1.75 1.72	0.00 0.35 0.34	0.47 0.58 0.47	0.00 0.23 0.27	0.44 0.44 0.52	0.048	0.11	1.79 1.88 1.70	2.35 3.33	(0.68) (2.03)
28.7 8.6 8.2 8.8	30.2 5.6 21.6 32.8	1.00 1.00 1.00 1.00	1.93 1.22 1.59 1.76	1.72 1.72 1.72 1.69	0.36 0.33 0.38 0.41	0.47 0.53 0.52 0.47	0.27 0.10 0.17 0.18	0.47 0.65 0.55 0.61	0.031	0.064	1.79 1.72 1.67 1.98	3.71 2.64 3.12 3.69	(4.10) (0.72) (2.98) (4.78)

TABLE I. Photolysis of C₃D₈-H₂S mixtures at 1236 Å.

^a C_sD_s+5% NO.

irradiated in the presence of H_2S with the expectation that thermal free radicals and D atoms would react as follows:

$$R \cdot + H_2 S \rightarrow R H + H S,$$
 (2)

(where R. represents a D atom or deuterated alkyl radical) to give partially deuterated products, RH, containing one H atom, which can thus be easily distinguished by a simple isotopic analysis from the fully deuterated products which would be formed by unimolecular decompositions, ion-molecule reactions and "hot" radical reactions or other fast bimolecular reactions.

EXPERIMENTAL

Materials

Propane- d_8 and propane-1, 1, 1, 3, 3, 3- d_6 , which were obtained from Merck, Sharp and Dohme Ltd. of Canada, were rigorously purified by gas chromatography and by low-temperature distillation in the vacuum line. Mass spectrometric analysis indicated that propane- d_8 contained 5% C₃D₇H. From the isotopic analysis of the methane formed in the pyrolysis of the propane- $1, 1, 1, 3, 3, 3 - d_6$, it could be deduced that it consisted of 94% CD₃CH₂CD₃ and 6%CD₂HCH₂CD₃. Hydrogen sulfide and hydrogen iodide were purified by low-temperature distillation.

Irradiation and Analysis

The photolysis experiments were carried out in a reaction vessel of 300 cc which was attached to a krypton resonance lamp by means of Apiezon W wax. The lamp consisted of an L-shaped Pyrex tube (1-cm i.d.) to which a CaF_2 window was attached with Torricelli seal. One end of the lamp was immersed in liquid nitrogen during operation in order to remove water impurity released from the Pyrex wall.8 During photolysis of H₂S-alkane mixtures the CaF₂ window, which passes only the 1236-Å resonance line,⁹ became coated with sulfur, which resulted in a decrease in intensity. Therefore, after each experiment the lamp was removed from the reaction vessel and the window was cleaned with CCl₄ and repolished.

The radiolysis and analytical procedure is the same as described in earlier publications from this laboratory.¹⁰ All irradiations were carried out in the NBS 50 000-Ci cobalt-60 source.

RESULTS

Photolysis

The photolysis experiments listed in Tables I and II were carried out at intensities which fluctuated between 5×10^{14} and 2×10^{15} quanta/sec. The percent decomposition in all experiments was between 0.05% and 0.1%. An increase in conversion from 0.01% to 0.1% in the photolysis of a C₃D₈-H₂S mixture containing 12.9% H₂S did not show any variation of the relative yields of the products or of the isotopic composition of the different fractions, within experimental error. All yields given in the tables have been expressed relative to that of CD₄ (Table I) or CD₃H (Table II).

Besides the data given in Tables I and II, the following information should be provided. In the $C_{3}D_{8}$ -H₂S experiments, the yields of propylene were strongly dependent on the condition of the CaF₂

TABLE II. Photolysis of CD₃CH₂CD₃+NO(1:0.05) mixtures at 1236 Å.

Torr Pressure	CD4	$CD_{3}H$	CD ₂ CDH	$\mathrm{CD}_{2}\mathrm{CH}_{2}$	$\mathrm{CD}_3\mathrm{CDH}_2$	C_3D_6	C₃D₅H	Acetylene	Isobutane	Butane
2.0 12.5 53.4 182.0	0.083 0.083 0.07 0.064	$1.00 \\ 1.00 \\ 1.00 \\ 1.00 $	0.72 0.80 0.86 0.90	0.85 0.87 0.83 0.80	0.33 0.37 0.39 0.37	0.41 0.53 0.64 0.46	0.72 0.83 0.84 0.80	0.63 0.60 0.50 0.39	$\begin{array}{c} 0.034 \\ 0.050 \\ 0.054 \\ 0.055 \end{array}$	$\begin{array}{c} 0.077 \\ 0.12_5 \\ 0.13_5 \\ 0.13_1 \end{array}$

⁸ H. Okabe, J. Opt. Soc. Am. 54, 478 (1964).
⁹ A. H. Laufer, J. A. Pirog, and J. R. McNesby, J. Opt. Soc. Am. 55, 64 (1965).
¹⁰ P. Ausloos and S. G. Lias, J. Chem. Phys. 41, 3962 (1964).

