On the Mechanism of the Isotopic Exchange of Tritium with Methane[1]

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The techniques of "high pressure" mass spectrometry have been used to identify some of the principal ionic intermediates in the "Wilzbach labeling" of methane with T_2. In mixtures of T_2 and CH_4 the long-lived transient is $C_2H_4T^+$. This ionic species appears to be involved in the nuclear-decay-induced part of the labeling mechanism. Mixtures of D_2 (as a stand-in for T_2) and methane were irradiated with electrons to study the radiation-induced part of the mechanism. The ionic interaction transients observed were CH_4D^+, $C_2H_4D^+$, $C_2H_3D_2^+$, and $C_2H_2D_3^+$. An investigation of the scavenging by xenon was attempted by irradiating mixtures of Xe and CH_4. The results are correlated with the ionic mechanisms previously proposed for the tritium labeling of CH_4.

A. Introduction

A widely used method of tagging organic molecules with radioactive tritium, originally described by Wilzbach,[2] consists in mixing the substance with T_2 and allowing the two to stand. On isolating the various tritiated products, one finds not only the tagged parent but various other radioactive substances resulting from destruction of the target molecule.[3,4] The mechanism of this "Wilzbach labeling" of several simple compounds has been investigated by Gant and Yang.[5] Methane in particular has been studied by Pratt and Wolfgang.[6] Both groups have concluded from kinetic and scavenger techniques that there are two modes of labeling with tritium: decay-induced labeling, which involves the reaction of the daughter ion $(THe^3)^+$ from the radioactive transformation; and radiation-induced labeling, which is initiated by the excitation and ionization of the parent molecule and the T_2 by the betas released in the nuclear decay and by secondary electrons. The latter process is in essence radiolysis of the mixture by internal self-radiation. Both modes are believed to be responsible for formation of tagged parent as well as other compounds. The mechanisms proposed for the two modes of isotopic tagging involve the reactions of positively-charged transient species.

If the ions suggested as intermediates are sufficiently long lived ($>10^{-5}$ sec.), they should be observable in the mass spectrometer operated at a source pressure high enough that ion–molecule reactions can occur. This paper describes the results of such a mass spectrometric approach to the identification of transient positively-charged species involved in isotopic tagging of CH_4 with tritium, the purpose being to establish the mechanisms by which tritium becomes incorporated into a methane molecule. Two methods were used. In the first, mixtures of CH_4 and D_2 (the deuterium being used as a stand-in for tritium) at source pressures of tenths of a millimeter were irradiated with electrons and the products were identified. These studies were designed to understand the mechanism of the radiation-induced part of the labeling mechanism. In a second line of investigation, mixtures of T_2 and CH_4 with and without added D_2 were introduced into the source chamber of the mass spectrometer in the hope of elucidating the decay-induced mechanism of tritium tagging. At gas pressures used a primary ion may be expected to undergo several collisions between formation, either by nuclear decay or by electron impact, and departure from the source chamber. For example, in a gas at 0.1 mm., an ion travelling 3.2 mm. between point

of origin and exit slit may collide with about three molecules on the average. For the $D_2 + CH_4$ runs, deuterium from the Stuart Oxygen Co. (>99.5% D_2) was mixed with Phillips Research Grade CH_4 (99.60%). The tritium gas was obtained from Oak Ridge National Laboratory. A description of the "high pressure" mass spectrometer appears elsewhere.[7]

B. Results

Table I lists the results of one of several such experiments which compared the intensities of various ionic species (with masses ranging from 1 to 48) that were

TABLE I

INTENSITIES OF SPECIES PRODUCED BY ELECTRON IMPACT OF $D_2 + CH_4$

		—Intensities in cts./sec.—		
				$D_2 + CH_4$
				D_2, 0.081
		D_2	CH_4	mm.
	Probable species	0.081	0.059	CH_4, 0.059
m/e	(singly charged)	mm.	mm.	mm.
1	H	<1	18	<2
2	H_2 or D	252	<1	<1
3	H_3	<1	<1	<1
4	D_2	5950	<1	132
5	D_2H	390	<1	<1
6	D_3	22000	<1	635
12	C	<2	70	<1
13	CH	<2	164	<1
14	CH_2	<2	683	265
15	CH_3	<2	12292	6597
16	$CH_4 + CH_2D$	6	9165	10628
17	$CH_5 + CHD_2 + CH_3D$	18	25500	30184
18	$H_2O + CH_4D + CD_3$	245	110	3393
19	$H_3O + CH_3D_2$	72	192	533
20	H_2DO	720	<1	55
25	C_2H	<2	44	30
26	C_2H_2	<2	674	399
27	C_2H_3	9	6985	6791
28	C_2H_4	8	2150	2800
29	C_2H_5	10	26953	29440
30	$C_2H_6 + C_2H_4D$	54	300	10850
31	$C_2H_7 + C_2H_3D_2$	<2	27	4810
32	$O_2 + C_2H_2D_3$	<3	71	720
33	O_2H	<3	5	20
38	C_3H_2	19	4	3
39	C_3H_3	6	126	125
40	C_3H_4	5	93	109
41	C_3H_5	10	497	1016
42	$C_3H_6 + C_3H_4D$	2	4	122
43	C_3H_7	30	73	166
44	C_3H_8	3	3	35
45	C_3H_9	8	1	13
46	C_3H_{10}	6	<1	4
47		<1	1	6
48		<1	5	<1

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) K. E. Wilzbach, J. Am. Chem. Soc., **79**, 1013 (1957).

(3) K. E. Wilzbach and P. Riesz, J. Phys. Chem., **62**, 6 (1958).

(4) W. R. Ahrens, M. C. Sauer and J. E. Willard, J. Am. Chem. Soc., **79**, 3284 (1957).

(5) P. L. Gant and K. Yang, J. Chem. Phys., **32**, 1757 (1960); **31**, 1589 (1959); **30**, 1108 (1959); J. Phys. Chem., **66**, 1619(1962).

