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Pulse Radiolysis of Methane*

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The pulse radiolysis of methane has been studied in the absence and presence of electron scavengers such as SF_6 and CD_3I and positive ion scavengers such as i-C_4D_{10} in order to define the role of the intermediates H, C, CH, CH_2, CH_3, CH_5^+, and $C_2H_5^+$ in product formation. The dose rate was varied from 0.68 to 15.2×10^{19} eV/g-s, the dose (number of pulses) was varied, and the duration of the pulse was changed from 3 ns to 100 ns. The variation of the yields of the ethylene and ethane products with dose is explained by the reaction of H-atoms with accumulated ethylene product. The fast reacting C, CH, and $^1CH_2$ species insert into methane to form acetylene, ethylene, and ethane products, but all of the reactions of these species cannot be completely specified since they may originate in upper electronic states, whose reactions with methane are unknown. Product formation by the slow reacting $^3CH_2$ and CH_3 radicals is also examined; for instance, evidence is presented for the occurrence of the reaction: $^3CH_2 + CH_3 \rightarrow C_2H_4 + H$. Results indicate that the ions CH_5^+ and $C_2H_5^+$ undergo neutralization mainly through the processes

$$CH_5^+ + e \rightarrow CH_4 + H$$

$$C_2H_5^+ + e \rightarrow (C_2H_4)^* + H \rightarrow C_2H_2 + H + H_2 (2H).$$

When i-C_4D_{10} is added, a fraction of the CH_5^+ and $C_2H_5^+$ react with the additive rather than undergo neutralization. A calculation demonstrates that the fraction of ions undergoing reaction with a given concentration of i-C_4D_{10} can be correctly predicted by assuming that the rate constant for neutralization of CH_5^+ and $C_2H_5^+$ is the same as that determined recently for the t-butyl ion.

Key words: Electron scavengers; gas phase; ion-molecule reactions; methane; neutralization; pulse radiolysis.

1. Introduction

The gas phase radiolysis of methane has been investigated extensively [1],[1] but is still not entirely understood. Three previous communications [2–4] have dealt with the yields of products formed in the pulse radiolysis of methane. The yields of the C_2 products were in poor agreement, even though in one of the studies, the conclusion was reached that the yields of these products were independent of the dose. Spectroscopic studies of the pulse radiolysis of methane have also appeared; in these studies $C(^1S)$ atoms [4] and $CH(^2\pi)$ [5] were shown to be formed.

An important question in the radiolysis of methane has been the ultimate fate of the major ions in the system, $C_2H_5^+$ and CH_5^+, which do not react with methane to produce any chemically different species at ambient temperatures. In the radiolysis at low dose rates, these ions will undergo many hundreds of collisions before being neutralized, and therefore will have a good chance of being intercepted first by small amounts of impurities or with accumulated radiolysis products [6]. Therefore, at low dose rates the chemical identities of the positive ions which eventually undergo neutralization will vary with dose, dose rate, condition of the wall, the purity of the CH_4, etc. At the high dose rates attained in pulse radiolysis experiments, on the other hand, the $C_2H_5^+$ and CH_5^+ ions will have a relatively short lifetime with respect to neutralization, and therefore are less likely to be intercepted by impurities or product molecules. The present investigation is essentially a continuation of an earlier study [7] which examined in detail the neutralization mechanism of the $C_2H_5^+$ ion in methane. The present investigation examines in more detail the effects of dose, dose rate, electron scavengers, and positive ion scavengers on the yields of the radiolytic products formed in methane under pulse radiolysis (high dose rate) conditions.

2. Experimental Procedure

2.1. Irradiation

The experimental procedure was identical to that described in two previous publications from this laboratory [7–8]. Two field emission sources (Febetron 705 and 706) [9] were used in this investigation. The dose per pulse (dose rate) was varied by (a) changing the charging voltage of the diode tube, or (b) inserting

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[1] Figures in brackets indicate the literature references at the end of this paper.

an aluminum plate (0.1 cm thick) between the face of the diode tube and the reaction vessel. These procedures result in changes in the pulse shape. However as will be shown later, the pulse shape or duration has no obvious effect on the product yields in the pulse radiolysis of CH_4. All irradiations carried out with the Febetron 705 and 706 will be henceforth designated as 60–100 ns and 3–5 ns pulse radiolysis, respectively. An accurate determination of the pulse shape is however required in the case of the $CH_4-i\text{-}C_4D_{10}$ experiments, where a quantitative treatment of the data in terms of the ion-molecule reactions is needed. The pulse shape for these experiments which were carried out with the 705 Febetron has been determined with a Faraday cup, and is given in a previous publication [8].

Nitrous oxide at 1 atm was used as a dosimeter. It was assumed that in the pulse radiolysis of nitrous oxide 12.4 molecules of N_2 are produced per 100 eV [10–11]. Relative stopping powers per electron relative to nitrous oxide were calculated from the tables of Berger and Seltzer [12].

2.2. Materials and Analysis

Methane and NO were purified by repeated low temperature distillation until the impurity level was less than 1 ppm. Isobutane-d_{10} was purified by gas chromatography. Mass spectrometric analysis showed that the methane-d_4 contained 5 percent CD_3H while the $i\text{-}C_4D_{10}$ contained 9 percent C_4D_9H.