			M/N _{CsDs}										
H ₂ S %	Ot S % scaver		CD_4	CD₃H	C_2D_4	C ₂ D ₃ H	C_2D_6	C₂D₅H	Acety- lene	Propy- lene	D_2	HD	H_2
2.5 4.5 10.7 19.0 23.4 37.7 54.4	NO:	13.0	0.28 0.28 0.28 0.27 0.27 0.27 0.26 0.28	0.61 0.62 0.64 0.009 0.62 0.61 0.71	0.22 0.23 0.24 0.25 0.27 0.29 0.35	$\begin{array}{c} 0.039\\ 0.040\\ 0.041\\ 0.008\\ 0.044\\ 0.047\\ 0.069\\ \end{array}$	0.45 0.44 0.39 0.36 0.34 0.27 0.23	$\begin{array}{c} 0.11\\ 0.12\\ 0.12\\ 0.009\\ 0.10\\ 0.088\\ 0.083 \end{array}$	0.10 0.09 0.081 0.12 0.11 0.10 0.092	$\begin{array}{c} 0.14\\ 0.14\\ 0.13\\ 0.13\\ 0.12\\ 0.092\\ 0.091 \end{array}$	0.39 0.41 0.40 0.37 0.39 0.35 0.35	0.85 0.94 0.94 0.84 0.94 0.89 0.89	$\begin{array}{c} (0.17) \\ (0.24) \\ (0.40) \\ (0.55) \\ (0.73) \\ (1.2) \\ (2.0) \end{array}$
	HI: HI: HI: NO: O ₂ :	3.2 8.4 21.8 4.9 7.3	0.30 0.32 0.38 0.29 0.29	$\begin{array}{c} 0.54 \\ 0.67 \\ 0.84 \\ 0.00 \\ 0.00 \end{array}$	$\begin{array}{c} 0.21 \\ 0.24 \\ 0.24 \\ 0.22 \\ 0.22 \\ 0.22 \end{array}$	$\begin{array}{c} 0.037 \\ 0.040 \\ 0.047 \\ 0.00 \\ 0.00 \end{array}$	$\begin{array}{c} 0.47 \\ 0.50 \\ 0.57 \\ 0.46 \\ 0.47 \end{array}$	$\begin{array}{c} 0.11 \\ 0.13 \\ 0.14 \\ 0.00 \\ 0.00 \end{array}$	0.11 0.10 0.10 0.094 0.11	0.44 0.28	0.41 0.41 0.37 0.37	0.70 0.90 0.87	(1.2) (1.8) (2.2)
Propane p	ressure:	33 ± 1 T	orr										

TABLE III. Radiolysis of C₃D₈ in the presence of H₂S, HI, NO, and O₂.

window. When the sulfur deposit on the window increased, a reduction in the yield of propylene was noted. This is true even if no H_2S is present in the reaction vessel, but a krypton lamp having a window coated with sulfur from a previous H₂S additive experiment is used. The use of such a lamp in an experiment with $CD_3CH_2CD_3$ showed that the yield of C₃D₆ is reduced while that of C₃D₅H remains unchanged. The yields of all other products are unaffected by the condition of the window. In order to avoid this complication, a few C₃D₈-H₂S experiments at a total pressure of 30 Torr were carried out at very short conversion (0.01%) using a newly polished CaF₂ window. The propylene yield in these experiments was the same as that observed in the photolysis of a C_3D_8 -NO mixture, 1.4 times the yield of CD_4 .

The propylene fraction in the C_3D_8 -H₂S experiments contained a maximum of about 4% C_3D_6H , the remainder being C_3D_6 . It should also be noted that in the photolysis of CD₃CH₂CD₃-NO mixtures, no other propylenes were observed except the ones listed in Table II.

Allene or methyl acetylene may be products, but could not be analyzed in the presence of propane on the chromatographic columns used in this investigation.

Radiolysis

The radiolytic products given in Tables III and IV are expressed as molecules (X) per ion pair formed by absorption of ionizing radiation by C_3D_8 , and are designated as $M(X)/N_{C_3D_8}$. Saturation ion currents were only measured for C_3D_8 -NO mixtures, containing 5% NO. The tentative assumption is made that addition of H₂S or HI to C_3D_8 has no effect on the ionization or excitation of C_3D_8 . It is shown in the Discussion that there are indications that this is actually so in the case of the C_3D_8 -H₂S mixtures but not for the C_3D_8 -HI mixtures.

Ninety-five percent of the propylene formed in the C_3D_8 -H₂S experiments was fully deuterated.

DISCUSSION

Before a detailed discussion of the photolytic and radiolytic reaction mechanism is undertaken, a few general remarks concerning the efficiency of H_2S and HI as free-radical interceptors are in order.

Because the methyl radical is the only alkyl radical for which the rates of the H abstraction reactions from H_2S , HI, and propane have been determined with some accuracy, it is convenient to consider the reactions of this radical in some detail.

Imai and Toyama^{6,7} obtained a value of $2.5 \times 10^{11} \exp(-2600/RT)$ mole⁻¹ cc sec⁻¹ for the rate of Reaction (3):

$$CD_3+H_2S\rightarrow CD_3H+HS.$$
 (3)

In addition, Jackson, McNesby, and Darwent¹¹ reported a rate constant of $3.2 \times 10^{11} \exp(-11.100/RT)$

TABLE IV. Radiolysis of C₃D₈-H₂S mixtures. Effect of pressure.