(6) T. H. Pratt and R. Wolfgang, J. Am. Chem. Soc., **83**, 10 (1961).

(7) S. Wexler and N. Jesse, ibid., **84**, 3425 (1962).

produced by electron impact at 140 e.v. in D_2, in CH_4, and in a mixture of $D_2 + CH_4$. The partial pressures of the constituents in the mixture were the same as for the individual gases bombarded alone. One sees that the species D_2^+ and D_3^+, which are very prominent in D_2 alone, are almost completely quenched in the mixture with methane. Accompanying these sharp drops in intensity, the intensities of the species with mass-to-charge ratios of 18, 19, 30, 31, and 32 are enhanced relative to that from CH_4 alone. The species of mass 14 and 15 decrease markedly in intensity and mass 16 is enhanced. The intensities of masses 41 and 42 also increase. In addition, the intensities of masses 30, 31, and 32 relative to that of mass 29 and the intensity of mass 18 relative to that of 17 (where the species with masses 29 and 17 are most probably the ions $C_2H_5^+$ and CH_5^+, respectively[7,8]) increase in a systematic manner with the relative concentration of D_2 in the mixture (Table II). The abundance ratio of mass 30 to mass 29 for each composition of gas was observed to be fairly insensitive to the total source pressure over the range of concentrations indicated in the table. Also, the 30/29 ratio for CH_4 alone remained constant (0.027 ± 0.001) over the entire range of partial pressures of methane used in this experiment. These sets of experimental data indicate that in all probability the enhancement of the species of mass 30 is due to the formation of the ion $C_2H_4D^+$, that of mass 31 to the formation of $C_2H_3D_2^+$, and that of mass 32 to $C_2H_2D_3^+$. The ionic species of mass 18 is probably CH_4D^+ and/or CD_3^+ or $CH_2D_2^+$.

TABLE II
EFFECT OF COMPOSITION OF $D_2 + CH_4$ MIXTURE ON SEVERAL INTENSITY RATIOS

Gas composition, mm.		Intensity ratio			
		$m/e = 30$	31	32	18
CH_4	D_2	$m/e = 29$	29	29	17
0.11	..	0.026	0.0015	0.0014	0.013
.23	0.03	.059	.015	.0014	.015
.11	.09	.26	.094	.015	.036
.07	.09	.42	.20	.039	.12
.02	.18	.90	.65	.25	.93

The appearance potentials of the principal interacting and product species were measured. Those of CH_4^+ and CH_4D^+ were the same, while those of $C_2H_4D^+$, $C_2H_3D_2^+$, and $C_2H_2D_3^+$ were equal to the appearance potentials of either CH_3^+ or D_2^+ within experimental error.

As a check on the isotopic exchange between D_2 and CH_4, the ionic products from electron impact on a mixture of H_2 with CH_4 were measured. In the latter experiment one would not expect to observe the effects of exchange, and the observed result should be that the intensities of CH_5^+ and particularly of $C_2H_5^+$ increase. That this indeed occurs is seen in the data of Table III, which is a compilation of a series of experiments in which H_2, CH_4, $H_2 + CH_4$, D_2, CH_4, and $D_2 + CH_4$ were irradiated with electrons. The partial pressures of the individual gases in each mixture were the same as for the pure component alone. Note that the effect of mixing H_2 with the methane is to enhance the intensities of CH_5^+ and $C_2H_5^+$, while D_2 greatly increases the intensities of $C_2H_4D^+$, $C_2H_3D_2^+$, $C_2H_2D_3^+$, and CH_4D^+.

Tables IV and V summarize the results of experiments in which mixtures of $CH_4 + T_2 + D_2$ in various proportions were introduced into the mass spectrometer. The primary ions observed were undoubtedly formed by the self-radiation of the gas mixture by the betas and secondary electrons, while the secondary ions $C_2H_5^+$,

(8) D. O. Schissler and D. P. Stevenson, J. Chem. Phys., **24**, 926 (1956).

TABLE III
INTENSITIES OF SPECIES IN $H_2 + CH_4$ AND $D_2 + CH_4$ SYSTEMS

		Intensity (cts./sec.) (pressures in mm.)					
		H_2 (0.036)	CH_4 (0.023)	$H_2 + CH_4$ (H_2, 0.036 CH_4, 0.023)	D_2 (0.036)	CH_4 (0.023)	$D_2 + CH_4$ (D_2, 0.036 CH_4, 0.023)
m/e	Probable species						
1	H	27	17	12		14	6
2	H_2	673		74	22		
3	H_3	1267		102	7		
4	D_2				1160		65
5	D_2H				13		
6	D_3				2100		93
12	C		25	18		28	12
13	CH		78	23		67	16
14	CH_2		250	94		188	73
15	CH_3		2600	2064	18	2121	1121
16	CH_4		2676	1608	31	2100	1605
17	CH_5		2321	3748	7	2184	2636
18	$H_2O + CH_4D$		5	1	6	<1	176
19	H_3O	8	14	22		6	12
26	C_2H_2		59	52		57	42
27	C_2H_3		402	584		390	387
28	C_2H_4		175	188		163	175
29	C_2H_5	16	2474	4186		2160	2347
30	$C_2H_6 + C_2H_4D$		12	6		11	545
31	$C_2H_7 + C_2H_3D_2$		<1	<1		2	169
32	$O_2 + C_2H_2D_3$		<1	<1		9	19
41	C_3H_5		16	54		21	27

TABLE IV
RELATIVE INTENSITIES OF SEVERAL SPECIES IN A $T_2 + D_2 + CH_4$ MIXTURE[a]

m/e	Probable species (singly charged)	Relative abundance
15	CH_3	0.32
16	CH_4	.10
17	CH_5	.042
19	CH_4T	< .02
29	C_2H_5	1.00
30	C_2H_4D	0.08
31	C_2H_4T	0.19

[a] The relative concentration of $CH_4/T_2/D_2$ in the mixture was 1.00/0.15/0.10. The total source pressure was 0.082 mm.

