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## The Self-induced Exchange of Tritium Gas with Methane

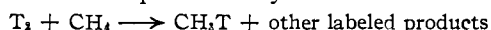
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The exchange of tritium atoms between  $T_2$  gas and methane as induced by radioactive decay of the tritium has been studied. Kinetic data indicate the existence of three distinct mechanisms: (1) Decay of tritium in  $T_2$  yields  $HeT^+$  which reacts rapidly with  $CH_4$  to yield excited  $CH_4T^+$ . This species reacts further to yield  $CH_3T$ . The mechanism shows the required first order dependence of  $T_2$  pressure and is insensitive to scavenging by xenon. (2) The tritium beta radiation causes formation of several species with lifetimes limited by recombination. One of these, probably  $CH_3^+$ , undergoes reaction with  $T_2$  leading to  $CH_3T$ . This mechanism gives an observed  $3/2$  power dependence on  $T_2$  pressure and is sensitive to ion scavengers. (3) A small square power term in the kinetics probably arises from the beta radiolysis of the  $T_2$  itself. The type of mechanisms postulated may be applied to the exchange of tritium with other substances. However, the present dearth of information on elementary ion-molecule processes makes it difficult to establish detailed, unique mechanisms for more complex systems.

### Introduction

We have attempted to determine the mechanism of a simple ion-induced reaction in the gas phase. In this reaction the exchange of  $T_2$  gas with methane is induced by the radioactive decay of the tritium and the beta radiation associated therewith. The system can be represented by



Interest in this type of system stems from two main sources. One is the growing pool of information on elementary ionic reactions in mass spectrometer ion sources. This provides some hope that one may be able to understand the more complex ionic reactions occurring in gaseous chemical systems at ordinary pressures in terms of the elementary processes found in the mass spectrometer. The system methane- $T_2$  was chosen for investigation because it is still sufficiently simple so that a relatively unique determination of the reaction path might be possible. This system also represents a simple case of the method of labeling developed by Wilzbach<sup>1</sup> in which tritium gas is mixed with the compound to be labeled. Despite several investigations,<sup>1-4</sup> including the quantitative studies of Yang and Gant, the mechanism of the self-induced tritium exchange process remains somewhat doubtful.

The experimental approach used in the present investigation involved mixing small amounts of tritium gas with methane in Pyrex bulbs. From time to time small aliquots were removed from each bulb, the labeled products separated by gas chromatography, and assayed by passage through an internal flow-proportional counter.<sup>5</sup> The proportions of reactants were varied from run to run and in some samples small amounts of various other substances were added. In this manner the dependence of the rate of exchange on the concentration of tritium gas and on the presence of the noble gases, iodine and nitric oxide was determined.

In developing a mechanism for the exchange from these results, it became necessary to consider certain possible ion-molecule reactions which had not been investigated previously. The criterion for predicting the direction of these re-

actions is that they must be exothermic. Furthermore resonant or near resonant reactions have a higher cross section than those in which there is a large energy difference.<sup>6</sup> The heats of reaction,  $\Delta H_r$ , for the ion-molecule reactions used in the discussion have been evaluated from the heats of formation of the ions.<sup>7-9</sup> The numbers to the right of the chemical equations in the discussion are the calculated  $\Delta H_r$  values in units of kilocalories per mole with a negative sign indicating that the reaction is exothermic as written.

### Experimental

**Procedures.**—The samples were prepared by expanding the gaseous constituents in the order of increasing pressure into previously evacuated (<0.1 micron) sample bulbs. These samples were analyzed immediately for tritium content and then allowed to stand for several days at ambient temperature (23°). At successive time intervals, aliquots were removed for separation and analysis by gas chromatography. The masses of the eluted constituents were monitored by a thermal conductivity detector using thermistors in a Wheatstone bridge circuit. The sensitivity of this apparatus was ca. one micromole, and there was never observed a mass peak of any hydrocarbon except methane. The radioactivities of the eluted constituents were monitored by a method described earlier which consists of mixing the effluent with methane and passing it directly into an internal flow counter.<sup>5</sup>

The sample vessels consisted of 30 cm.<sup>3</sup> Pyrex spheres equipped with a capillary tee stopcock. One outlet of this stopcock connected with the bulb, the outlet opposite was sealed off to enclose a small volume and the outlet in between connected to the analytical vacuum line. This configuration allows withdrawal of an aliquot which is negligible compared to the whole, but adequate for analysis, by rotating the stopcock back and forth through 90°. The vacuum system was calibrated so that a known portion of a sample could be admitted to the gas chromatographic apparatus. Then, from the number of observed disintegrations of tritium, the flow rates of the eluents, the volume of the counter and the fraction of the sample analyzed, the concentration of the labeled reaction products could be determined. It was found that the reproducibility of this procedure was within 3%.

The substrates used in the gas chromatographic apparatus were (a) 40-60 mesh silica gel for the separation and analysis of hydrogen, methane, ethane, ethylene and acetylene; and (b) silicone oil (Dow Corning #703) on 40-60 mesh firebrick for the separation and analysis of the higher hydrocarbons. The aliquots were removed from the sample bulbs by expansion into a vacuum line and injected into the gas chromatographic apparatus by sweeping the line with helium. With this procedure, one would expect some

- (1) K. E. Wilzbach, *THIS JOURNAL*, **79**, 1013 (1957).
- (2) P. Riesz and K. E. Wilzbach, *J. Phys. Chem.*, **62**, 6 (1958).
- (3) K. Yang and P. L. Gant, *J. Chem. Phys.*, **30**, 1108 (1959).
- (4) K. Yang and P. L. Gant, *ibid.*, **31**, 1589 (1959).
- (5) R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).  
R. Wolfgang and C. MacKay, *Nucleonics*, **16**, #10, 69 (1958).

- (6) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952.
- (7) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.
- (8) F. W. Lampe and F. H. Field, *Tetrahedron*, **7**, 189 (1959).
- (9) O. A. Schaeffer and S. O. Thompson, *Rad. Res.*, **10**, 671 (1959).

fractionation of the higher boiling hydrocarbons; therefore, no quantitative results were taken for labeled hydrocarbons above the butanes even though hexanes and above were observed.

**Materials Used.**—Phillips Petroleum Co. "Research Grade" methane, stated to contain less than 0.04% impurities, was admitted to the vacuum line by a bulb to bulb distillation from liquid nitrogen temperatures taking a center cut from each of the three bulbs used. This procedure was used each time that a series of samples was prepared.