	$M/N_{C_3D_5}$											
Pressure C ₃ D ₈ (Torr)	H₂S %	CD₄	CD₃H	C_2D_4	C₂D₃H	C_2D_6	C₂D₅H	Acety- lene	Propy- lene	D_2	HD	$\rm H_2$
5 33.5 425	8.4 10.7 9.4	0.31 0.28 0.26	0.63 0.64 0.64	0.27 0.24 0.22	0.040 0.041 0.034	0.42 0.39 0.38	0.11 0.12 0.100	0.13 0.081 0.049	0.13 0.100	0.39 0.40 0.37	0.88 0.94 0.95	(0.34) (0.40) (0.35)

¹¹ W. M. Jackson, J. R. McNesby, and B. de B. Darwent, J. Chem. Phys. 37, 1610 (1962).

 $mole^{-1}$ cc sec⁻¹ for the abstraction of a secondary D atom from $CH_3CD_2CH_3$, and it can be surmised from their data that the activation energy for the abstraction of a primary deuterium atom from C₃D₈ is as high as 12.5 kcal/mole. It may thus be concluded that if the experiments are carried out around 20 C°, the rate of Reaction (3) is about 2.5×10^5 times higher than that of the abstraction reaction

$$CD_3 + C_3D_8 \rightarrow CD_4 + C_3D_7, \tag{4}$$

so that when about 0.5% H₂S is added to C₃D₈, 99.9% of the thermal methyl radicals will react with H₂S according to Reaction (3), provided that reaction of the methyl radical with other alkyl radicals, hydrogen atoms, or HS radicals can be excluded. In a homogenous system, reactions between the smaller reactive radicals can be prevented by simply keeping the intensity sufficiently low, or by having a high enough concentration of H₂S in the system. The HS radical will then react with HS or with the larger alkyl radicals which react more slowly with H₂S.

That H₂S is indeed quite efficient in intercepting D atoms, CD₃, C₂D₃, and C₂D₅ radicals is seen in the radiolysis of C₃D₈-H₂S mixtures (Table III). There is apparently no significant increase in the yields of HD, CD₃H, C₂D₃H, and C₂D₅H when the H₂S percentage is increased from 2.5 to 10.7, indicating that the addition of 2.5% H₂S is sufficient to have the majority of these radicals react according to Reaction (2). The small increase in the yields of the partially deuterated products which is noticed when the H₂S concentration is augmented may be due in part to the fact that some of the excited radicals which are formed in the primary fragmentations can only be intercepted at the higher concentration of H₂S.

In the photolysis, however, much higher percentages of H₂S are needed than in the radiolysis to intercept the radicals effectively. It is seen in Table I that at least 10% H₂S must be added to C₃D₈ before the ratios¹² CD_3H/CD_4 , C_2D_5H/C_2D_6 , C_2D_3H/C_2D_4 , and HD/D_2 become invariant with the percentage of H₂S. The fact that H₂S is a less-efficient interceptor in the photolysis than in the radiolysis is most likely due to the high extinction coefficient of C₃D₈, which is 108 atm⁻¹·cm⁻¹ at 1470 Å¹³ and probably higher at 1236 Å. There is consequently a very high steady-state concentration of free radicals in the neighborhood of the CaF₂ window.

Of course, in both the radiolysis and photolysis, H₂S itself absorbs a fraction of the radiation. The extinction coefficient of H₂S at 1236 Å has not been

measured, but in view of the fact that the yield of H_2 at the highest H_2S/C_3D_8 ratios is comparable to that of the deuterium labeled products, it may be surmised that the extinction coefficient of H₂S is comparable to that of C₃D₈. The excited H₂S molecules will probably decompose to form H atoms with excess kinetic energy, so that some of the HD formed at high H₂S concentrations may be produced by the abstraction reaction

$$H^* + C_3 D_8 \rightarrow HD + C_3 D_7, \qquad (5)$$

where H* represents a "hot" H atom. However, Reaction (5) is unimportant in the radiolysis and in the photolysis, since the yield of HD does not increase significantly as the percentage of H₂S is increased above 10%.

Similar remarks can be made concerning the use of HI as a radical scavenger in the radiolysis. O'Neal and Benson¹⁴ reported a value of 1.3 ± 0.5 kcal for the difference in activation energy E_6 - E_7 , corresponding to reactions

$$CH_3 + HI \rightarrow CH_4 + I,$$
 (6)

$$CH_3+I_2 \rightarrow CH_3I+I.$$
 (7)

Thus, if one accepts a value of 0.5 kcal¹⁵ for the activation energy of Reaction (7), Reaction (6) is at least 10^5 times faster than Reaction (4). It is clear, however, that when HI is used as a free-radical interceptor the experiments must be carried out at short conversions, since reaction of the alkyl radicals with the product I_2 can be several times faster than Reaction (6). The results given in Table III, indicate that when 3.2% HI are added to C3D8, ion pair yields of CD3H, C₂D₅H, C₂D₃H, and HD are surprisingly close to those obtained in the radiolysis of C3D8-H2S mixtures. In contrast with the C₃D₈-H₂S experiments it is seen that when the concentration of HI is increased the yields of most products, expressed as $M/N_{C_3D_8}$, are augmented. This would indicate that energy partition in the C_3D_8 -HI mixtures may not simply be derived from the electron fraction of the two components. For a heavy atom such as iodine, the Auger electrons may play an important role.16

It is now of interest to reconsider the photolytic and radiolytic mechanisms proposed in earlier studies, making use of the additional information available from the C₃D₈-H₂S experiments.