TABLE V
RELATIVE INTENSITIES OF $C_2H_4T^+$, $C_2H_4D^+$, AND $C_2H_5^+$ AS FUNCTION OF COMPOSITION OF $T_2 + D_2 + CH_4$ MIXTURES

Expt.	Pressure range, mm.	Relative concn. of mixture ($CH_4/T_2/D_2$)	Relative intensities	
			$I(C_2H_4T^+)/I(C_2H_5^+)$	$I(C_2H_4D^+)/I(C_2H_5^+)$
1	0.10–0.13	1./0.12/0	0.07	0
			.07	0
2	.08– .13	1.0/ .12/0	.17	0
3	.08– .17	1.0/ .15/0.10	.19	0.08
			.16	
			.19	0.09
			.24	0.08
4	.11– .15	1.0/ .12/ .10	.19	0
			.31	<0.01
5	.05– .08	1.0/ .12/ .10	.19	.03
			.25	.05
6	.12– .16	1.0/ .12/ .26	.22	.12
			.16	.08

$C_2H_4T^+$, and $C_2H_4D^+$ detected in these experiments were the result of ion–molecule reactions of $(THe^3)^+$ and of the primaries; the electron gun was not used. Because of the low intensities of the species, counting techniques were employed. Signals ranging from about 5 to 800 counts/min. above background were recorded. Deuterium gas was added to assess the effects of radia-

tion-induced reaction of D_2 (and thus T_2) with CH_4, the assumption being made that T_2 and D_2 react in identical ways with electrons, CH_4, etc. One notes that the ratio of the intensity of mass 31 ($C_2H_4T^+$) to that of mass 29 ($C_2H_5^+$) is invariably greater than the ratio of 30/29 ($C_2H_4D^+/C_2H_5^+$), corrected for $C^{12}C^{13}H_5^+$). Since the $C_2H_5^+$ and $C_2H_4D^+$ ions observed can be formed only by radiation-induced processes, it is clear that the numbers of $C_2H_4T^+$ and of $C_2H_4D^+$ ions formed in radiation-induced reactions must be directly proportional to the partial pressures of T_2 and D_2, respectively. In determining the amount of decay-induced $C_2H_4T^+$, its production by radiation-induced reactions must therefore be taken into account. This is done by multiplying the intensity ratio $C_2H_4D^+/C_2H_5^+$ (column 5) by the concentration ratio T_2/D_2 and subtracting the product from the intensity ratio $C_2H_4T^+/C_2H_5^+$ (column 4). When this is done, the net ratio $C_2H_4T^+/C_2H_5$ is always found to be significantly greater than zero. Casual perusal of Table V shows this to be the case. Clearly, a large fraction of the $C_2H_4T^+$ must be formed by reactions not initiated by the radiation field in the source volume of the mass spectrometer. A logical source of these $C_2H_4T^+$ ions is the reaction between the CH_4 and the $(THe^3)^+$ daughter produced in the beta transformation. Note (Table IV) that the other possible ion produced by interaction of T_2^+ and $(THe^3)^+$ with methane, namely, CH_4T^+, is of very low abundance.

In an effort to study the mechanism of supposedly ionic scavenging by xenon in the labeling process, $Xe + CH_4$ mixtures of widely differing ratios of concentration were prepared and irradiated by 140-e.v. electrons. The mass patterns measured for the blends appear in Table VI along with the spectra of ions found in pure CH_4 and Xe at the same respective partial pressures as in the mixtures. Among the hydrocarbon fragments, one notes that all species except $C_2H_4^+$ are much less intense in the mixtures than in pure CH_4. The abundances of the xenon isotopes are also reduced in the mixture relative to Xe alone. Low yields of XeH^+ and ionic combinations of Xe and hydrocarbon fragments are found in the mixture.

C. Discussion

From conventional studies of reaction kinetics and of scavenging, Pratt and Wolfgang[6] have concluded that the isotopic tagging of CH_4 with tritium takes place by at least three independent sequences of reactions. In gaseous mixtures of CH_4 and T_2 in the range of ratios $10^3:1$ to $10^4:1$, they found the rate of production of CH_3T to be given by the expression

$$R(CH_3T) = 9.2 \times 10^6[T_2] + 7.4 \times 10^7[T_2]^{3/2} + 7.8 \times 10^5[T_2]^2 \quad (1)$$

where R is the limiting rate of formation of CH_3T at zero time, expressed in molecules per cm.^{3} per sec., and $[T_2]$ is the concentration of tritium in millicuries per cm.^{3}. In equation 1, the linear term in tritium concentration was ascribed to formation of tritiated methane by a decay-induced ionic mechanism, i.e., by a reaction between CH_4 and the daughter molecular ion $(THe^3)^+$ from the beta decay of T_2. The three-halves-power term was attributed to a radiation-induced species which has a recombination limited lifetime. They suggested a sequence of ionic reactions that was started by the production of CH_4^+ from ionization of methane by betas and secondary electrons as the most plausible example of such a process. Finally, a small term that varies with the square of the tritium concentration represents the effect of the radiation field on the T_2 in the gas mixture. When Xe was added, the $[T]^{3/2}$ term

TABLE VI
Intensities of Positively Charged Species in $CH_4 + Xe$ Systems

		Intensity (cts./sec.)[a] (pressures in mm.)				
			CH₄, 0.13		CH₄, 0.072		CH₄, 0.08
	Probable	CH₄,	Xe,	CH₄,	Xe,	CH₄,	Xe,
m/e	species	0.13	0.09	0.072	0.19	0.08	0.03
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14	CH_2	71	61	506	49	344	192
15	CH_3	1869	1100	10105	677	7073	3435
16	CH_4	941	128	4945	91	4270	1353
17	CH_5	25570	7580	22693	7076	22700	15959
18	H_2O	140	35	173	18	163	46
19	H_3O	446	235	330	168	330	168
25	C_2H	25	15	39	12	37	24
26	C_2H_2	179	103	500	58	474	255
27	C_2H_3	7870	3630	6908	3065	7142	5105
28	C_2H_4	3080	3700	2273	4533	2301	2650
29	C_2H_5	31610	6310	26264	5931	26315	16293
30	C_2H_6	552	235	364	356	378	363
31	C_2H_7	151	24	36	34	41	45
32	O_2	70	59	84	59	83	52
33	O_2H	6	6	10		8	