Hydrogen was analyzed by low temperature distillation using liquid hydrogen as a refrigerant. All other products were analyzed by gas chromatography and in those experiments where deuterium labeled compounds were used, the different hydrocarbon products were collected at the exit of the gas chromatograph and subsequently analyzed by mass spectrometry.

3. Results

3.1. Product Yields

The yields of the measured products are given as molecules, M, of product X produced per ion pair, N_+, formed as a result of the absorption or radiation by methane ($M(X)/N_+$). A W-value of 27 for methane was chosen [13] to convert the number of molecules per eV to the number of molecules per ion pair.

Figure 1 shows the effect of the number of pulses on the major products. These experiments were carried out with the 705 Febetron (60–100 ns) at dose rates ($\sim 10^{26}$ eV/g-s) which were at least a factor of 20 below the maximum dose rate obtainable from a Febetron 705. Product yields obtained at higher dose rates are given in table 1. It can be noted that it is the total dose rather than the dose rate which determines the product yields. The product yields observed for one pulse at a dose per pulse of $3.3\ \text{eV/g} \times 10^{19}$ (second row of table 1) corresponds roughly to that observed for five pulses delivered at a five fold lower dose rate (fig. 1). Apparently the duration of the pulse has no effect on the product yields as long as the total dose is the same. Indeed, the experiments carried out with a 706 Febetron (3–5 ns) given in table 1, show that an increase in the number of pulses has qualitatively and quantitatively the same effect on the product yields as that observed for the 60–100 ns pulse experiments (fig. 1); the dose per pulse in the two series of experiments was comparable.

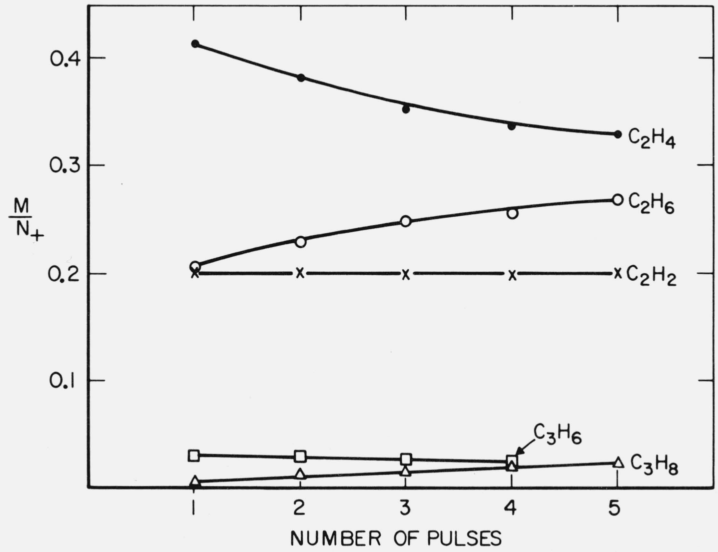

FIGURE 1. *Ion pair yields of* C_2H_4, C_2H_6, C_2H_2, C_3H_6, *and* C_3H_8 *formed in 300 torr of methane as a function of dose (number of pulses).*

Dose/pulse = 0.68×10^{19} eV/g and pulse duration = 60–100 ns.

TABLE 1. *Pulse radiolysis of pure methane*

Duration of pulse ns	Dose/pulse eV/g× 10^{-19}	Number of pulses	Pressure torr	C_2H_2	C_2H_4	C_2H_6	C_3H_4	C_3H_6	C_3H_8	Reference
				Molecules per ion pair (M/N_+)						
60–100	0.68	1	300	0.205	0.420	0.202	0.010	0.029	0.008	This work
60–100	3.3	1	300	.210	.326	.262	.012	.024	.018	
60–100	15.2	2	100	.210	.191	.284	.011	.016	.024	This work
60–100	~ 70	1	400–700	.185	.258	.258				2
60–100	~ 70	10	400–700	.148	.185	.332				2
3–5	0.83	1	300	.218	.432	.212	.011	.029	.008	This work
3–5	0.83	2	300	.204	.370	.230	.011	.025	.012	This work
3–5	0.83	4	300	.210	.343	.279	.012	.024	.019	This work
3–5	0.49	1 to 16	760	.23	.28	.52				3
3–5	0.58		100	.162	.324	.567			.019	5
Low Dose Rate			731	.00	.001	.595		.00	.097	26

The main effect of an increase in total dose is to raise $M(C_2H_6)/N_+$ and $M(C_3H_8)/N_+$ and to diminish $M(C_2H_4)/N_+$. Comparable effects of dose on yields of C_2H_6 and C_2H_4 were also reported by Cahill et al. [2] (table 1). In addition, the latter investigators did observe a decrease of $M(C_2H_2)/N_+$ with increasing dose while none was seen in the present study. The dose range in the study of Cahill et al. was however higher than in our investigation. In contrast, Hummel and Hearne [3] did not find any obvious effect of dose on the yields of C_2H_6, C_2H_4, and C_2H_2 (table 1). The fact that the dose per pulse, the methane pressure and the reaction vessel design were comparable in the two studies, makes it difficult to provide any clues as to the cause of these conflicting observations. The scatter in the product yield data reported by Hummel and Hearne [3] is however unusually high, if one considers the reproducibility of the dose per pulse delivered by the 706 Febetron (see Experimental Procedure of Ref. [19]).