Photolysis

"Molecular" Elimination Processes

On the basis of recent studies^{13,17} and some additional results on the photolysis of CD₃CH₂CD₃-NO mixtures

¹⁴ E. O'Neal and S. W. Benson, J. Chem. Phys. 36, 2196

(1962). ¹⁵ H. C. Andersen and G. B. Kistiakowski, J. Chem. Phys. 11,

¹⁶ A. J. Swallow, Discussions Faraday Soc. 36, 273 (1963).
 ¹⁷ P. Ausloos, S. G. Lias, and I. B. Sandoval, Discussions Faraday Soc. 36, 66 (1963).

¹² The partially deuterated product yields are compared with the fully deuterated product yields because at high H_2S concentrations, the relative yields of D_2 , CD_4 , C_2D_6 , C_2D_2 , and C_2D_4 are identical to those obtained in the photolysis of a C₈D₈-NO mixture, thus indicating that H₂S does not affect the primary fragmentation processes which, as is pointed out later in the Discussion are responsible for the formation of these fully deuterated products.

¹³ H. Okabe and J. R. McNesby, J. Chem. Phys. 37, 1340 (1962).

presented in this paper (Table II), the following molecular elmination processes may be expected to occur in the photolysis of C_3D_8 :

$$C_3D_8 \rightarrow C_2D_6 + CD_2, \tag{8}$$

$$\rightarrow CD_4 + CD_3CD,$$
 (9)

$$\rightarrow CD_4 + CD_2CD_2,$$
 (10)

$$\rightarrow D_2 + CD_3 CCD_3. \tag{11}$$

The fact that the relative yields of the fully deuterated products in the C₃D₈-H₂S mixtures are the same as those in the photolysis of a C_3D_8 -NO mixture (Table I) demonstrates that addition of H2S does not significantly affect the relative probabilities of the different primary processes.

Process (8) is justified on the basis of the fact that in the photolysis of C₃H₈-C₃D₈-NO mixtures, ethane consists entirely of C2D6 and C2H6. Furthermore, CD_3CDH_2 is the only ethane formed in the photolysis of CD₃CH₂CD₃-NO mixtures.¹⁷

$$CD_3CH_2CD_3 \rightarrow CD_3CH_2D + CD_2.$$
 (12)

At 1236 Å, about 125 kcal must be partitioned between the two fragments produced in Process (12), so that the CD_2 radicals may be rather highly excited. Isobutane and *n*-butane, which are both formed in the NO scavenged system, may be ascribed to the insertion of methylene into propane. The gradual increase in the yields of these two products relative to that of "molecular" methane or ethane can be ascribed to a collisional deactivation of the internally excited butane molecule. Because, at the higher pressures, the yield of the butanes seems to level off to a value which is only 50%of that of "molecular" ethane, it may be surmised that methylene can also undergo other reactions such as abstraction.¹⁸ It is of interest to note that, in agreement with earlier studies in which diazomethane¹⁹ was used, insertion of methylene into the secondary C-H bond occurs with a probability which is higher than insertion in the primary C–D bond by about 20%.

Processes (9) and (10) were originally proposed^{13,17} to account for the fact that methane in the photolysis of C₃H₈-C₃D₈ mixtures consists mainly of CH₄ and CD₄. Experiments carried out with CD₃CH₂CD₃ and CH₃CD₂CH₃ indicate that at 1236 Å, Process (9) accounts for at least 85% of the "molecular" methane.17 It should be noted that the occurrence of Process (9) is particularly well founded by the observation that in the photolysis of CD₃CH₂CD₃-NO mixtures (Table II), CD₃H, which would be formed by the analogous reaction

$$CD_3CH_2CD_3^* \rightarrow CD_3H + CD_3CH$$
 (13)

becomes equal to the yield of CD₂CDH at high pressures, where the majority of the internally excited CD₂CDH' molecules formed in the rearrangement process

$$CD_3CH \rightarrow CD_2CDH'$$
 (14)

are collisionally stabilized.

The occurrence of Process (11) at 1470 Å is established by the facts that, at that wavelength, the hydrogen is formed by a molecular elimination process,¹³ and the hydrogen formed in the photolysis of CH₃CD₂CH₃ and CD₃CH₂CD₃ consists mainly of D₂ and H₂, respectively.^{13,17} Furthermore, it would be difficult to explain the formation¹⁷ of C₃D₆ as the major propylene formed at 1470 Å by a mechanism other than

$$CD_3CH_2CD_3^* \rightarrow CD_3CCD_3 + H_2,$$
 (15)

$$CD_3CCD_3 \rightarrow C_3D_6'$$
, (16)

$$C_{3}D_{6}' + M \rightarrow C_{3}D_{6} + M, \qquad (17)$$

where C_3D_6' is an internally excited propylene molecule.