TABLE VIA

		Intensity (cts./sec.)[a]	
		CH₄, 0.072 mm.	Xe,
m/e	Probable species	Xe, 0.19 mm.	0.19 mm
126	Xe^{126}	36	56
127		41	62
128	Xe^{128}	701	1150
129	Xe^{129}	9300	13000
130	Xe^{130}	1550	2375
131	Xe^{131}	7500	10700
132	Xe^{132}	9300	12800
133	HXe^{132}	102	36
134	Xe^{134}	3600	5700
135	HXe^{134}	35	14
136	Xe^{136}	3300	5000
137	HXe^{136}	41	6
140		5	
141		2	
142	CH_2Xe^{128}	25	
143	$CH_3Xe^{128} + CH_2Xe^{129}$	150	
144	$CH_4Xe^{128} + CH_3Xe^{129}$	51	
145	$CH_4Xe^{129} + CH_3Xe^{130}$	167	
146	$CH_4Xe^{130} + CH_3Xe^{131}$	166	
147	$CH_4Xe^{131} + CH_3Xe^{132}$	11	
148	CH_4Xe^{132}	59	
149	CH_3Xe^{134}	12	
150	CH_4Xe^{136}	60	

[a] Intensities corrected for naturally occurring C^{13}.

was completely quenched, but the other two contributions to the rate were unaffected.

1. Mechanism of Decay-Induced Reaction.—The ionic mechanism proposed by Pratt and Wolfgang to account for the decay-induced part of the Wilzbach labeling of methane appears in Fig. 1. One notes that the proposed transient species $C_2H_4T^+$ must be very long lived to be neutralized by electron capture, for Stevenson[9] has calculated that the lifetime of an ion against electron capture is about 10^6 times as long as the lifetime against an ion–molecule reaction in a gas at a pressure near one atmosphere if the dose rate is 300 R./sec. Under Pratt and Wolfgang's and our experimental conditions the factor would be even greater. The present results from study of $CH_4 + T_2 + D_2$ mixtures (Table V) indicate that the species $C_2H_4T^+$ is formed partially by ion–molecule reactions initiated by a primary precursor not produced by the radiation field. The most likely primary species that is not radiation induced is the molecular ion $(THe^3)^+$ formed as the daughter of the beta decay of T_2. This ionic species has a lifetime greater than 10^{-5} sec. in collision-free space, for it has been shown by mass spectrometric techniques to be formed in 94.5% of the beta transitions of T_2.[10] Furthermore, ions of the $C_2H_5^+$ type were found to be unreactive with methane.[7] Thus, our
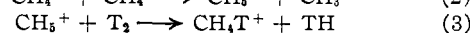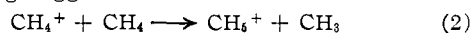
(9) D. P. Stevenson. *J. Phys. Chem.*, **61**, 1453 (1957).

(10) S. Wexler, *J. Inorg. and Nuclear Chem.*, **10**, 8 (1959); see also A. H. Snell, F. Pleasonton and H. E. Leming, *ibid.*, **5**, 112 (1957).

observation of the transient species $C_2H_4T^+$ tends to support the mechanism (Fig. 1) proposed by Pratt and Wolfgang. However, it should be emphasized that the inference that $C_2H_4T^+$ is produced by reactions of ions not formed by the radiation field (as well as by reactions of radiolytically formed primary ions) is based on the observation that the measured ratio $C_2H_4T^+/ C_2H_5^+$ is greater than $C_2H_4D^+/C_2H_5^+$ in $T_2 + D_2 + CH_4$ gas mixtures. The ions $C_2H_5^+$ and $C_2H_4D^+$ can conceivably be formed only by radiation-induced mechanisms. Implicit in the conclusions from these experiments is the assumption that T_2 and D_2 react identically in radiation-induced reactions, i.e., there is no large isotope effect. Relatively large isotopic variations in the cross sections of ionic reactions of H_2 and D_2 with rare gas atoms and O_2 have been reported,[9,11] but the higher reaction probability is always that for the lighter molecule. This would suggest that in $D_2 + T_2 + CH_4$ mixtures the $(D_2 + CH_4)^+$ reaction occurs more readily than that of $(T_2 + CH_4)^+$. Consequently, the present finding of much more $C_2H_4T^+$ than $C_2H_4D^+$ relative to $C_2H_5^+$ (Table V) is contrary to the result that would have been expected solely from the isotopic difference between the reaction rates. This leaves no alternative to the conclusion that $C_2H_4T^+$ is produced by a decay-induced mechanism. Furthermore, when the data from electron impact on $CH_4 + H_2$ are compared with those for $CH_4 + D_2$ gas mixtures (Table III), a similar isotope effect appears—H_2 being more reactive than D_2. The intensity of $C_2H_5^+$ from the mixture $CH_4 + H_2$ exceeds that from pure CH_4 by 1712 cts./sec. In the change from pure CH_4 to its mixture with D_2, the sum of the intensity increases of $C_2H_5^+$, $C_2H_4D^+$, $C_2H_3D_2^+$, and $C_2H_2D_3^+$ was 898 cts./sec., only about half that for the mixture with H_2.