The tritium purchased from Oak Ridge National Laboratories was found to contain trace amounts of labeled hydrocarbons as well as its  $\text{He}^3$  decay product. These impurities were removed by diffusing the tritium through the walls of a hot nickel tube.<sup>10</sup> Samples then could be prepared which contained no detectable labeled hydrocarbons at zero time. The manufacturers stipulated the tritium to be carrier free; it is assumed to be in the form of  $\text{T}_2$  when the samples are initiated.

Air Reduction Co. "Assayed Reagent Grade" noble gases were admitted to the samples without further purification. They were stipulated, by mass spectrographic analysis, to contain less than these mole per cent. impurities: Ne, 0.005%; Ar, 0.005%; Kr, 0.03%; and Xe, 0.01%. Matheson regular grade helium, stated to be of 99.99% purity, was admitted to the samples through a liquid nitrogen trap.

Matheson regular grade nitric oxide, stated to be of 99.0% purity, was passed into a previously evacuated liquid nitrogen trap from which a center cut was distilled slowly into the sample vessel.

Baker and Adamson Co. "Reagent Grade" iodine was purified by vacuum sublimation into small Pyrex ampoules equipped with fragile break off tips. These ampoules were inserted into the sample bulbs prior to filling; after the samples were prepared, the ampoules were broken open by vigorous shaking of the sample bulbs.

A further purification step was taken by placing a Dry Ice trap at the entrance of the sample bulb. This prevented the mercury vapors of the vacuum system from entering the samples.

TABLE I  
LIMITING RATES OF FORMATION OF  $\text{CH}_3\text{T}$

No.	Additive and pressure (mm. Hg)	Tritium activity, <sup>a</sup> (mc./cm. <sup>3</sup> )	$\left(\frac{d\text{CH}_3\text{T}}{dt}\right)_0 \times 10^{-7}$ (molecules/cm. <sup>3</sup> sec.)	R/R <sub>0</sub>
1		0.15	0.47	0.84
2		0.90	6.88	2.1
3		1.8	12.7	1.8
4		2.4	29.6	3.4
5		3.1	43.8	3.8
6		5.6	107	5.2
7 <sup>a</sup>		6.4	115	4.8
8 <sup>a</sup>		8.7	168	5.4
9 <sup>b</sup>		6.7	164	6.6
10 <sup>b</sup>		5.6	121	5.8
11	He 14	4.2	74.6	4.8
12	Ne 12	1.5	27.0	4.8
13	A 10	1.4	20.0	3.8
14	Kr 20	1.8	28.2	4.2
15	Xe 31	1.2	1.17	0.27
16	Xe 27	3.8	4.59	.34
17	Xe 27	7.1	10.4	.40
18	Xe 6	6.9	9.95	.40
19	I <sub>2</sub> (satd.)	0.93	0.86	.25
20	I <sub>2</sub> (satd.)	1.2	1.22	.27
21	I <sub>2</sub> /Xe (satd.)/20	1.0	1.05	.28
22	NO 20	2.8	<0.36	< .036
23	NO 26	3.6	<0.18	< .02
24	Xe/Ne 13/29	5.3	5.8	.30

<sup>a</sup> Total pressure 327 mm. <sup>b</sup> Total pressure 153 mm.

**Energy Absorption.**—Dorfman<sup>11</sup> has shown that when the product of the radius of the spherical container and the gas

density is 0.08 mg./cm., one half of the energy of the tritium beta is absorbed. In the present investigation, the radii of the sample bulbs were 2.0 cm. (30–31 cm.<sup>3</sup>) in which case the methane "half-pressure" is calculated to be 41 mm. (at 25°). All of the samples were filled to a total pressure of  $675 \pm 3$  mm., except where noted in Table I; therefore, the absorption of energy is virtually complete. Since all of the energy is absorbed, the initial step in the radiolysis of the methane, *i.e.*, production of ions, radicals, etc., is dependent only on the concentration of tritium.

## Results

The limiting rates of formation of labeled methane, reported in Table I, were determined by taking the slope of the concentration *vs.* time curves at zero time. These curves were of four types. Fig. 1 is representative of samples 1 through 10 containing no additives which show a slight decrease in the rate of production of labeled meth-

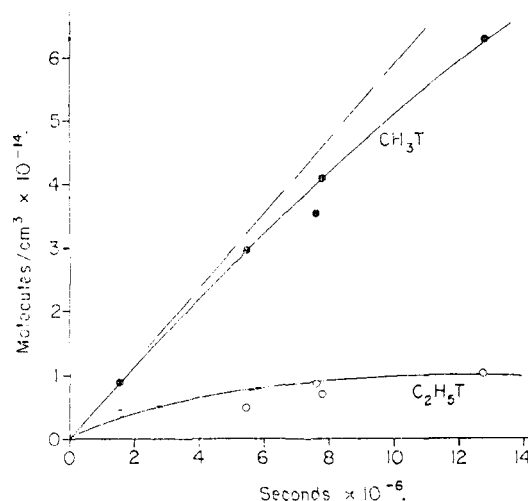


Fig. 1.—Concentration of labeled methane and ethane *vs.* time in sample 2: ●,  $\text{CH}_3\text{T}$ ; ○,  $\text{C}_2\text{H}_5\text{T}$ . Activity: 0.90 mc./cm.<sup>3</sup>.

ane and ethane with time. Samples containing noble gases with ionization potentials above that of methane show a greater decrease in the rate of production of labeled methane with time, and the concentration of labeled methane has a maximum value. In samples containing xenon there is an increase in the rate of production of labeled methane and ethane with time. The presence of iodine, however, results in rates of production of both labeled methane and ethane that are constant with time. Addition of iodine plus xenon results in behavior similar to that of samples containing only iodine, and the xenon plus neon sample behaved similarly to the samples containing only xenon. The amount of labeled methane and ethane formed in samples with nitric oxide additive were too small to monitor quantitatively; however, upper limits to the rates of production of labeled methane were determined and are reported in Table I.

The limiting rates of production of labeled methane at zero time *vs.* the activity of tritium are plotted in Fig. 2. There are two distinct loci: one for samples 1–6 containing no additives (un-scavenged); and one for samples 15–21 scavenged either by xenon or by iodine. Experiments with added He, Ne or Kr give points falling above

(10) K. Landecker and A. J. Gray, *Rev. Sci. Instr.*, **25**, 1151 (1954).

(11) L. M. Dorfman, *Phys. Rev.*, **95**, 393 (1954).