In the last row of table 1 we presented a typical product distribution observed in the radiolysis of CH_4 at the relatively low dose rates provided by a 3 MeV Van de Graaff electron accelerator. In certain other low dose rate studies which were carried out at extremely low doses, higher ion pair yields of ethylene (up to 0.2) have been obtained than in the example given, but in all of the published investigations the ion pair yield of acetylene in pure methane was found to be no higher than 0.07.

Figure 2 shows the effect of pressure on the product yields obtained with the 705 Febetron (60–100 ns). The samples were exposed to only one pulse.

The effect of electron scavengers, SF_6 and CD_3I, and free radical scavengers, O_2 and NO, on the products was explored. The CH_4-SF_6 and CH_4-CD_3I experiments were performed with a 705 Febetron, while the CH_4-O_2 and CH_4-NO experiments were carried out with the 706 Febetron. The electron scavengers inhibit the formation of acetylene, allene, and propyne and increase the yield of ethylene. A threefold increase of the pressure of SF_6 has no noticeable effect on the product yields, while an increase of the pressure of CD_3I raises the yield of ethane. The free radical scavengers, oxygen and nitric oxide diminish the yields of essentially all products. The effect on the production of acetylene and ethylene is however much less pronounced than on that of ethane and propane. An increase in the number of pulses from 1 to 4 had no noticeable effect on the product yields produced in the pulse radiolysis of the CH_4-O_2 or CH_4-NO mixtures. Product yields reported in a conventional NO scavenged radiolysis experiment carried out with a 3 MeV Van de Graaff electron accelerator are included in table 2 for comparison.

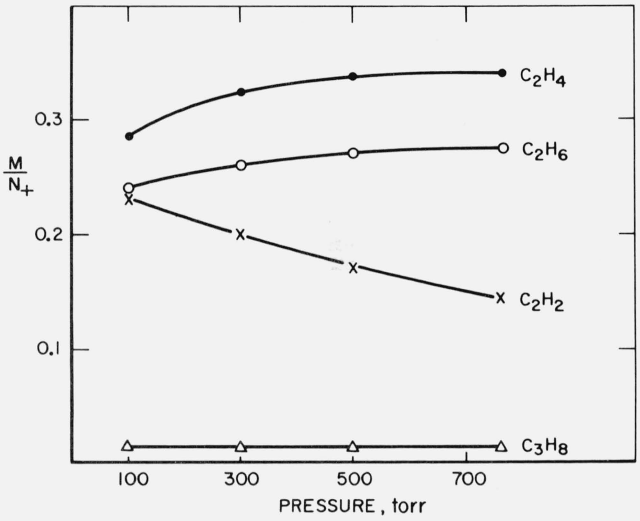

FIGURE 2. *Ion pair yields of* C_2H_4, C_2H_6, C_2H_2, *and* C_3H_8 *formed in methane by one* 3.3×10^{19} *eV/g pulse of* 60–100 ns *duration, as a function of pressure.*

3.2. Deuterium Labeling Experiments

We determined the isotopic composition and ion pair yields of the hydrogen formed in the pulse radiolysis (dose/pulse: 0.68×10^{19} eV/g, pulse duration 60–100 ns, total pressure: 300 torr) of CH_4-CD_4 (1:1) mixture in the presence and absence of SF_6. These results are represented in table 3. Because of their complexity, the isotopic compositions of the ethane formed in these experiments could not be established. They were however quite similar to those obtained in low dose rate experiments. In contrast, the mass spectrum of the ethane fraction formed in the pulse radiolysis of a CH_4-CD_4-NO (1:1:0.06) mixture was easy to interpret. The small contributions of

TABLE 2. *Effect of electron and free radical scavengers*

Duration of pulse ns	Dose/pulse eV/g× 10^{-19}	CH_4 pressure,	additive torr	C_2H_2	C_2H_4	C_2H_6	C_3H_4	C_3H_6	C_3H_8
				Molecules per Ion Pair (M/N_+)					
60	0.68	300		0.205	0.420	0.202	0.010	0.029	0.008
60	0.68	300	$SF_6-3.0$	.028	.575	.333	.002	.033	.025
60	3.3	100		.240	.286	.241	.011	.021	.016
60	3.3	100	$SF_6-1.0$	.034	.623	.261	.004	.027	.017
60	3.3	100	$SF_6-3.2$	.034	.651	.295	.003	.026	.018
60	3.3	300		.195	.305	.245	.010	.022	.016
60	3.3	300	$CD_3I-1.0$	.042	.424	.744	.001	.018	.039
60	3.3	300	$CD_3I-3.6$	.042	.479	1.11	.001	.015	.048
Low Dose Rate [a]		731	NO−7		.190	.043		.011	.008

[a] Reference [26].