2. Mechanisms of Radiation-Induced Reactions.—

To account for the major part of the radiation-induced labeling of methane at pressures near one atmosphere and with a T_2 admixture of about 1 part in 10^4, Pratt and Wolfgang suggested a set of consecutive reactions

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad (2)$$
$$CH_5^+ + T_2 \longrightarrow CH_4T^+ + TH \qquad (3)$$
$$CH_4T^+ + CH_4 \longrightarrow CH_3T + CH_5^+ \qquad (4)$$

Reaction 3 apparently is slow since it requires an activation energy of 2–4 kcal./mole. These reactions obviously are initiated by the action of the radiation field on the methane. They were proposed to account for the $[T_2]^{3/2}$ term in the concentration dependence of the rate of labeling (eq. 1). The authors did not present a detailed mechanism for the labeling process started by ionization of the T_2.

The transient ionic species formed in reactions of ions produced by the action of the radiation field on the $CH_4 + T_2$ mixture were investigated by experiments in which D_2 was used as a stand-in for T_2 and a beam of 140-e.v. electrons served as the radiation field. The ratio of CH_4 to D_2 in these experiments was varied between 0.1 and 10. Indeed, reaction between the two components was difficult to detect at the higher values of CH_4/D_2. Because of the limitations on the ratio of reactants and on the total pressure (0.1–0.2 mm.) in the source chamber of the mass spectrometer, ionic products would be expected from the reaction of the primary ions of methane (particularly CH_4^+ and CH_3^+) with D_2, from the interaction of D_2^+ with CH_4, and from the chemical reaction of the primary ions of methane with methane and of D_2^+ with D_2. In addition, the secondary ion D_3^+ may react with methane and the secondary ions CH_5^+ and $C_2H_5^+$ may react with D_2.

(11) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955); **24**, 926 (1956); G. Gioumousis and D. P. Stevenson, *ibid.*, **29**, 294 (1958).
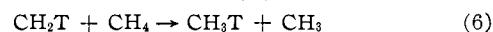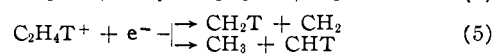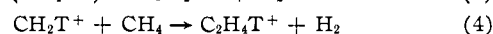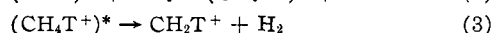
$$T_2^+ \rightarrow (THe^3)^+ + \beta^- \qquad (1)$$
$$(THe^3)^+ + CH_4 \rightarrow (CH_4T^+)^* + He^3 \qquad (2)$$
$$(CH_4T^+)^* \rightarrow CH_2T^+ + H_2 \qquad (3)$$
$$CH_2T^+ + CH_4 \rightarrow C_2H_4T^+ + H_2 \qquad (4)$$
$$C_2H_4T^+ + e^- - \begin{array}{l} \rightarrow CH_2T + CH_2 \\ \rightarrow CH_3 + CHT \end{array} \qquad (5)$$
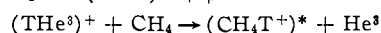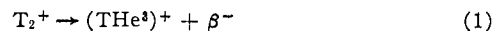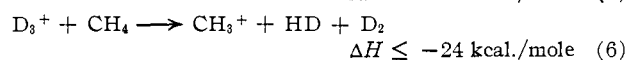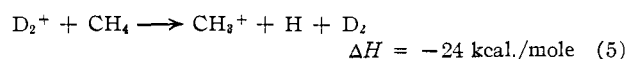$$CH_2T + CH_4 \rightarrow CH_3T + CH_3 \qquad (6)$$

Fig. 1.—Proposed ionic mechanism of decay-induced part of Wilzbach labeling of CH_4 (Pratt and Wolfgang, 1961).

The mass pattern obtained by electron impact on a mixture of CH_4 and D_2 (Table I) is therefore the composite result of several different sequences of ion–molecule reactions, and the problem is to sort out the evidence for each series of reactions. The spectra of ions from direct electron impact and from ion–molecule reactions in methane alone may be subtracted off that from the mixture $D_2 + CH_4$. This may be done by comparison of columns 4 and 5 in Table I. When this is done, one sees that most of the primary ions from methane react with D_2. Also, the decreases in the intensities of D_2^+ and D_3^+ in going from pure D_2 gas to the mixture with methane is more than an order of magnitude (in some runs it was more than two orders of magnitude) greater than would be expected from the attenuation of the electron beam in the mixture. This almost complete disappearance of D_2^+ and D_3^+ in the mixture indicates that these species react with methane. The large increases in the intensities of several entities in the mixture suggest that the products of the ionic reactions between the two constituents are CH_4D^+, $C_2H_4D^+$, $C_2H_3D_2^+$, $C_2H_2D_3^+$, and $C_3H_4D^+$. The coincidence of appearance potentials indicates that the CH_4^+ ion is the precursor of CH_4D^+, but either CH_3^+ or D_2^+ ions or both are the primary precursors of the species $C_2H_4D^+$, $C_2H_3D_2^+$, and $C_2H_2D_3^+$.

The disappearance of D_2^+ and D_3^+ may conceivably be the result of dissociative charge exchange with methane, since this process is energetically possible for both ions. These reactions are

$$D_2^+ + CH_4 \longrightarrow CH_3^+ + H + D_2$$
$$\Delta H = -24 \text{ kcal./mole} \quad (5)$$
$$D_3^+ + CH_4 \longrightarrow CH_3^+ + HD + D_2$$
$$\Delta H \leq -24 \text{ kcal./mole} \quad (6)$$

However, cross sections for these nonresonance charge exchange reactions should be less than for exoergic ion–molecule reactions of the condensation type.[12–14] Furthermore, reactions corresponding to 5 and 6 do not result in the characteristics of the labeling of CH_4 by T_2^+ observed. Also, the reaction cross section for $(D_2 + CH_4)^+ \rightarrow CH_4D^+ + D$ is very small.[15] Consequently, it is very likely that reactions between CH_4 and the ions D_2^+ and D_3^+ occur which lead to $C_2H_4D^+$, $C_2H_3D_2^+$, and $C_2H_2D_3^+$. An additional indication of this is that a species with $m/e = 32$, most likely $C_2H_2D_3^+$, is found in the $D_2 + CH_4$ mixture. This ion could not be formed by the reactions of methane ions with D_2.