At 1236 Å, the situation is obviously more complex. Only 29% of the total hydrogen formed in the photolysis of CD₃CH₂CD₃ is H₂ and a fraction of that is probably formed by bimolecular processes, as is indicated by the presence of HD in the photolysis of C₃D₈-C₃H₈-NO mixtures.¹⁷ Hydrogen is, however, eliminated from the center carbon atom, as is indicated by the presence of C_3D_6 in the propylene fraction formed in the photolysis of CD₃CH₂CD₃ (Table II). Reaction (17) is substantiated by the observation that the relative yield of C_3D_6 increases gradually with an increase in pressure up to 53.4 Torr.²⁰ It may be surmised that, at the lower pressures, internally excited C₃D₆ species decompose further to yield smaller fragments such as acetylene. Although this is consistent with the observation that there is a gradual pressure, it should be noted that acetylene may also result from the secondary decomposition of other fragments.

It may be noted that at 1236 Å, there is no evidence for the elimination of a D₂ molecule from the primary carbon atom of CD₃CH₂CD₃. The CDCH₂CD₃ radical, which would result from such a process would be expected to rearrange, at least in part, to propylene- d_4 , but no propylene- d_4 was observed at pressures ranging from 2 to 182 Torr. It should finally be noted that elimination of an HD molecule from two adjacent carbon atoms

$CD_3CH_2CD_3^* \rightarrow CD_2CHCD_3 + HD$, (18)

is a likely process at 1236 Å. Propylene- d_5 and HD

decrease in the yield of acetylene with increase in

¹⁸ H. M. Frey, Proc. Chem. Soc. 1959, 318.

¹⁹ H. M. Frey, J. Am. Chem. Soc. 80, 5005 (1958).

²⁰ It is believed that the drop in the yield of C_8D_6 at pressures above 53.4 Torr (Table II) is due to the removal of CD_8CDCD_9 by reaction on the CaF₂ window (see Results).

account for more than 60% and 50% of the propylene and hydrogen¹⁷ fractions, respectively. It is also of interest to note that there is no effect of pressure on the yield of C_3D_5H relative to that of "molecular" methane (Table II).

Free-Radical Formation

The results of Table I indicate that CD_3 is the major alkyl radical produced in the photolysis of C_3D_8 . Because of the presence of C_2D_5 in the photolysis of C_3D_8 -H₂S mixtures, it can be concluded that a fraction of the CD_3 radicals is formed by the dissociative process

$$C_3 D_8^* \rightarrow C D_3 + C_2 D_5. \tag{19}$$

The actual importance of this process is, however, difficult to evaluate because C_2D_5 radicals formed in processes such as (19) are vibrationally excited, and may thus be expected to decompose further. The CH₂CD₂ formed in the photolysis of CD₃CH₂CD₃-NO mixtures (Table II) may, for instance, be ascribed to the sequence of reactions:

$$CD_3CH_2CD_3^* \rightarrow CD_3 + CH_2CD_3',$$
 (20)

$$CH_2CD_3' \rightarrow D + CH_2CD_2.$$
 (21)

Reactions (20) and (21) are, however, indistinguishable from the reaction sequence

$$CD_3CH_2CD_3^* \rightarrow D + CD_2CH_2CD_3',$$
 (22)

$$CD_2CH_2CD_3' \rightarrow CD_2CH_2 + CD_3,$$
 (23)

unless experiments are carried out at pressures which are sufficiently high that CD_3CH_2 and/or $CD_3CH_2CD_2$ are collisionally stabilized. It is of interest to note that there is a small decrease in the yield of CH_2CD_2 in the photolysis of $CD_3CH_2CD_3$ -NO mixtures when the pressure is raised from 12.5 to 182 Torr. Furthermore, the C_3D_8 -H₂S experiments in Table I indicate that there is a corresponding increase in the relative yield of C_2D_5H . It is clear, however, that pressures well above 182 Torr are required to stabilize the majority of the ethyl and/or propyl radicals formed in the primary process.

The fact that in the $C_3D_8-H_2S$ experiments, the yield of CD_3H is considerably higher than that of $[C_2D_5H+(C_2D_4-CD_4)]$ indicates that Processes (20) and (23) do not entirely account for all methyl radicals formed. However, if one takes into account the yields of C_2D_3H and C_2D_2 , a good material balance is obtained between the C_1 and C_2 products. It can indeed be seen that at high H₂S concentrations, CD_4+CD_8H is equal to 2.93, while a value of 2.82 is obtained for the sum $C_2D_4+C_2D_3H+C_2D_5H+C_2D_2$. Reaction of CD_2 with C_3D_8 may account for the slight excess of C_1 species. Although the material balance demonstrates that one CD_3 radical is formed for each C_2D_3 radicals and the acetylene remain in question. The photolysis of CD₃CH₂CD₃-NO mixtures (Table II) clearly indicates that acetylene is not exclusively formed by decomposition of the ethylidene radical formed in Process (13), because at elevated pressures where C_2D_3H becomes equal to CD₃H, acetylene is still an important product. Furthermore, although decomposition of the ethylene formed in Processes (21) and (23) cannot be excluded as a source of acetylene, it is unlikely that the ethylene formed in such secondary fragmentations would still retain enough energy to decompose further, especially after about 90 kcal are expended in the primary process. Secondary decomposition of the propylene formed by elimination of a hydrogen molecule from two adjacent carbon atoms is, however, a likely source of C_2D_2 and C_2D_3 especially since at 1236 Å the propylene could be formed with up to 190-kcal excess energy.