C_2D_5H, C_2DH_5, and $C_2D_3H_3$ found in the ethane fraction (C_2D_6 − 22%, C_2D_5H − 2%, $C_2D_4H_2$ − 23.5%, $C_2D_3H_3$ − 2.7%, $C_2D_2H_4$ − 22%, C_2DH_5 − 2%, C_2H_6 − 25.8%) shows that 3 mol percent NO scavenged the majority of the methyl radicals under the conditions of this experiment (dose/pulse: 0.83 × 10^{19} eV/g, pulse duration 3–5 ns, total pressure: 500 torr).

TABLE 3. *Radiolysis of* CH_4-CD_4 (1:1). *The formation of hydrogen*

	Methane pressure	Additive (torr)	H_2	HD	D_2
			M/N_+		
Pulse radiolysis (60–100 ns).	300		0.67	0.36	0.44
	300	SF_6, 3	.57	.23	.37
(Difference)			.10	.13	.07
^{60}Co-Gamma radiolysis	39	NO, 0.06	.45	.20	.36

The isotopic composition of the hydrogen formed in the pulse radiolysis of CH_4-CD_4 (1:1) both in the presence and absence of SF_6 is given in table 3. The total yield of hydrogen was within 5 percent independent of pulse duration (3–100 ns) and dose (0.78–15.2 eV/g × 10^{19}).

4. Discussion

4.1. Formation of Products in the Pulse Radiolysis of Methane

Before beginning our discussion of the specific modes of product formation in irradiated methane, it is useful to summarize the major processes which are known to occur in this system. Products will, of course, originate from the dissociation of the parent CH_4^+ ion, i.e.:

$$CH_4^+ \rightarrow CH_3^+ + H \tag{1}$$

from ion-molecule reactions [1] such as:

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \tag{2}$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \tag{3}$$

and from the neutralization of positive ions [7]. (The CH_4^+ and CH_3^+ ions comprise at least 90 percent of the initially formed positive ions in methane; CH_2^+ may be formed but in small yield.) Since ion-molecule reactions 2 and 3 occur at essentially every collision, the major ions which will undergo neutralization in methane at high dose rates (where reaction with impurities or accumulated products can not compete with neutralization) will be $C_2H_5^+$, which is neutralize according to the mechanism:

$$C_2H_5^+ + e \rightarrow [C_2H_4]^* + H \rightarrow C_2H_2 + H_2 + H \tag{4}$$

and CH_5^+ whose neutralization mechanism is unknown. We will present evidence in this paper that CH_5^+ is neutralized to give mainly methane and an H atom:

$$CH_5^+ + e \rightarrow CH_4 + H. \tag{5}$$

In addition to these ionic processes, products formed in irradiated methane will originate from the decomposition of neutral excited methane molecules [1]:

$$CH_4^* \rightarrow CH_2 + H_2\ (2H) \tag{6}$$

$$\rightarrow CH + H + H_2\ (2H) \tag{7}$$

$$\rightarrow C + H_2\ (2H) + H_2\ (2H) \tag{8}$$

and from the subsequent reactions of the radical intermediates formed in dissociation reactions 6 through 8 as well as in reactions such as 1, 3, 4 and 5. (We exclude from this discussion product formation through reaction with accumulated products.) The prediction of the modes of reaction of these radical intermediates is complicated by the fact that we do not know in which excited states they may be formed. For instance CH_2 may be formed [14] in the ground $\tilde{X}\,{}^3\bar{\Sigma}_g$ state, which is unreactive with methane, in the lowest singlet state, $\tilde{a}\,{}^1A_1$, which will insert into methane [15]:

$${}^1CH_2 + CH_4 \rightarrow (C_2H_6)^* \begin{array}{l} \rightarrow 2CH_3 \\ \xrightarrow{M} C_2H_6 \end{array} \tag{9}$$

as well as undergo conversion to the triplet upon collision with methane [16]:

$$^1CH_2 + CH_4 \rightarrow {}^3CH_2 + CH_4 \qquad (10)$$

or in a higher excited state [17] such as $\tilde{b}\ {}^1B_1$ or $\tilde{c}\ {}^1A_1$ whose reactions with methane are unknown. It is not inconceivable that these excited species undergo some reaction other than reaction (9), possibly H atom abstraction. Similarly, the CH species from reaction (7) is formed [17] not only in the ground $X^2\pi$ state, but also in the $A^2\Delta$ and $B^2\ \Sigma^-$ states. It has been shown that some of the ethylene formed in irradiated methane originates in a reaction in which a CH species inserts into methane [18]:

$$CH + CH_4 \rightarrow C_2H_4 + H. \qquad (11)$$

The ground state CH does undergo reaction (11), but the reactions of the excited CH species are unknown. Finally, the C atoms may be in the unreactive ^3P state, or in the ^1S or ^1D states. It has recently been demonstrated that the insertion of C atoms into methane results in the formation of acetylene [7]:

$$C(^1S \text{ or } {}^1D) + CH_4 \rightarrow C_2H_2 + H_2. \qquad (12)$$

It is interesting to consider the various intermediate species generated in methane in terms of their lifetimes in the pulsed system. As mentioned before, it is to be expected that the primary ions will react at the first collision to give CH_5^+ and $C_2H_5^+$, most of which, under our conditions will be neutralized (reactions 4 and 5) during the duration of the pulse, generating H atoms and stable product molecules. At least some of the $^1CH_2$, CH, and ^1C species (depending on the electronic state, as discussed above) will disappear by reaction with methane at essentially every collision (through reactions 9–12), so these species also will have effectively disappeared by the end of the pulse. On the other hand, the H atoms, methyl radicals, and the triplet CH_2 species, do not react to any appreciable extent with methane under these conditions, and therefore will survive in the system until they encounter a species with which they can react. This means that we should expect to see reactions among these long-lived intermediate species as major sources of product formation.