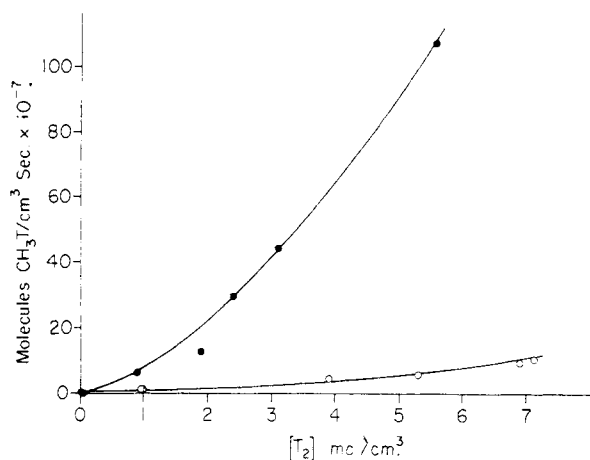


Fig. 2.—Rate of formation of labeled methane vs. concentration of tritium: ●, unscavenged; ○, scavenged.

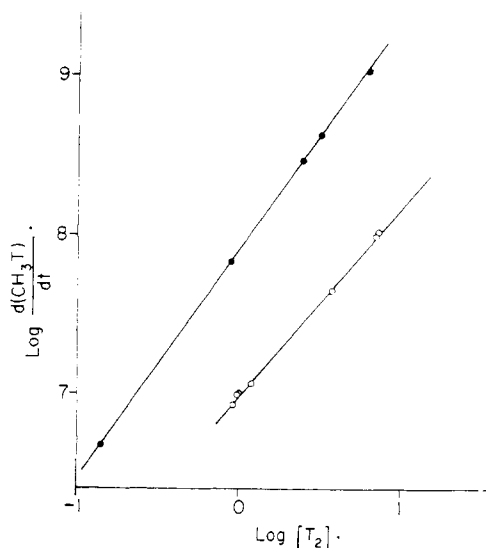


Fig. 3.—Logarithm of the rate of formation of labeled methane vs. the logarithm of the tritium concentration: ●, unscavenged; ○, scavenged.

both curves, and with added NO the points fall below both curves. A plot of the logarithm of the rate of formation of labeled methane vs. the logarithm of the concentration of tritium, Fig. 3, results in straight lines for both I<sub>2</sub> or Xe scavenged and unscavenged samples. These correspond to the empirical rate equations

$$R_u = 8.0 \times 10^7 a^{1.50} \quad (1)$$

$$R_s = 9.3 \times 10^6 a^{1.20} \quad (2)$$

where  $R_u$  and  $R_s$  are the rates of formation of labeled methane in the unscavenged and scavenged samples, respectively, and  $a$  is the concentration of tritium in the sample in units of mc./cm.<sup>3</sup>. Expression 1 shows that the rate of production of labeled methane in the unscavenged samples is dependent on the 3/2 power of the tritium concentration. However, the 1.2 power of the tritium concentration in expression 2 suggests that there are two or more competing reactions which lead to labeled methane in the scavenged samples. A more convenient way to express these data is

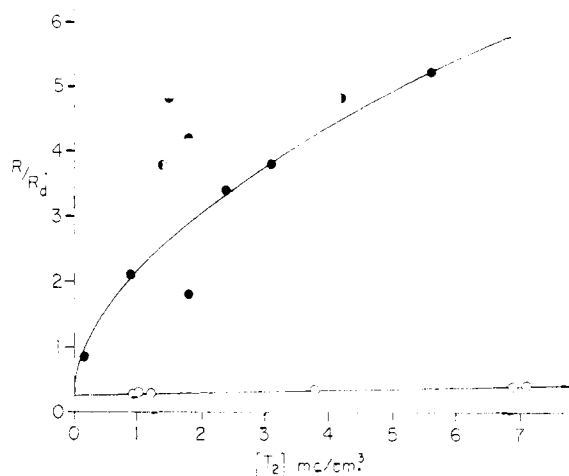


Fig. 4.— $R/R_d$  values vs. the tritium concentration: ●, no additive; ○, xenon and/or iodine added; ⊙, He added; ⊕, Ne added; ⊖, Ar added; ⊗, Kr added.  $R/R_d$  = rate of exchange as fraction of rate of decay.

to calculate the ratios of the observed rates,  $R_u$  or  $R_s$ , to the rate of decay of tritium,  $R_d$ , in the sample. These ratios are given in Table I and plotted against the tritium concentration in Fig. 4. Here the scavenged samples form a straight line with an intercept of 0.25 and a slope of 0.021 from which we obtain the expression

$$R_s/R_d = 0.25 + 0.021a \quad (3)$$

Now, remembering that

$$R_d = 3.70 \times 10^7 a \quad (4)$$

we can express the limiting rate in the scavenged runs

$$R_s = 9.2 \times 10^6 a + 7.8 \times 10^5 a^2 \quad (5)$$

This expression, with integer exponents of  $a$ , yields essentially the same curve as does (2) in Figs. 2 and 3.

At this point, it is assumed that the reactions responsible for the labeling of methane in the scavenged samples are also occurring in the unscavenged samples as well. Therefore, the combination of equations 1 and 5 forms the over-all empirical rate equation

$$R_u = 9.2 \times 10^6 a + 7.4 \times 10^7 a^{1/2} + 7.8 \times 10^5 a^2 \quad (6)$$

which is an equivalent expression for (1), within the experimental error.

Labeled hydrocarbons up to and including the C<sub>6</sub>'s have been observed as reaction products. All of these hydrocarbons were saturated except in the samples containing iodine in which case labeled ethylene also was detected. Table II gives the distribution of products in terms of the number of tritium disintegrations observed in a typical sam-

TABLE II  
PRODUCTS OBSERVED FROM THE INTERACTION OF TRITIUM AND METHANE

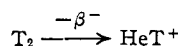
Additive	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> I
None (#2)	100,000	44,800	0	8020	2400	3500	..
Xe (#15)	12,400	3,240	0	2190	88	960	..
I <sub>2</sub> (#19)	11,900	2,360	2710	191	86	192	1980
Xe + I <sub>2</sub> (#20)	13,300	2,280	1500	182	55	158	3500

ple, normalized to the same initial tritium concentration, time, and 100,000 counts of methane in an unscavenged sample.

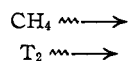
The experimental error in the determination of the number of counts observed as a constituent passes through the flow counter is  $\pm 4\%$ . This is a result of the accuracy with which the flow of the eluting gas was determined. An error analysis of the calibration of the analytical vacuum system showed that the determinations would be expected to have a precision of  $\pm 3\%$  and an absolute accuracy of  $30\%$ . An error of this nature would of course be reflected in the magnitudes of the rate constants but would not change the nature of the following arguments since the relative concentrations of all radioactive constituents would be the same.