The relatively large yield of HD in the photolysis of C_3D_8 -H₂S mixtures (Table I) indicates that D atoms play an important role in the photolysis of C_3D_8 . It is, however, not possible to establish the mode of formation of the D atoms from the data reported in this paper, since the formation of many of the products may involve the elmination of either a D₂ molecule or of two D atoms. For instance, propylene is probably formed by elimination of D₂ from C_3D_8 as well as by the removal of two D atoms in two consecutive processes. Products such as C_2D_2 and C_3D_4 can also be formed in many different ways.

It is finally of interest to note that summation of all carbon and deuterium atoms of the products formed in the photolysis of a mixture of C_3D_8 with 30.2% H₂S yields the material balance $C_3D_{8,4}$. If the reasonable assumption is made that C_3D_4 , which was not measured, is formed with a yield comparable to that of acetylene, the value for the D/C ratio becomes, within experimental error, equal to that of propane. It may thus be surmised that stable propyl radicals are formed only in very small yields in the primary process.

Radiolysis

Formation of Methane

The results given in Table I, which lists the yields of products formed when C_3D_8 is irradiated in the presence of NO, O₂, and varying concentrations of H₂S, show that CD₃H is a product in experiments where H₂S is an additive. When NO is added to C_3D_8 -H₂S mixtures, however, this product disappears, indicating that its precursor is a free radical. Thus, one may conclude that the CD₃H is formed by Reaction (3). The results of Table I also show that the yield of CD₄ obtained in the radiolysis of C_3D_8 -H₂S mixtures is independent of the amount of H₂S added to C_3D_8 , and that it is furthermore equal to the yield of CD₄ observed in the radiolysis of C_3D_8 -NO, C_3D_8 -O₂, and C_3D_8 -H₂S-NO mixtures. Since the methane produced in the radiolysis of propane in the presence of O2, NO, or iodine is formed mainly by the unimolecular decomposition of the parent ion

$$C_3D_8^+ \rightarrow CD_4 + C_2D_4^+, \qquad (24)$$

and of the neutral excited propane molecule¹⁷ [Processes (9) and (10)], this observation indicates that the addition of H₂S has little effect on the primary fragmentation of the parent ion or of the neutral excited molecule. Since it may be expected that the CD₃ radicals are formed mainly by the parent ion fragmentation processes

$$C_3D_8^+ \longrightarrow CD_3 + C_2D_5^+, \qquad (25)$$

$$CD_3 + C_2D_3^+ + D_2,$$
 (26)

it is thus not surprising that the yields of CD₃H are also, within experimental error, independent of the concentration of H₂S in the system.

Assuming that all CD₃ radicals produced by fragmentation of the parent ion are formed in Processes (25) and (26), it can be estimated from the sum $M(C_2D_5^++C_2D_3^+)N_{C_3D_8}$ as derived²¹ from the 70-eV mass-spectral cracking pattern of C3D8 that the ion pair yield of CD₃ radicals resulting from the fragmentation of the parent ion^{21} is 0.48. It is true that the actual yields of these ions measured in the mass spectrometer cannot be expected to correspond to yields formed at the much higher pressures of the radiolytic system, but since $C_2D_3^+$ is apparently primarily formed by a secondary fragmentation

$$C_2 D_5^+ \rightarrow C_2 D_3^+ + D_2 \tag{27}$$

it may be expected that an increase in pressure tends to increase the contribution of the $C_2D_5^+$ ion at the expense of the $C_2D_3^+$ ion,^{17,22} so that the sum of the two remains constant. There is evidence¹⁷ that the ion pair yield of the primary decomposition 25 is diminished appreciably only at pressures above one atmosphere. The foregoing is substantiated by the fact that an ion-pair yield of 0.5 can actually be derived for $M(C_2D_5^++C_2D_3^+)/N_{C_3D_8}$ in the radiolysis of a $C_3D_8^-$ C₃H₈-NO mixture at 30 Torr,²³ assuming that essentially all $C_2D_5^+$ ions and 70% of the $C_2D_3^+$ ions^{24,25} undergo hydride-ion transfer reactions with propane.

The latter value, which is in satisfactory agreement with the one derived from the mass spectrometric cracking pattern, provides us with a dependable estimate of the number of CD₃ radicals formed by fragmentation of the parent ion. The difference between this value and the measured ion pair yield of CD₃H can be tentatively ascribed to decomposition of the neutral excited propane molecule.

Formation of Ethane

The C₂D₆ formed in the radiolysis of C₃D₈ in the presence of a radical scavenger is, in contrast to the CD₄ discussed above, mainly formed by bimolecular reactions such as²³⁻²⁵:

$$C_2D_5^+ + C_3D_8 \longrightarrow C_2D_6 + C_3D_7^+, \qquad (28)$$

$$C_2D_4^+ + C_3D_8 \rightarrow C_2D_6 + C_3D_6^+,$$
 (29)

$$C_2D_3^+ + C_3D_8 \longrightarrow C_2D_6 + C_3D_5^+.$$
(30)

From results obtained in an earlier study²³ it can be estimated that at a pressure of 30 Torr, about 80% of the total ethane is formed by Reaction (28), about 10% by Reaction (29), and the remaining 10%, by Reaction (30) and the unimolecular process (8). At more elevated pressures, the contribution to the total ethane yield of Reaction (29) relative to Reactions (28) and (30) becomes smaller because of the diminishing importance^{17,23} of the fragmentation process (24).