Unfortunately, it is difficult to accurately predict the yields of the long-lived H, CH_3, and triplet CH_2 species, so a quantitative unraveling of all the mechanisms of product formation in the pulse radiolysis of methane is not actually feasible at the present time. Although the yields and reactions of the ionic species are well understood, the initial yield of excited CH_4 can only be estimated in a rough way.

We can, however, predict that most H atoms will combine with polyatomic radicals, mostly CH_3:

$$H + CH_3 \rightarrow CH_4^* \qquad (13)$$

$$CH_4^* + M \rightarrow CH_4 + M \qquad (14)$$

H–H recombination will be very slow because of the third body requirement and will not effectively compete with reaction with polyatomic radicals as long as such species remain in the system. The occurrence of reaction (13) as the most probable fate of H atoms on the pulse radiolysis of neopentane has been demonstrated [19]. That reaction (13) is important in this system is qualitatively confirmed by the results of experiments in which the yield of H atoms is reduced. It has recently been shown [7] that the addition of SF_6 as an electron scavenger in the pulse radiolysis of methane eliminates reaction (4) as a source of ethylene and H atoms, probably through the occurrence of a reaction such as:

$$C_2H_5^+ + SF_6^- \rightarrow C_2H_4 + HF + SF_5. \qquad (15)$$

Thus, in the presence of SF_6, a major source of H atom formation is eliminated. Under these conditions, the yield of ethane is increased (table 2) because of the increased importance of methyl-methyl combination:

$$CH_3 + CH_3 \rightarrow C_2H_6. \qquad (16)$$

The same interpretation explains the fact that in the low dose rate radiolysis of methane (where neutralization processes 4 and 5 will not occur to any appreciable extent, and where the steady state concentration of H atoms will be much lower, so that diffusion to the wall and recombination there to form H_2 will be much more important), the yield of ethane and hydrogen is much higher than in the pulse radiolysis experiments. It is difficult to explain the high ethane yields obtained in a recent pulse radiolysis study [3], which, fortuitously, agreed with the low dose rate ethane yield.

4.2. The Formation of Ethylene and Acetylene Products

As discussed above, it is expected that ethylene and acetylene should be formed in the radiolysis of methane under high dose rate conditions [7] from the neutralization of the ethyl ion according to reaction (4), as well as from reaction (11) (ethylene formation) and reaction (12) (acetylene formation). Also, it is possible that other sources of these products exist, for instance, reactions of excited CH_2 species with methane, or reactions of triplet CH_2 with other radicals. There is actually some experimental evidence for the formation of ethylene from a reaction involving triplet CH_2 (which is unreactive with methane) and methyl radicals. In one experiment, CD_3I was added to methane as an electron and H atom scavenger:

$$CD_3I + H \rightarrow CD_3 + HI \qquad (17)$$

$$CD_3I + e \rightarrow CD_3 + I^-. \qquad (18)$$

In this experiment, it was seen that about 15 percent of the ethylene consisted of $C_2D_2H_2$ and C_2D_3H, formed in a ratio of 4.3 : 1. This demonstrates that some reaction involving methyl radicals contributes to ethylene formation. A plausible reaction is:

$$^3CH_2 + CD_3 \rightarrow (C_2D_3H_2)^* \begin{cases} \rightarrow C_2D_2H_2 + D \\ \rightarrow C_2D_3H + H. \end{cases} \qquad (19)$$

An isotopic analysis of the ethane formed in this experiment indicated that the ratio of CH_3 to CD_3 radicals was 2.38. Thus, if one accepts the occurrence of reaction 19, it can be estimated (table 2) that the ion pair yield of $^3CH_2$ reacting to give ethylene is about 0.1. It should be pointed out that this methyl radical reaction leading to ethylene formation is more plausible than the reaction suggested earlier [20]:

$$CH_3 + CH_3 \rightarrow C_2H_6^* \rightarrow C_2H_4 + H_2. \qquad (20)$$

It is well known [21] that ethylene is not a product in systems where methyl radicals are the major intermediate reactants.

As pointed out before [7], the substantial reduction of the yield of acetylene on addition of electron scavengers such as SF_6 and CD_3I (table 2) can be accounted for by a change in the neutralization mechanism of the $C_2H_5^+$ ion (reactions 4 and 15). The reduction in the yield of acetylene observed when the pressure is increased (fig. 2) can at least in part be explained by the collisional deactivation of the ethylene precursor in reaction (4).