### Discussion

Equation 6 indicates that there are at least three separate mechanisms by which methane can be labeled. Two classes of reactions must be considered: (a) The initiating species is  $\text{HeT}^+$  formed by the decay of  $\text{T}_2$ .<sup>3,4,12</sup> This is termed the decay-induced mechanism. (b) The initiating species is produced by the self-irradiation of the mixture with the tritium beta rays. This is termed the irradiation-induced mechanism. Thus we have three initiating steps

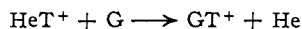


for the decay-induced<sup>13</sup> mechanism and

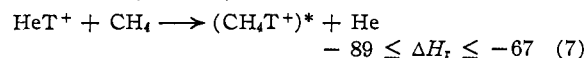


for the irradiation induced mechanism. It will be shown that these initiating steps each give rise to a term in the empirical rate equation 6.

**I. Decay Induced Mechanism.**—A mechanism accounting for the first term in equation 6 must be consistent with the first order concentration of tritium, scavenging by NO, but no scavenging by Xe and  $\text{I}_2$ . The rate of production of  $\text{HeT}^+$  is first order in tritium. Now, if the subsequent reactions of this species lead to labeled methane with the same probability at all dose rates, then the overall kinetics will be first order. It is therefore postulated that the formation of  $\text{HeT}^+$  is rate determining. This species must have a short lifetime in methane, since if it did not, it would be scavenged by rare gas additives in exothermic reactions of the type



$\text{HeT}^+$  probably reacts in the first few collisions with methane  $(\text{CH}_4\text{T}^+)^*$



The state of high excitation of the resulting  $(\text{CH}_4\text{T}^+)^*$  makes its fate somewhat uncertain. If

(12) A. H. Snell, F. Pleasonton and H. E. Leming, *J. Inorg. Nuclear Chem.*, **5**, 112 (1957).

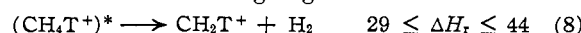
(13) Gant and Yang have used the term "recoil labeling" to describe the postulated interactions of  $\text{HeT}^+$ . This term previously has been applied<sup>14</sup> to the chemical reactions of high energy tritium atoms recoiling from nuclear reactions. We find it somewhat misleading to use the same term to describe the reaction of  $\text{HeT}^+$ , which has no significant recoil energy.

(14) M. A. El-Sayed, P. J. Z. Estrup and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

it survived long enough it could form  $\text{CH}_3\text{T}$  by transferring a proton to  $\text{CH}_4$  (reaction 18) or to a molecule of scavenger. Its lifetime can be estimated using the Kassel model of unimolecular dissociation.<sup>15</sup> According to this the unimolecular rate constant  $k_E$ , which is the inverse of the mean life  $T$ , is given by

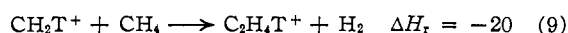
$$k_E = A \left(1 - \frac{E_0}{E}\right)^{r-1} = \frac{1}{T}$$

$A$ , the frequency factor for intramolecular energy transfer is taken as  $10^{14}$ ,  $E_0$  as about 50 and  $E$  about 70. The treatment appears to give best results for simple molecules when  $r$  is taken as  $2/3$  the number of internal degrees of freedom. Thus  $r - 1 \sim 7$  is used here.  $T$  is then approximately  $10^{-11}$  sec. which is an order of magnitude less than the period of a molecular collision. It is therefore likely (though hardly certain in view of the approximate nature of the calculation) that  $(\text{CH}_4\text{T}^+)^*$  will dissociate before undergoing bimolecular reaction

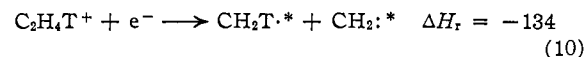


We now consider two possible mechanisms for the conversion of  $\text{CH}_2\text{T}^+$  to  $\text{CH}_3\text{T}$ . They are denoted IA and IB.

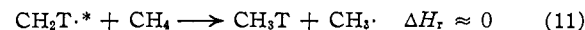
**Mechanism IA.**—In the mass spectrometer  $\text{CH}_2\text{T}^+$  ions will react rapidly with methane by the reaction



There is no direct evidence from mass spectrometry on the further reaction of  $\text{C}_2\text{H}_5^+$  with methane; but it is energetically possible for the  $\text{C}_2\text{H}_4\text{T}^+$  ion to undergo such reaction to yield higher labeled hydrocarbon ions. However, the lifetimes of these higher hydrocarbon ions must be correspondingly longer or else once the chain is initiated the reaction will continue rapidly to give polymer. The radiation chemistry of methane shows that the yield of higher hydrocarbons decreases with the number of carbon atoms.<sup>16</sup> In this study it was found that the longer the carbon chain the smaller the yield of the labeled hydrocarbon; see Table II. It is therefore to be expected that the lifetime of the  $\text{C}_2\text{H}_4\text{T}^+$  ion would be sufficiently long so that neutralization processes become significant. If this is the case, then the reaction



would yield a hot  $\text{CH}_2\text{T}\cdot^*$  radical. By virtue of its excess energy this could then suffer an exchange reaction with methane to yield labeled methane; *viz.*



If the tritium remains with the  $\text{CH}_2\cdot^*$  fragment, then labeled ethane could result from the reaction

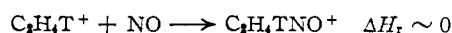


Although the lifetime of  $\text{C}_2\text{H}_4\text{T}^+$  is postulated to be long, no effect of xenon or iodine scavenging is expected since the charge transfer reactions (electron or proton) of this ion with xenon and/or iodine are all endothermic. This is in accord with the experimental result that reactions which give rise

(15) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publications, London, 1955, p. 61 *et seq.*

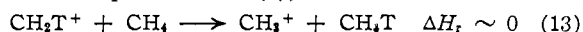
(16) F. W. Lampe, *THIS JOURNAL*, **79**, 1055 (1957).

to the first order term in (6) are not affected by xenon or iodine. However, inhibition of the reaction sequence by nitric oxide is observed. This could result from

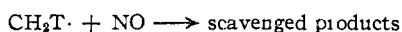
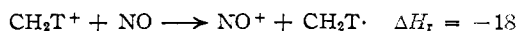


which is exothermic unless the heat of formation of  $\text{C}_2\text{H}_5\text{NO}^+$  differs from that of  $\text{CH}_3\text{NO}^+$  by some 64 kcal./mole, which is unlikely. ( $\Delta H_f(\text{CH}_3\text{NO}^+) = 184$  kcal./mole.<sup>7</sup>)