Considerations such as the foregoing lead to a proposed sequence of ion–molecule reactions (Fig. 2) taking place as a result of electron impact on $D_2 + CH_4$ mixtures at pressures of tenths of millimeters. It is seen that isotopic exchange occurs in the interactions of D_3^+ and of primary ions from both CH_4 and D_2.

(12) G. K. Lavrovskaya, M. I. Markin and V. L. Tal'roze, *Kinetika i Kataliz*, **2**, 21 (1961).

(13) E. Gustafsson and E. Lindholm, *Arkiv Fysik*, **18**, 219 (1960).

(14) For a compilation of cross sections of ion–molecule reactions, see F. W. Lampe, J. L. Franklin and F. H. Field, *Progr. in Reaction Kinetics*, **1**, 87 (1961).

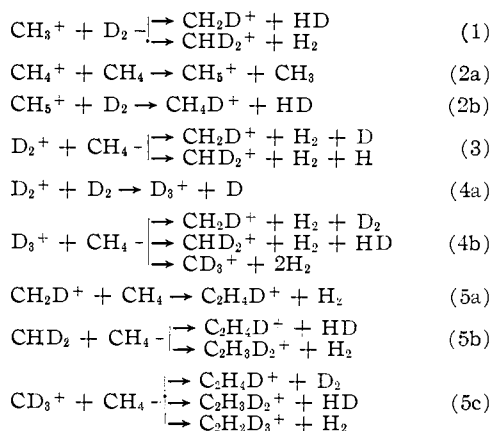(15) F. W. Lampe and F. H. Field, *J. Am. Chem. Soc.*, **81**, 3242 (1959).

$$CH_3^+ + D_2 -\begin{cases}\rightarrow CH_2D^+ + HD \\ \rightarrow CHD_2^+ + H_2\end{cases} \quad (1)$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \quad (2a)$$

$$CH_5^+ + D_2 \rightarrow CH_4D^+ + HD \quad (2b)$$

$$D_2^+ + CH_4 -\begin{cases}\rightarrow CH_2D^+ + H_2 + D \\ \rightarrow CHD_2^+ + H_2 + H\end{cases} \quad (3)$$

$$D_2^+ + D_2 \rightarrow D_3^+ + D \quad (4a)$$

$$D_3^+ + CH_4 -\begin{cases}\rightarrow CH_2D^+ + H_2 + D_2 \\ \rightarrow CHD_2^+ + H_2 + HD \\ \rightarrow CD_3^+ + 2H_2\end{cases} \quad (4b)$$

$$CH_2D^+ + CH_4 \rightarrow C_2H_4D^+ + H_2 \quad (5a)$$

$$CHD_2 + CH_4 -\begin{cases}\rightarrow C_2H_4D^+ + HD \\ \rightarrow C_2H_3D_2^+ + H_2\end{cases} \quad (5b)$$

$$CD_3^+ + CH_4 -\begin{cases}\rightarrow C_2H_4D^+ + D_2 \\ \rightarrow C_2H_3D_2^+ + HD \\ \rightarrow C_2H_2D_3^+ + H_2\end{cases} \quad (5c)$$

Fig. 2.—Possible ionic reactions in isotopic exchange in D_2 + CH_4 mixtures.

The present results give no direct evidence that the principal secondary ions from CH_4 participate in further reactions such as

$$C_2H_5^+ + D_2 \longrightarrow C_2H_4D^+ + HD \quad (7)$$

$$CH_5^+ + D_2 \longrightarrow CH_4D^+ + HD \quad (8)$$
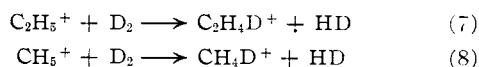
If these reactions were prominent, the species with masses 29 and 17 would be expected to be less intense in the mixture than in pure methane, and the species with masses 30 and 18 would be expected to be correspondingly more intense. The decreases in abundances of species with masses 17 and 29 are not shown by the data of Table I. However, reaction (8) may occur and be masked because of the small amount of CH_4D^+ relative to CH_5^+ and the formation of CHD_2^+ as a product of $CH_3^+ + D_2$ and $D_2^+ + CH_4$. Likewise, the isotopic exchange reducing $C_2H_5^+$ may be masked by a reaction of CH_2D^+ with CH_4 to give $C_2H_5^+$. Another explanation may be that (7) and (8) are endoergic for reactants in their ground electronic states, and consequently they should be difficult to observe in the mass spectrometer.

Part of the variations in abundances of species noted in Table I may, from the considerations presented above, be ascribed to the interaction of D_2^+ ions with methane to form a relatively long-lived[7] ion analogous to $C_2H_5^+$ but containing one or two deuteriums. In the radiation-induced mechanism of Wilzbach labeling of methane, therefore, these reactions would be expected to constitute the part starting with the ionization of T_2 by betas and secondary electrons, i.e., these reactions correspond to the $[T_2]^2$ term in the rate expression 1. The mechanism proposed here is given in Fig. 3. It is of considerable interest to note that the same long-lived ion $C_2H_4T^+$ is depicted as being formed both in the decay-induced mechanism and in this part of the radiation-induced mechanism of the labeling process. Indeed, the sequences of reactions are almost identical (as is seen by comparison of Fig. 1 and 3).

3. Studies on the Mechanism of Xe Scavenging.—

The close similarity between the two sequences of reactions described above leads one to expect that an ion scavenger such as Xe should have the same effect on these two parts of the tagging—in agreement with the observation of Pratt and Wolfgang that xenon has no effect on either of these mechanisms. Since cross sections of ion-molecule reactions are so large, and the xenon concentration in their experiments was about 0.1 of the CH_4 concentration, the tritium should have been incorporated into the hydrocarbon ion $C_2H_4T^+$ long before the ion encountered a xenon atom. The question then becomes whether a Xe will react with a $C_2H_4T^+$.