4.3. The Formation of Hydrogen Product

The most important sources of unscavengeable hydrogen in the radiolysis of methane [22] would be expected to be reactions (2) and probably (6–8), with additional contributions from reactions such as (12). In the high dose rate pulse radiolysis [7], an additional source of unscavengeable hydrogen will be the neutralization of the $C_2H_5^+$ ion through reaction (4). (As mentioned before, this ion will react with impurities or accumulated products before undergoing neutralization under low dose rate conditions [6].) However, if SF_6 is added to pulse-irradiated methane, the ethyl ion will be neutralized through reaction (15) and will not produce H_2 as a neutralization product. Since the other hydrogen-forming reactions would not be expected to be dependent on dose rate, it is not surprising that the isotopic distribution and total yield of the hydrogen produced in the low intensity gamma radiolysis [22] of a CH_4-CD_4 (1:1) mixture in the presence of a radical scavenger (NO) is quite similar to that of the hydrogen produced in the pulse radiolysis of such a mixture in the presence of SF_6 (tab. 3). These distributions and yields are compared with those observed in the pulse radiolysis of a CH_4-CD_4 mixture in the absence of added SF_6, where neutralization mechanism 4 would be expected to prevail. Although the drop in the total yield of hydrogen product (0.30) when SF_6 is added is somewhat larger than the corresponding drop in the yield of acetylene, i.e., the yield of reaction (4) in the absence of SF_6 (0.18), it should be remembered that H atom reactions may contribute to hydrogen formation to some extent in the absence of SF_6.

4.4. Neutralization of CH_5^+

As mentioned above, the neutralization mechanism of CH_5^+ has been a matter of speculation in the past. For instance, it has been suggested [23] that CH_5^+ neutralization results in the formation of CH_2 radicals:

$$CH_5^+ + e \rightarrow CH_2 + H_2 + H \qquad (21)$$

The occurrence of this reaction to give three H atoms as products can be excluded on energetic grounds; this process would be 25 kcal/mol endothermic. However, the formation of CH_2 species in a neutralization reaction can be excluded entirely on the grounds that the yield of CH_2 species is the same in the pulse radiolysis (where CH_5^+ undergoes neutralization) as in the low dose rate radiolysis (where it does not). That is, the yield of stabilized ethane formed in CH_2 insertion reaction (9) is 0.054 in the low dose rate radiolysis of a methane−NO mixture at a pressure of 500 torr; the yield of this product in the pulse radiolysis of a CH_4-CD_4-NO mixture (see Results) is 0.058. (The insertion product will consist of C_2D_6, $C_2D_4H_2$, $C_2H_4D_2$, and C_2H_6, as more than 90 percent of the ethane formed in this experiment did.) The occurrence of process (21) was suggested [23] on the basis of an analysis of C_5 product yields formed in the low dose rate radiolysis of CH_4 containing 10 percent 2-butene. In such a mixture, neutralization of CH_5^+ could not possibly compete with the fast exothermic proton transfer reaction:

$$CH_5^+ + C_4H_8 \rightarrow CH_4 + C_4H_9^+. \qquad (22)$$

Another plausible neutralization process which CH_5^+ could undergo would be:

$$CH_5^+ + e \rightarrow CH_3 + H_2. \qquad (23)$$

We cannot exclude the occurrence of this process on the basis of our results, but can conclude that this is not the major neutralization mechanism of this ion since the hydrogen which is formed in the pulse radiolysis can largely be accounted for by reactions (2, 4, 6–8), and 12). Also, if we consider that when SF_6 is added, the energy available to the neutralization process is reduced, and one generally observes a change in neutralization mechanism [7] (as seen for $C_2H_5^+$, reaction (4) being replaced by reaction (15)). Thus, it is pertinent that when SF_6 is added to methane (at a pressure of 300 torr), the total yield of hydrogen is reduced from 1.47 to 1.16, a drop of 0.31. Of this, 60 percent can be accounted for by the elimination of reaction (4) (as evidenced by the drop in the acetylene yield). Thus, the maximum yield which could be attributed to process (21) or (23) is 0.13 (i.e., not more than 30% of the CH_5^+). However, if one examines the isotopic distribution of the differential hydrogen, given in table 3, one notices that HD is the main component; such a distribution would be inconsistent with the loss of a molecule of hydrogen from the various isotopically labeled CX_5^+ ions (where X is H or D). Even if we assume that SF_6 does not affect the occurrence of neutralization mechanism (23), we can say that the maximum yield which could be attributed to this process would be the difference between the hydrogen yield in the low dose rate radiolysis [22] of a CH_4—NO mixture (0.95) where neutralization processes do not contribute, and that observed in the pulse radiolysis in the presence of SF_6 (1.16), a difference of 0.21.

By elimination, then, we write as the most probable neutralization reaction of CH_5^+, process (5), the formation of an H atom and a methane molecule. It is interesting to note that the maximum amount of energy which can be contained in this product CH_4 molecule is 8.1 eV; this is about 0.4 eV below the onset for singlet-singlet excitation, so we may conclude that the CH_4 is excited to the triplet state (onset at 7.5 eV) or is a vibrationally excited ground state molecule. In the latter case, further dissociation would involve cleavage of a C-H bond.