**Mechanism IB.**—An alternative mechanism for the decay-induced labeling of methane can be postulated which involves hydride ion transfer<sup>8</sup> to  $\text{CH}_2\text{T}^+$ , produced in (8); *viz.*



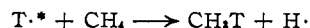
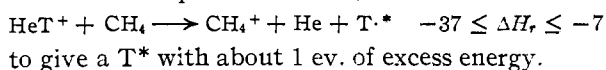
If (13) is to account for the labeling it is necessary that it compete successfully with (9) and that the  $\text{CH}_2\text{T}^+$  ion must have a lifetime long enough to be scavenged by nitric oxide. It is possible that the  $\text{CH}_3^+$  ions produced from methane by electron impact are in different energy states than those produced by other processes. If this is the case then the  $\text{CH}_2\text{T}^+$  ion produced in (8) may suffer several collisions with the surrounding molecules before any reaction occurs, while  $\text{CH}_3^+$  ions produced by the irradiation of the methane will react on first collision to yield  $\text{C}_2\text{H}_5^+$ — as they do in the mass spectrometer. On this hypothesis the scavenging properties of xenon and nitric oxide can be accounted for. Scavenging by xenon would not be expected because the charge transfer reaction to xenon from  $\text{CH}_2\text{T}^+$  is endothermic. The action of nitric oxide could result from the reactions



Scavenging by iodine, through charge transfer from  $\text{CH}_2\text{T}^+$ , is energetically favorable, but this term in the rate equation is not affected by iodine. Even though the concentration of  $\text{I}_2$  is one-thirtieth that of  $\text{NO}$ , the absence of such a scavenging effect casts some doubt on this mechanism, IB, and would favor mechanism IA instead.

The maximum rate of formation of labeled methane by the above mechanisms is the decay rate of tritium; *i.e.*, no more than one  $\text{CH}_3\text{T}$  can result per  $\text{HeT}^+$  formed. However, one would expect that  $\text{CH}_2\text{T}^+$  would be produced by (8) in only 60% of the events, neglecting isotope effects. Since the  $\text{C}_2\text{H}_4\text{T}^+$  ion as produced in (a) would also lead to the formation of labeled higher hydrocarbons, *e.g.* reaction 12, the 0.25 intercept of the  $R_s/R_d$  vs. activity curve, Fig. 4, is not unreasonable. The decay-induced mechanisms, reactions 8–13, are thus compatible with experiment in view of the observations of first order kinetics, scavenging by nitric oxide, no scavenging by xenon and/or iodine, and production of labeled higher hydrocarbons.

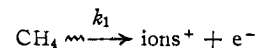
The above decay-induced mechanisms are not unique for the production of  $\text{CH}_3\text{T}$  from  $\text{HeT}^+$  and several other alternatives have been considered but discarded as improbable. For example, the  $\text{HeT}^+$  could react with methane by an electron rather than a proton transfer, *i.e.*



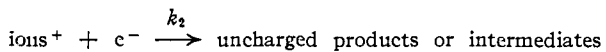
The latter reaction, however, is unlikely since Schwartz, Williams and Hamill have shown<sup>17</sup> that it does not occur with 1–2 ev. hydrogen atoms.

**II. Radiation Induced Exchange.**—The second term in the kinetic expression (6) is also believed to be due to ion-molecule reactions. The data indicating this are the scavenging action of xenon, which eliminates this term, and the 3/2 power dependence of the latter becomes apparent in developing the kinetics of a general reaction mechanism involving exchange with radiation produced ions.

The concentration of ions originating in the radiolysis of methane and eliminated primarily by neutralization is governed by the rate of production



and neutralization



(A homogeneous reaction is assumed since the lifetime of an ion does not permit migration to the walls. This can be justified by comparing the diffusion rate as calculated by Schaeffer and Thompson,<sup>9</sup> with the recombination lifetime estimated using the method of Stevenson.<sup>18</sup>) Invoking the steady state condition and assuming that there are no doubly charged ions

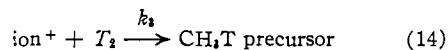
$$\frac{d(\text{ion}^+)}{dt} = k_1(\text{T}_2) - k_2(\text{ion}^+)(\text{e}^-) = 0$$

then since

$$(\text{ion}^+) = (\text{e}^-)$$

$$(\text{ion}^+) = \sqrt{\frac{k_1}{k_2}} (\text{T}_2)$$

If exchange then occurs involving a rate determining step of the type



then

$$\frac{d(\text{CH}_3\text{T})}{dt} = k_3(\text{ion}^+)(\text{T}_2) = k_4(\text{T}_2)^{3/2}$$

where  $k_4 = k_3 \sqrt{k_1/k_2}$ . This is the form of equation 1.<sup>19</sup>

Exchange of  $\text{T}_2$  with ions, the lifetime of which is limited by recombination, thus gives the experimentally observed form of kinetic expression and can also account for the scavenging. It is difficult to postulate any other type of reaction which will meet these criteria. However, although it is thus very probable that this class of mechanism accounts for the 3/2 power term in equation 6 in a unique manner, a determination of the exact ion or ions involved cannot be made with the same degree of assurance.

The ions which are formed by the action of beta rays on methane and their relative abundances may

(17) H. A. Schwartz, R. R. Williams and W. H. Hamill, *THIS JOURNAL*, **74**, 6007 (1952).

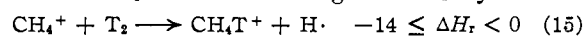
(18) D. P. Stevenson, *J. Phys. Chem.*, **61**, 1453 (1957).

(19) This conclusion is contrary to a statement of Gant and Yang<sup>4</sup> that the amount of labeling caused by the radiation *per decay* should increase linearly with  $\text{T}_2$  concentration; *i.e.*, that the *total* radiation induced labeling should be second order in the concentration of  $\text{T}_2$ .