When 2.5 to 4.5% H₂S is added to C₃D₈, the C₂D₆ yield is quite close to that obtained in the oxygen or NO scavenged system. However, when the H₂S concentration is increased, there is a gradual decrease in the yield of C_2D_6 . It is apparent, therefore, that the $C_2D_5^+$ ion, which is the major precursor of C_2D_6 , reacts with H₂S to form products other than ethane. The occurrence of the proton-transfer reaction

$$C_2D_5^+ + H_2S \rightarrow C_2D_4 + H_2SD^+$$
(31)

could, in part, account for the experimental observations. Reaction (31), which is exothermic by at least 19 kcal/mole assuming that the heat of formation of H_3S^+ is less than 187 kcal/mole,²⁶ could also account for the increase in the yield of C_2D_4 with increasing H_2S concentration. It should be noted, however, that the drop in the yield of C_2D_6 is not entirely compensated for by the increment in the yield of C_2D_4 . From the results given in Table III, it can actually be derived that roughly one-third of the ethyl ions which are removed from the system by H_2S take part in Reaction (31). The remainder may undergo an alternative reaction such as:

$$C_2H_5^+ + H_2S \rightarrow C_2H_5S^+ + H_2. \tag{32}$$

The above reaction seems plausible in view of the fact

²¹ The major fragment ions produced by the decomposition of the $C_3D_8^+$ ion in the mass spectrometer at an ionizing energy of 70 eV, and their relative abundances, expressed as fractions of the total ionization, are: CD_3^+ , 0.027; $C_2D_3^+$, 0.134; $C_2D_4^+$, 0.205; $C_2D_5^+$, 0.347; $C_3D_5^+$, 0.029; $C_3D_6^+$, 0.012; $C_3D_7^+$, 0.041; $C_3D_8^+$, 0.084. All values have been corrected for the isotopic abundance of C13 and for insufficient deuteration of the C3D8 sample used for the determination.

 ²² M. Vestal, A. L. Wahrhaftig, and W. H. Johnson, "Theoretical Studies in Basic Radiation Chemistry," ARL 62-426, September 1962. Available from the Office of Technical Services, U.S.

Department of Commerce. ²³ P. Ausloos and R. Gorden, Jr., J. Chem. Phys. 41, 1278 (1964).

²⁴ G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G.

Volpi, J. Chem. Phys. 41, 2998 (1964). ²⁵ M. S. B. Munson, J. L. Franklin, and F. H. Field, J. Phys. Chem. 68, 3098 (1964).

²⁶ F. W. Lampe, J. L. Franklin, and F. H. Field, Progr. Reaction Kinetics 1, 69 (1961).

that the analogous reaction between a methyl ion and H₂S has been reported to occur in the mass spectrometer.27

The yield of C₂D₅H, which remains within experimental error unchanged from 2.5% to 10% H₂S can be ascribed to the C₂D₅ radical. It should be noted that when NO is added to a C₃D₈-H₂S mixture, the yield of C₂D₅H is reduced by more than a factor of ten while that of C₂D₆ remains unchanged. According to the 70eV cracking pattern, the ion pair yield of CD_3^+ which would correspond to that of the C_2D_5 radical

$$C_3D_8^+ \rightarrow CD_3^+ + CD_3CD_2$$
 (33)

is only 0.027, and this is a maximum value for $M(C_2D_5)/N_{C_3D_8}$ since it is possible that a fraction of the C_2D_5 radicals are formed with enough excess kinetic energy that they will undergo further decomposition. Also, at a pressure of 30 Torr, high-energy process such as (33) may be less important than in the mass spectrometer. Thus, C_2D_5 radicals corresponding to an ion pair yield of about 0.09 must be accounted for by processes other than 33. The hydride-transfer reaction

$$C_2D_4^+ + C_3D_8 \rightarrow C_2D_5 + C_3D_7^+,$$
 (34)

which has recently been reported^{24,25} to occur in the mass spectrometer, may be expected to contribute to the formation of C_2D_5 . From the results of an earlier study²³ it can be estimated that the ion-pair yield which can be attributed to Reaction (29) is about 0.04. Taking a value²⁵ of 1.73 for the ratio k_{34}/k_{29} , an ion pair yield of 0.07 can be ascribed to the C_2D_5 radicals formed by Reaction (34). The ethyl radicals still unaccounted for, which correspond to an ion-pair yield of approximately 0.02 ± 0.01 could then be ascribed to the decomposition of neutral excited propane. The fact that $M(C_2D_4^+)/N_{C_3D_8}$, thus inferred from the product yields ascribed to Reactions (29) and (34), is only 0.11, as compared to a value of 0.2 which can be derived from the 70-eV mass spectral cracking pattern, is not too surprising if one considers that disproportionation processes such as (24) occur with a low-frequency factor which makes them more strongly pressure dependent than a C-H or C-C cleavage.^{10,17} This is also corroborated by the results given in Table IV which demonstrate that an increase in pressure from 5 to 425 Torr results in a decrease of $M(CD_4)/N_{C_3D_8}$, while $M(CD_3H)/N_{C_3D_8}$ $N_{C_{3}D_{8}}$ remains essentially constant.