Studies on several Xe–CH_4 mixtures were undertaken to answer this question. The observed species

Reactions Starting with T_2^+

$$T_2^+ + CH_4 -\begin{cases}\rightarrow CH_2T^+ + H_2 + T \\ \rightarrow CHT_2^+ + H_2 + H\end{cases} \quad (1)$$

$$CH_2T^+ + CH_4 \rightarrow C_2H_4T^+ + H_2 \quad (2a)$$

$$CHT_2^+ + CH_4 \rightarrow C_2H_3T_2^+ + H_2 \quad (2b)$$

$$C_2H_4T^+ + e^- -\begin{cases}\rightarrow CH_2T + CH_2 \\ \rightarrow CH_3 + CHT\end{cases} \quad (3)$$

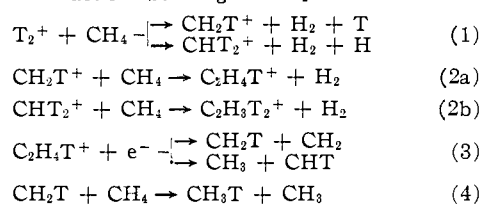$$CH_2T + CH_4 \rightarrow CH_3T + CH_3 \quad (4)$$

Fig. 3.—Proposed partial ionic mechanism of radiation-induced part of Wilzbach labeling of CH_4.

and their intensities are listed in Table VI. It is seen that the abundances of the Xe isotopes and of all hydrocarbon ions except $C_2H_4^+$ are lower in the mixture than in pure Xe and methane, respectively, but the difference is somewhat smaller for Xe than for the hydrocarbons. These lowerings of the abundance in the mixture are believed to be mainly due to attenuation of the electron beam by the relatively high concentrations of CH_4 and Xe along the path between the entrance hole for the electrons and the critical region of ionization adjacent to the slit. For the source configuration used, calculation shows that methane at 0.1 mm. will attenuate the electron beam by 65% while xenon at the same pressure will decrease the electron beam strength by 81%.

Table VII lists the hydrocarbon ions from the Xe–CH_4 mixtures as fractional intensities. For these calculations, the sum of all ion abundances from mass 14 through mass 32 was used for the total intensity I(total). These species account for more than 90% of the intensity of all ions from methane.[7] In arriving at conclusions from this table, we assume that changes in I-(total) when Xe is added reflect the attenuation of the electron beam by Xe between the entrance hole and the exit slit; but variations in fractional intensity are assumed to be caused by ionic reactions involving the particular species. One sees that the fractional intensities of the primary ions from methane usually decrease in

TABLE VII
Effect of Xe on Fractional Intensities of Species in CH_4

	Fractional intensity I_i/I(total)[a] (pressures in mm.)					
Probable species	CH_4 (0.13)	CH_4 + Xe (CH_4, 0.13 Xe, 0.09)	CH_4 (0.072)	CH_4 + Xe (CH_4, 0.072 Xe, 0.19)	CH_4 (0.08)	CH_4 + Xe (CH_4, 0.08 Xe, 0.03)
CH_2	0.00099	0.0027	0.0068	0.0022	0.0048	0.0042
CH_3	.026	.048	.136	.031	.100	.075
CH_4	.013	.0056	.066	.0042	.060	.030
CH_5	.36	.33	.30	.32	.32	.35
C_2H	.00035	.00066	.00052	.00055	.00052	.00053
C_2H_2	.0025	.0045	.0067	.0027	.0067	.0056
C_2H_3	.109	.159	.093	.14	.100	.112
C_2H_4	.043	.162	.030	.21	.032	.058
C_2H_5	.44	.28	.35	.27	.37	.36
C_2H_6	.0077	.010	.0049	.016	.0053	.0080
C_2H_7	.0021	.0010	.00048	.0016	.00058	.0010

[a] The sum of all hydrocarbon species from mass 14 through mass 32 was taken as I(total). These ions account for more than 90% of the total intensity of all ions from methane in the range of pressures studied.
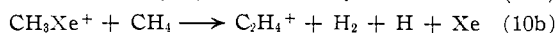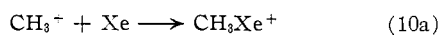
the mixture, while those of the more abundant secondary ions (except $C_2H_5^+$ and CH_5^+) usually increase. This suggests that the former are reacting with xenon. The yields of HXe^+ and CH_3Xe^+ in the mixture are very low (Table VI) in agreement with previous studies of Field and Franklin on CH_4–Xe mixtures,[16] and these are formed by the action of Xe^+ on methane.[16] Hence the reactions responsible for the abnormal drop in the abundances of CH_4^+ and CH_2^+ and the rise in the yield of

(16) F. H. Field and J. L. Franklin, J. Am. Chem. Soc., 83, 4509 (1961).

$C_2H_4{}^+$ are probably a simple charge exchange

$$CH_4{}^+ + Xe \longrightarrow CH_4 + Xe^+ \qquad (9)$$
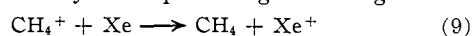
and the consecutive ion–molecule reactions

$$CH_3{}^+ + Xe \longrightarrow CH_3Xe^+ \qquad (10a)$$

$$CH_3Xe^+ + CH_4 \longrightarrow C_2H_4{}^+ + H_2 + H + Xe \qquad (10b)$$

However, the central question of whether the principal secondary ions from methane, $CH_5{}^+$ and $C_2H_5{}^+$ (and therefore CH_4T^+ and $C_2H_4T^+$), react with xenon is not unambiguously answered by the data of Tables VI and VII. The ion $CH_5{}^+$ apparently does not react with xenon because $I(CH_5{}^+)/I(\text{total})$ is the same in CH_4 alone as it is in the $CH_4 + Xe$ mixture (Table VII). The observation that $I(C_2H_5{}^+)/I(\text{total})$ is less in the mixture than in pure CH_4 could suggest reaction between this secondary ion and xenon; but it should be remembered that the primary precursor of $C_2H_5{}^+$ is $CH_3{}^+$, and the latter may interact with Xe by a competitive process (equation 10a); and this may be the correct explanation for the lower value of the intensity ratio $I(C_2H_5{}^+)/I(\text{total})$ in the mixture. The proton transfer reaction