4.5. Effect of Dose on the Product Yields

Figure 1 shows the yields of the ethylene, ethane, acetylene, propylene, and propane products formed in methane as a function of the total absorbed dose (number of pulses). It is seen that the yields of some of these products do change with the number of pulses. Additional results confirming this observation are given in table 1. Since this observation is in contradiction to results reported in a recent pulse radiolysis study of methane [3], the effect of dose on product yields merits some examination.

At the high dose rates and relatively low total dose used in pulse radiolysis studies, nearly all of the unreactive ions (mainly $C_2H_5^+$ and CH_5^+) formed in pure methane will undergo charge recombination, and will not survive long enough to undergo reactions with accumulated products, so this can be discounted as a possible source of the dose effects shown in figure 1 and table 1. On the other hand, it is to be expected that as the total dose is increased, accumulated products, especially ethylene, will begin to intercept H atoms formed in the system. In the low dose rate radiolysis of methane, the formation of propane and *n*-butane is ascribed [23–25] to the reaction sequence:

$$C_2H_4 + H \rightarrow C_2H_5 \tag{24}$$

$$C_2H_5 + CH_3 \rightarrow C_3H_8 \tag{25}$$

$$C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10}. \tag{26}$$

The observed dose effects given in figure 1 and table 1 can in part be accounted for by the occurrence of this reaction sequence in the pulse radiolysis of methane. For instance, the yield of ethylene decreases with increasing dose, while the yield of propane increases (and the yield of *n*-butane increases also, but the total ion pair yield of this product was less than 0.01 so it has not been included in the figure). The fact that the increment in the yield of propane is less than the decrease in the yield of ethylene can be explained by the combination reaction

$$C_2H_5 + H \rightarrow C_2H_6. \tag{27}$$

Reaction (27) would also account in part for the increase in the yield of ethane with increasing dose. As mentioned before, the high concentration of free radicals in the pulse radiolysis experiments favors reactions such as (27) over the termolecular combination of H atoms [19].

$$H + H + M \rightarrow H_2 + M. \tag{28}$$

The inhibition of the formation of propane in the presence of a free radical scavenger such as NO is consistent with the formation of this product is a free radical reaction (reaction 25).

The lack of any noticeable effect of dose on $M(C_2H_2)/N_+$ can easily be explained, since the rate constant for the addition of H to C_2H_2 is nearly a factor of ten lower than that of reaction (24) [27]. Therefore, for a 30 percent decrease of $M(C_2H_4)/N_+$ as a function of dose (fig. 1) one can only expect an ~3 percent decrease of $M(C_2H_2)/N_+$. Although such a minor decrease would go unnoticed over this limited dose range it might account for the low yields of $M(C_2H_2)/N_+$ reported by Cahill et al. [2] (table 1) for their experiments performed at a relatively high total dose.

4.6. Pulse Radiolysis of CH_4—i-C_4D_{10} Mixtures

As discussed in the foregoing sections of this paper, the major change in the radiolytic mechanism of methane which occurs in going from low dose rate conditions (i.e., gamma radiolysis) to high dose rate conditions (pulse radiolysis) is the change in the fate of the two major ions in the system, $C_2H_5^+$ and CH_5^+. At low dose rates, the steady state concentration of electrons is low, and the ions, consequently, will survive many collisions before undergoing neutralization (at one atmosphere and a dose rate such that 10^{10}-ions/s-ml are formed, it can be estimated that these ions would undergo 10^5 to 10^6 collisions before being neutralized), and consequently will have ample opportunity to react with accumulated products or any other foreign compounds which may be present in small concentrations. This was illustrated in an earlier radiolysis study [6], where it was shown that at a dose rate of 4×10^{17} eV/g-s, addition of 0.01 mol percent propane resulted in the interception of all $C_2H_5^+$ and CH_5^+ ions, through the reactions:

$$C_2H_5^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_7^+ \tag{29}$$

$$CH_5^+ + C_3H_8 \rightarrow (C_3H_9^+)^* + CH_4. \tag{30}$$

Reactions of this type were shown [6] to be of general occurrence for all higher hydrocarbon additives. (This was later confirmed mass spectrometrically [28–31]; the occurrence of such ion molecule reactions in gas mixtures in high pressure mass spectrometers now finds application as an analytical technique called "chemical ionization mass spectrometry".)

At high dose rates, on the other hand, the $C_2H_5^+$ and CH_5^+ will undergo neutralization before being able to react with small amounts of foreign compounds. In a recent pulse radiolysis study [8], the rate of neturalization of unreactive ions (*t*-butyl ions in neopentane) was examined by allowing the neutralization process to compete with a reaction between the ion and a reactive additive. In this section we report the results of similar experiments in methane, in which the neutralization of $C_2H_5^+$ and CH_5^+ competes with their reactions with isobutane-d_{10}:

$$C_2H_5^+ + i\text{-}C_4D_{10} \rightarrow C_2H_5D + C_4D_9^+ \tag{31}$$

$$CH_5^+ + i\text{-}C_4D_{10} \rightarrow (C_4D_{10}H^+)^* + CH_4 \tag{32}$$

$$(C_4D_{10}H^+)^* \rightarrow CD_3H + C_3D_7^+ \tag{33}$$

$$C_3D_7^+ + i\text{-}C_4D_{10} \rightarrow C_3D_8 + C_4D_9^+. \tag{34}$$

At low dose rates [6], where every $C_2H_5^+$ ion can be expected to undergo reaction (31), the ion pair yield of C_2H_5D observed in a $CH_4-i\text{-}C_4D_{10}$ mixture (at a total sample pressure of 460 torr) was 0.32. The CH_5^+ ions reacting with $i\text{-}C_4D_{10}$ will lead mainly to the formation of C_3D_8 as a neutral product through reactions (33) and (34) (although a fraction of the $C_4D_{10}H^+$ ions formed in reaction (32) undergo fragmentation reactions other than (33)); under low dose rate conditions [6], the observed ion pair yield of C_3D_8 was 0.36. At the highest dose rates used in that study (4×10^{17} eV/g-s), all the $C_2H_5^+$ and CH_5^+ ions were intercepted by the isobutane, as evidenced by the fact that the yields of C_2H_5D and C_3D_8 were independent of isobutane concentration from 0.01 to 1 mol percent.

Similar $CH_4-i\text{-}C_4D_{10}$ mixtures were irradiated here at high dose rates in the presence and absence of the electron scavenger, SF_6. As the results given in figure 3 show, neutralization does compete with reactions (31) and (32) under these conditions; not only are the yields of C_2H_5D and C_3D_8 strongly dependent on the concentration of $i\text{-}C_4D_{10}$ at high dose rates, but also, even at an isobutane concentration of 1 percent, the yields of these products are lower than the corresponding yields in the low dose rate radiolysis.

In order to evaluate these results, the yields of C_2H_5D and C_3D_8 which one would expect in these experiments were calculated using a modified WR-16 computer program [32]. In the calculation, reaction mechanism (31–34) was assumed to occur, and in addition it was assumed that $C_2H_5^+$, CH_5^+, $C_3D_7^+$ (formed in reaction (33)), and $C_4D_9^+$ (formed in reactions (31) and (34)) will undergo neutralization in competition with reaction. The neutralization rate constants for all these ions were assumed to be equal to those recently determined [8] for the *t*-butyl ion; that is, the rate constant for neutralization by an electron was taken to be 1.9×10^{-6} cm³/molecule-s, while that for neutralization by SF_6^- (for experiments in the presence of SF_6) was taken to be 0.4×10^{-6}. In the presence of SF_6, a calculation indicates that more than 99 percent of the electrons will attach to SF_6 to form SF_6^-, taking a rate constant of 2.6×10^{-7} cm³/molecule-s for thermal electron attachment [33–34]. The rate constants for the ion-molecule reactions (31) and (34) were taken to be 0.7×10^{-9} cm³/molecule-s and 0.33×10^{-9} cm³/molecule-s respectively [35–36]. Reaction (32) was assumed to occur at every collision ($k_{30} = 1.1 \times 10^{-9}$ cm³/molecule-s). Finally it was assumed that the $(C_4D_{10}H^+)$ species formed in reaction (32) does not survive long enough to be neutralized.

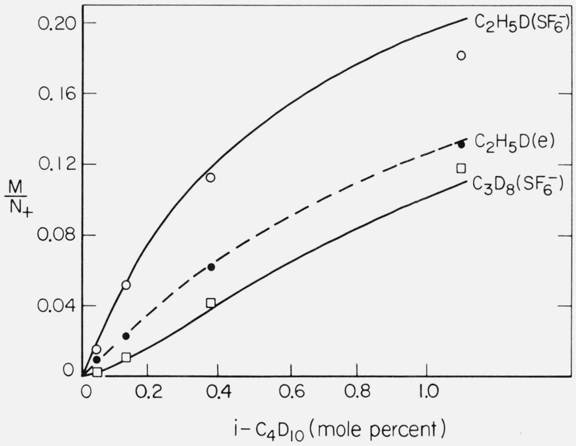

FIGURE 3. *Ion pair yields of* C_2H_5D *formed in* 300 *torr of methane to which various concentrations of* i-C_4D_{10} *have been added, in the absence and presence of* SF_6, *and the yield of* C_3D_8 *in the presence of* SF_6.

Dose/pulse = 3.3×10^{19} eV/g. Lines represent yields of these products predicted by by calculation (see Discussion).

The yields of C_2H_5D and C_3D_8 predicted by these calculations are shown by the lines in figure 3. (The yield of C_3D_8 was not measured in the absence of SF_6 so this line has not been given in the plot.) Considering the fact that the mechanism here is fairly complicated, and several assumptions or approximations had to be made in the calculations (i.e., the lifetime of $(C_4D_{10}H^+)^*$, the neutralization rate constants, the rate constant of reaction (32)), the calculations predict the observed yields of C_2H_5D and C_3D_8 as a function of $i\text{-}C_4D_{10}$ concentration remarkably well. This indicates that the neutralization rate constants of these ions probably are not much different from those determined [8] for the neutralization of the *t*-butyl ion.

It is interesting that the calculation actually predicts the observed slight *s*-shaped curvature of the plot of C_3D_8 yield as a function of $i\text{-}C_4D_{10}$ concentration (fig. 3).

5. References and Note

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