Formation of Ethylene

The formation of C_2D_3H in the radiolysis of C_3D_8- H₂S mixtures indicates that C₂D₃ radicals are produced in the radiolysis of propane. The facts that the yield of C_2D_3H undergoes only a minor increase when the H_2S concentration is increased²⁸ from 2.5 to 10.7%, and that NO quenches its formation by 80%, indicate that C_2D_3H is formed mainly by Reaction (35).

$$C_2D_3 + H_2S \rightarrow C_2D_3H + HS. \tag{35}$$

According to the mass-spectral cracking pattern, C₂D₃ radicals are not produced by the fragmentation of the parent ion. Therefore, it may be tentatively assumed that the decomposition of neutral excited propane molecules accounts for the presence of these radicals in the radiolytic system.

Formation of Propylene and Acetylene

It can be seen in Table III that the propylene yield is consistently lower in the C₃D₈-H₂S experiments than in the radiolysis of C₃D₈-NO mixtures. This is probably due to the fact that, as noted before, 17,29 part of the propylene does originate from the sec- $C_3D_7^+$ ion. Because this ion is not known to react with propane, it may be expected that it will react with H_2S , even when H_2S is present in very small percentage. However, the proton-transfer reaction between the sec-C₃D₇⁺ ion and H₂S is endothermic, if one accepts a value²⁶ of 187 kcal/mole for $\Delta H_f(H_3S^+)$. It is actually shown in a later study on C₄D₁₀-H₂S mixtures that although the yield of C_3D_8 , which originates mainly from the propyl ion, is diminished at high H₂S concentrations, there is no corresponding increase in the yield of propylene. The residual propylene in the C_3D_8 -H₂S experiments can thus be tentatively ascribed to the hydride-ion transfer reaction

$$C_3D_5^+ + C_3D_8 \rightarrow C_3D_6 + C_3D_7^+ \tag{36}$$

and to the decomposition of neutral excited C₃D₈. The gradual reduction in $M(C_3D_6)/N_{C_3D_8}$ at high H₂S concentrations can be tentatively ascribed to reaction of the $C_3D_5^+$ ion with H_2S .

The formation of acetylene in the radiolysis of C₃D₈ remains to be accounted for. The fact that its yield is independent of the amount of added H₂S, and is, within experimental error, the same when H₂S is replaced by either HI, NO, or O₂ strongly indicates that it is formed in the fragmentation of an internally excited neutral species. It is of interest that an increase in pressure (Table IV) reduces the yield of acetylene in much the same way as in the photolysis (Table II).

²⁷ F. H. Field and F. W. Lampe, J. Am. Chem. Soc. 80, 5583 (1958).

²⁸ It may be surmised that the increase of C₂D₃H at higher H₂S concentrations, which parallels the increase in C₂D₄, may be due to an ionic process such as $C_2D_5^++H_2S\rightarrow C_2D_3H+D_2HS^+$. The residual yield of C₂D₈H formed in the C₈D₈-H₂S-NO experi-²⁹ J. H. Futrell and T. O. Tiernan, J. Chem. Phys. 37, 1694

^{(1962).}

Formation of Hydrogen

It can be noted that the yield of D_2 is, within experimental error, the same in all experiments listed in Table III. This is not surprising in view of the fact that this nonscavengable hydrogen must be largely formed by the elimination of D_2 molecules from the parent ion and neutral excited molecule as well as from fragments thereof.¹⁷ Of interest are the high values of M(HD) $N_{C_3D_8}$ which are very nearly independent of the percentage of H₂S. On the basis of the information now available concerning the modes of decomposition of neutral excited C₃D₈ and of the role of neutral excited molecules in the radiolysis,23 it can be estimated that roughly 20 to 30% of the HD yield can be ascribed to D atoms originating from the unimolecular decomposition of C₃D₈. On the other hand, elimination of D atoms from the parent ion occurs with a low probability.^{21,30} Therefore, the origin of most of the HD remains unknown; the most likely sources of this HD are one or more bimolecular processes probably involving relatively unreactive ions which are the only species which have not yet been taken into consideration in the radiolytic mechanism. A major ion which reacts at very low rate with propane is the $C_3D_7^+$ ion which is formed mainly as a reaction product in the hydride ion transfer reaction between most fragment ions and propane. When H₂S is added to the system, even in small concentration, all $C_3D_7^+$ may be expected to react with H₂S. Although the exact nature of the ion molecule reaction is not known, it may be surmised that the occurrence of such a process will eventually result in the formation of D atoms or HD.

Formation of Neutral Excited Molecules in the Radiolysis

In view of the uncertainty concerning the modes of formation of acetylene and propylene, the present data on the radiolysis of C_3D_8 -H₂S mixtures do not provide us with a much more accurate evaluation for γ (number of neutral excited molecules per ion pair) than that derived in a previous study.²³ However, because C_2D_3 radicals and acetylene were not taken into consideration it may be surmised that the earlier estimate of 0.3 ± 0.1 for γ may have to be revised upward to 0.4 ± 0.1 .

It is gratifying to note that the relative yields of the product radicals and molecules attributed to neutral excited molecule decomposition as derived in this and in earlier studies^{17,28} do not depart drastically from the product distribution observed in the photolysis.

³⁰ A. Kropf, E. M. Eyring, A. L. Wahrhaftig, and H. Eyring, J. Chem. Phys. **32**, 149 (1960).