$$Xe + C_2H_4T^+ \longrightarrow XeH^+ + C_2H_3T$$
$$\Delta H \approx + 10 \text{ kcal./mole} \qquad (11)$$
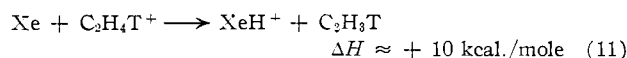
may be unlikely for energetic reasons, but error limits in the ionic heats of formation make this uncertain. But the low yields of XeH^+ in experiments with mixtures of $CH_4 + Xe$ (Table VI) indicate that proton transfer such as reaction 11 is very inefficient if it occurs at all. The recent results of Field and Franklin[16] on $CH_4 + Xe$ show that the XeH^+ is produced in reactions of Xe^+ with CH_4, and presumably not by alternative modes involving hydrocarbon ions reacting with Xe.

The intensity of $C_2H_4{}^+$ from electron bombardment of $CH_4 + Xe$ mixtures is greater than that from pure CH_4, in contrast to the behaviors of all the other hydrocarbon ions (Table VI). Such an enhancement could not occur as a result of the collision-induced decomposition

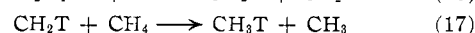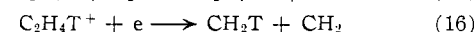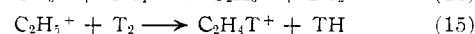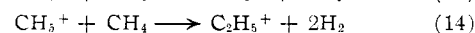$$C_2H_5{}^+ + Xe \longrightarrow C_2H_4{}^+ + H + Xe \qquad (12)$$
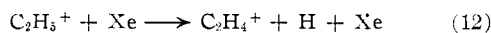
since the reaction requires 86 kcal./mole of energy. Therefore, it is likely that the increase in $C_2H_4{}^+$ ions results from reactions (such as in equation 10a and 10b) not involving $C_2H_5{}^+$.

In conclusion, the experiment gives no conclusive evidence for a reaction between $C_2H_5{}^+$ and Xe, and this again may support the conclusion of Pratt and Wolfgang that xenon has no quenching action on ionic mechanisms involving the long-lived species $C_2H_4T^+$.

4. Considerations of the Radiation-Induced Mechanism Initiated by Ions from CH_4.—Plausible mechanisms, based on identification of long-lived ionic species, have been proposed in the foregoing discussion. These may account for the decay-induced labeling of methane with tritium and a part of the radiation-induced labeling; but, as shown by equation 1, they account for a relatively minor fraction of the rate of formation of CH_3T. What can be said about the

radiation-induced part initiated by the action of the radiation field on methane, the predominant constituent? Since the ratio of the concentration of CH_4 to that of T_2 was about 10^4 in Pratt and Wolfgang's work, primary methane ions produced by betas and secondary electrons would react with CH_4 rather than T_2. Only long-lived ionic species would react with the tritium. From previous studies[7] on CH_4 at source pressures of tenths of a millimeter, the secondary ion $C_2H_5{}^+$ appears to be the only long-lived ion of great abundance. The other prominent secondary ion $CH_5{}^+$ appears to react with CH_4, although relatively inefficiently. Unfortunately the present experiment cannot distinguish between the intensity of a species in CH_4 and the intensity in a mixture of CH_4 and D_2 unless the D_2 constitutes at least 10% of the mixture, as seen in Table II. The principal mechanism of the labeling process therefore remains a subject of speculation on the basis of the methane investigations.[7]

In contrast to reactions 2–4 proposed by Pratt and Wolfgang, the set of consecutive reactions suggested by these investigations is

$$CH_4{}^+ + CH_4 \longrightarrow CH_5{}^+ + CH_3 \qquad (13)$$
$$CH_5{}^+ + CH_4 \longrightarrow C_2H_5{}^+ + 2H_2 \qquad (14)$$
$$C_2H_5{}^+ + T_2 \longrightarrow C_2H_4T^+ + TH \qquad (15)$$
$$C_2H_4T^+ + e \longrightarrow CH_2T + CH_2 \qquad (16)$$
$$CH_2T + CH_4 \longrightarrow CH_3T + CH_3 \qquad (17)$$

The occurrence of the isotopic exchange (reaction 15) should be evidenced by a marked decrease in the intensity of $C_2H_5{}^+$ when D_2 is added to CH_4. Actually Table I indicates an increase in this ion. However, as discussed above, the process involved (reaction 7) could have been masked by reactions that increase the intensity of the $C_2H_5{}^+$. Or, as Pratt and Wolfgang have concluded for the analogous reaction involving $CH_5{}^+$, reaction 15 is slow, as it requires an activation energy. Therefore, it would not be observed in the mass spectrometer.

The mechanism by which xenon inhibits this mode of tagging methane is at present not understood. As pointed out above, the experiments of Pratt and Wolfgang were carried out at about 300 mm. pressure of CH_4 and about 30 mm. of Xe. Therefore, Xe could interfere with the series of reactions 13–17 only by way of some reaction with the secondary ions $CH_5{}^+$ and $C_2H_5{}^+$. But the studies on Xe–CH_4 mixtures (Tables VI and VII) give no unequivocal evidence for any such reactions. Pratt and Wolfgang suggest that proton exchange between Xe and $CH_5{}^+$ is the mode of quenching, but there is a lack of evidence for this in Tables VI and VII. On the other hand, the suggested sequence of reactions 13–17 does not take into account the observed quenching by xenon.