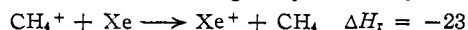
be assumed to be similar to those produced in the mass spectrometer.<sup>20</sup> This is justified by the fact that essentially all of the ionization of the methane is caused by low energy electrons or delta rays. The rate of production of ions in the CH<sub>4</sub>-T<sub>2</sub> system can be calculated using an average beta ray energy of 5.69 kev. and an energy requirement per ion pair of 26.8 ev.<sup>21</sup> The rate of production of ions, I, comes to  $7.8 \times 10^9$  ions/mc. sec. or  $7.8 \times 10^9$  a ions/cm.<sup>3</sup> sec. Considering the 3/2 power term of (6) and using  $\alpha = 5$  mc./cm.<sup>3</sup>, it is seen that the relative abundance of the ion or ions responsible for this term must exceed 2%. The most abundant ions in the mass spectrum of methane are 51% CH<sub>4</sub><sup>+</sup>, 40% CH<sub>3</sub><sup>+</sup> and 4% CH<sub>2</sub><sup>+</sup>.<sup>19</sup> We may therefore limit our considerations to these ions, and possible other ions formed by their reaction with methane.

The charge exchange of CH<sub>2</sub><sup>+</sup> and CH<sub>3</sub><sup>+</sup> with xenon is energetically unfavorable. Thus even if their lifetime is long enough to permit reaction 14 to occur, it would be difficult to account for the observed xenon scavenging.

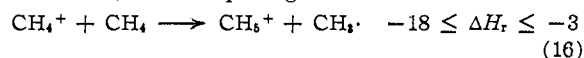
The CH<sub>4</sub><sup>+</sup> ion can exchange with T<sub>2</sub><sup>8</sup> by



and it also can be scavenged by xenon by

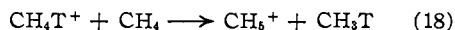


However, the competing reaction with methane



has a rate constant which is two orders of magnitude larger than (15).<sup>8</sup> Furthermore, the concentration of CH<sub>4</sub> is larger than that of T<sub>2</sub> by a factor of  $10^4$ – $10^5$ . Therefore, we may exclude reaction 15 as a significant factor in the exchange.

The lifetime of the CH<sub>5</sub><sup>+</sup> ion formed in equation 16 is thought<sup>22</sup> to be limited only by its rate of recombination with electrons. We may thus postulate the exchange



The proton transfer reaction 18 is a familiar type of ion mechanism,<sup>8</sup> but there is no precedent for exchange reaction 17. However, if we assume that it is the rate determining step for the 3/2 term in the kinetic expression 6, its activation energy may be estimated. This is done by comparing the rate law for this mechanism with the second term of the rate equation 6.

$$\frac{d(\text{CH}_3\text{T})}{dt} = k_5(\text{CH}_5^+)(\text{T}_2) = 7.4 \times 10^7(\text{T}_2)^{3/2}$$

To approximate (CH<sub>5</sub><sup>+</sup>) we take the relative abundance of the ions in the mass spectrum of methane<sup>20</sup> and assume that all CH<sub>4</sub><sup>+</sup> reacts to yield CH<sub>5</sub><sup>+</sup>. Then from the rate of production of the ions and the rate of neutralization we estimate (CH<sub>5</sub><sup>+</sup>) =  $4.4 \times 10^7$  a<sup>1/2</sup> ions/cm.<sup>3</sup> From this a value of  $k_5$  of  $1.6 \times 10^{-6}$  cm.<sup>3</sup>/molecule sec. is obtained. Comparing this with the prediction from transition state theory

(20) L. G. Smith, *Phys. Rev.*, **51**, 263 (1937).

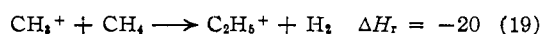
(21) J. Weiss and W. Bernstein, *ibid.*, **98**, 1828 (1955).

(22) G. C. Meisels, W. H. Hamill and R. R. Williams, Jr., *J. Phys. Chem.*, **61**, 1456 (1957).

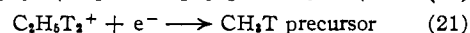
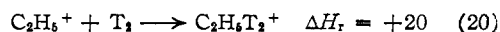
of a value of  $10^{-14}$ – $10^{-13}$  for the pre-exponential factor of a reaction of a linear with a non-linear molecule, we can approximate the activation energy as being 2–4 kcal./mole. The value thus obtained on the basis of regular "non-sticky" collision kinetics is perhaps unexpectedly low, although there is very little relevant information on which such a judgment can be based. This suggests that CH<sub>5</sub><sup>+</sup> and T<sub>2</sub> may form an ion cluster, such as have again been postulated recently.<sup>9,23,24</sup>

Charge exchange of CH<sub>5</sub><sup>+</sup> with Xe, NO and I<sub>2</sub> is exoergic and its concentration should therefore be negligible in the presence of these species. This accounts for the observed scavenging of the 3/2 power term in equation 6.

Many other specific mechanisms of type 14 may be considered since other types of ions, both known and unknown, may be present in sufficient abundance. However, we have not been able to establish any more satisfactory medium for this exchange than the CH<sub>5</sub><sup>+</sup> exchange 17 and 18. Thus CH<sub>3</sub><sup>+</sup> produced by electron impact has been shown (*e.g.*, ref. 8) to react rapidly with CH<sub>4</sub> to produce C<sub>2</sub>H<sub>5</sub><sup>+</sup>.



A sequence involving C<sub>2</sub>H<sub>7</sub><sup>+</sup> (*e.g.*, ref. 9)



might be possible if it were not for the fact that (20) appears exoergic. We have considered and discarded a number of such mechanisms.

### III. Exchange of Radiation Activated Tritium.—

Another series of reactions which could produce labeled methane must be considered. This is a possible sequence initiated by the action of the betas, or secondary electrons, on tritium molecules. Such a mechanism would yield a kinetic expression dependent on the square of the tritium concentration. The square term in the empirical rate equation 6 can be ascribed to a mechanism involving initiation reactions of this type. However, there are other mechanisms (discussed below) which also may be used to explain the square dependence.

IV. Radical and Other Mechanisms.—Kinetic considerations show that reactions involving free radicals produced by the irradiation of the methane are not likely to be involved in the production of labeled methane. Mechanisms involving the reaction of these radicals with tritium to yield a CH<sub>3</sub>T precursor in a rate determining step lead to kinetic expressions of the form

$$\frac{d(\text{CH}_3\text{T})}{dt} = k[\text{T}_2]^n$$

when a steady state condition is invoked. If the steady state concentration of radicals is limited by a second order process such as radical-radical recombinations, then  $n = 3/2$ ; but if it is limited by a first order process, such as diffusion to the walls, then  $n = 2$ . If, however, first and second order processes compete, then  $2 \geq n \geq 3/2$  (neglecting zero and/or third order processes). With this in mind, it is difficult to imagine radical mechanisms

(23) J. L. Magee and K. Funabashi, *Rad. Res.*, **10**, 622 (1959).

(24) R. F. Pottie and W. H. Hamill, *J. Phys. Chem.*, **63**, 877 (1959).

which could lead to the first order term in the empirical rate equation, (6). It is also unlikely that the 3/2 term in (6) comes from a radical reaction since with such a mechanism it is difficult to account for the scavenging by xenon. However, this possibility cannot be excluded.

In the case of excited states,  $n = 2$  if one supposes that the steady state concentration of excited methane is limited by a first order decay of the excitation and that there are no significant second order mechanisms by which the excitation can be quenched. It is therefore unlikely that the linear and/or 3/2 term in (6) are due to excited states. However, the square term may be due, at least in part, to reactions involving radicals or excited states.

**V. Higher Products.**—In discussing at some length the exchange to give  $\text{CH}_3\text{T}$ , we have so far largely ignored the formation of higher labeled hydrocarbons (see Table II). The production of the latter can be rationalized readily by invoking ion condensation reactions such as (9). However, not enough is known about the elementary processes involved to make it possible to decide the relative importance of a large number of possible reaction paths.

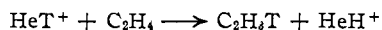
**VI. Secondary Reactions.**—It is obvious that as the reaction proceeds and products accumulate the system becomes too complex for meaningful analysis. The decrease in the rate of formation of methane with time (*cf.* Fig. 1) could be due to (a) the dilution of the  $\text{T}_2$  by the HT formed as a reaction product, and/or (b) the formation of reaction products of low ionization potentials (*e.g.*,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ) which act as ion scavengers. The increase in the rate of formation of labeled methane with time in the xenon samples probably results from a secondary reaction which is not itself scavenged by xenon.

The increase in the initial reaction rate caused by the addition of He, Ne, Ar or Kr (*cf.* Fig. 4) could arise from the reaction

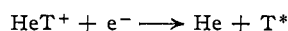


where G is one of the noble gases mentioned above. The origin of the  $\text{GT}^+$  ion-molecule is, however, unknown.

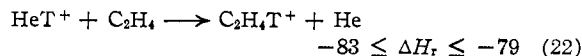
**VII. Other Systems.**—Several other tritium-hydrocarbon systems have been investigated<sup>2-4</sup> with the aim of studying the exchange mechanism rather than merely labeling compounds. However, the only extensive kinetic investigation is that of Gant and Yang<sup>4</sup> for the tritium-ethylene system. A rate expression derived from their data exhibits a first and a second power term in the tritium concentration. The first power term is stated as probably resulting from exchange of  $\text{HeT}^+$  with ethylene



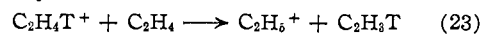
or possibly the reaction of energetic tritium atoms produced by its neutralization



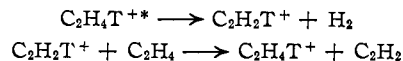
However, the neutralization mechanism is slow and so, most probably, is the exchange. These reactions probably would not be able to compete with the rapid charge transfer that must be expected.



A resonant proton transfer reaction can then yield labeled ethylene.



(The  $\text{C}_2\text{H}_3\text{T}^+$  formed by (22) has sufficient excitation energy so that it may dissociate before the next collision. If so, the following reactions will intervene between (22) and (23)



The latter of these has been identified in the mass spectrometer.<sup>8</sup>)

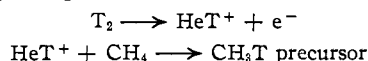
The second power term in the tritium concentration apparently is in accord with a mechanism involving radiation activated tritium. However, the system appears too complex to establish a unique and detailed mechanism. Nevertheless, this term appears analogous with a similar one in the tritium methane exchange.

The tritium ethylene reaction does not exhibit a 3/2 power term. This suggests that ethylene itself is acting as a scavenger so that there are no long lived ions (or radicals) in the system which can react with tritium to yield labeled ethylene.

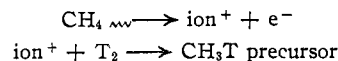
This comparison between methane and ethylene points up the differences that may be expected between systems. The mechanism types postulated probably are generally applicable but their particular modes and relative importance will vary greatly depending on the molecules involved. In view of the scarcity of relevant information on elementary ion-molecule processes, it will be difficult to ascribe detailed and unique mechanisms in more complex systems.

**Conclusions.**—(1) Three general types of mechanisms for the exchange between  $\text{T}_2$  and  $\text{CH}_4$  have been identified.

(a) A decay induced mechanism which is first order in the concentration of  $\text{T}_2$  and may be described by the process



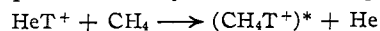
(b) Exchange of tritium with a radiation produced species, probably an ion, the lifetime of which is recombination limited. This leads to a 3/2 order term in the concentration of  $\text{T}_2$  and may be described by the process



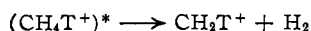
(c) Exchange of a radiation activated tritium species which is second order in the concentration of tritium.

Unfortunately, assignment of specific and unique reaction paths corresponding to these general types of mechanisms cannot be made with the same degree of assurance.

(2) For the decay induced mechanism the following sequence is likely to be occurring

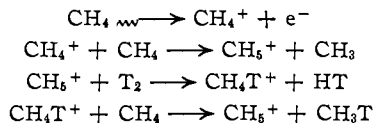


The  $(\text{CH}_4\text{T}^+)^*$  may form  $\text{CH}_3\text{T}$  directly by transferring a proton to a  $\text{CH}_4$  molecule. However it is more likely to decompose



There are then at least two possible paths by which  $\text{CH}_2\text{T}^+$  can lead to  $\text{CH}_3\text{T}$ .

(3) For the exchange of tritium with a radiation produced ion the specific sequence postulated is



(4) The general types of mechanisms as given in (1) are applicable to the exchange of  $\text{T}_2$  with other systems. In this sense the results of this

work can be applied to  $\text{T}_2$  exchange with other compounds to provide general mechanisms for Wilzbach labeling. However, with larger molecules the knowledge of the ions present, their state of excitation and their reactivity is so fragmentary as to make assignment of unique and detailed reaction paths for the exchange process very difficult.

**Acknowledgments.**—This work was presented by T. H. Pratt in partial fulfillment of the requirements for the Ph.D. degree at Yale University. He wishes to thank the Procter & Gamble Corporation for a fellowship during his last year of study. These studies were supported by the U. S. Atomic Energy Commission.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

## Ionic and Free Radical Processes in the Radiolysis of Liquid Methyl and Ethyl Iodides<sup>1</sup>

BY H. A. GILLIS, R. R. WILLIAMS, JR., AND W. H. HAMILL

RECEIVED APRIL 22, 1960

Liquid methyl and ethyl iodides have been irradiated at room temperature with a  $\text{Co}^{60}$  source at dose rates approximating  $10^{19}$  e.v. hr.<sup>-1</sup> ml.<sup>-1</sup> in air-free samples with added HI and  $\text{I}_2$ . In ethyl iodide,  $\text{C}_4\text{H}_{10}$  is a small but significant product;  $G(\text{C}_2\text{H}_4)$  decreases at HI or  $\text{I}_2$  concentrations  $> 10^{-2} M$ ;  $G(\text{C}_2\text{H}_6)$  increases at HI concentrations  $> 10^{-2} M$  provided  $\text{I}_2/\text{HI} \sim 0$ ;  $G(\text{C}_2\text{H}_6)$  decreases at  $\text{I}_2$  concentrations  $> 10^{-2} M$  provided  $\text{HI}/\text{I}_2 \sim 0$ ;  $G(\text{C}_4\text{H}_{10})$  decreases at HI or  $\text{I}_2$  concentrations  $> 10^{-2} M$ . In methyl iodide,  $G(\text{CH}_4)$  increases at HI concentrations  $> 10^{-2} M$ , and  $G(\text{C}_2\text{H}_6)$  decreases at  $\text{I}_2$  or HI concentrations  $> 10^{-2} M$ . These results indicate that  $\text{C}_2\text{H}_5$  and  $\text{CH}_3$  are involved in diffusion-controlled reactions, as  $2\text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10}$ ;  $\text{C}_2\text{H}_5 + \text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$ ;  $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ , etc., Disposition of radicals favorable to diffusion controlled reencounters may arise from track effects in general. In particular they would be favored by the pairing of alkyl radicals following charge neutralization of the products of ion-molecule reactions, as  $\text{CH}_3\text{I}^+ + \text{CH}_3\text{I} \rightarrow \text{C}_2\text{H}_6\text{I}^+ + \text{I}$  and  $\text{C}_2\text{H}_5\text{I}^+ + \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_4\text{H}_{10}\text{I}^+ + \text{I}$  which have been observed in the mass spectrometer. The reaction products are qualitatively and quantitatively consistent with electron impact cracking patterns as determined by mass spectrometry.

### Introduction

There are several features common to the photolysis<sup>2</sup> and radiolysis<sup>3</sup> of ethyl iodide in the liquid phase. In particular the correlation between structure of alkyl iodides and yields of iodine in both photolysis<sup>4</sup> and radiolysis<sup>4,5</sup> in the liquid phase suggests that common mechanisms are involved. This correlation is that the quantum yield, or  $G$ - (100 e.v. yield), for iodine production increases with increasing number of hydrogen atoms in the  $\beta$ -position. The rate controlling steps are assumed to be competitive processes, e.g.,  $\text{C}_2\text{H}_5 + \text{I} \rightarrow \text{C}_2\text{H}_5\text{I}$  and  $\text{C}_2\text{H}_5 + \text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$ . Iodine definitely results from the reaction<sup>6</sup>  $\text{C}_2\text{H}_5 + \text{HI} \rightarrow \text{C}_2\text{H}_6 + \text{I}$ . The relation between the number of  $\beta$ -hydrogens and the relative efficiency of reactions of disproportionation and dimerization is not peculiar to reactions between alkyl radicals and iodine atoms. Striking examples of the  $\beta$ -effect have been observed for several alkyl radicals.<sup>7</sup>

(1) From the Ph.D. dissertation of H. A. Gillis, University of Notre Dame, August, 1957. A contribution from the Radiation Project of the University of Notre Dame, supported in part under AEC contract AT(11-1)-38 and Navy equipment loan contract Nonr-06900.

(2) R. H. Schuler and W. H. Hamill, *THIS JOURNAL*, **73**, 3466 (1951).

(3) R. H. Schuler and W. H. Hamill, *ibid.*, **74**, 6171 (1952); R. H. S. doctoral dissertation, University of Notre Dame, June, 1949.

(4) E. L. Cochran, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **76**, 2145 (1954).

(5) E. O. Hornig and J. E. Willard, *ibid.*, **79**, 2429 (1957).

(6) D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **78**, 6228 (1956).

(7) (a) J. W. Kraus and J. G. Calvert, *ibid.*, **79**, 5921 (1957); (b) A. S. Newton, *J. Phys. Chem.*, **61**, 1485 (1957).

The effect of added hydrogen iodide, over a range of concentration, upon the photolysis of ethyl iodide has been interpreted<sup>6</sup> in terms of a diffusion-controlled reaction between the neighboring ethyl radical-iodine atom pair following dissociation of the C-I bond. The present work is a parallel study of evidence which might indicate diffusion-controlled processes in the radiolysis of liquid methyl and ethyl iodides from measurements of the yields of hydrocarbon products as functions of the concentrations of iodine and of hydrogen iodide.

### Experimental

**Materials.**—Methyl and ethyl iodides were purified by the same procedure. After passing through a 60 cm. column of silica gel they were distilled through a 4 ft. glass-helix packed distilling column. The middle cut of ethyl iodide retained boiled at  $72.4^\circ$  (760 mm.) and  $n_D^{20}$  was 1.5138. Methyl iodide boiled at  $42.5^\circ$  (760 mm.) and  $n_D^{20}$  was 1.5307. Resublimed iodine was used as received. Hydrogen iodide was prepared from phosphoric acid and potassium iodide. Phosphorus pentoxide was added to 85% phosphoric acid until it dissolved only very slowly. This acid was added in vacuum to finely ground potassium iodide until evolution of gas virtually stopped. The gas was freed of most of the contaminating iodine by three distillations and then dried with phosphorus pentoxide at  $-45^\circ$ .  $n\text{-C}_4\text{D}_{10}$  was prepared by exchange between butane and deuterium over a platinum catalyst at  $75^\circ$  (courtesy of Dr. A. Kupperman).

**Apparatus.**—The 150 curie  $\text{Co}^{60}$  source has been described by Lazo.<sup>8</sup> In one run X-rays from a Van de Graaff generator were used at a target current of 78  $\mu\text{amp}$ . and 1.5 m.e.v. **Procedure.**—Samples of 5 ml. in 1.6 cm. i.d. Pyrex cells were used for all gamma irradiations. They were first outgassed by three cycles of freezing and pumping, then thaw-

(8) R. M. Lazo, Ph.D. thesis, University of Notre Dame, 1953.