also seem to be required[1c,9] to explain gas phase halogen atom recoil reactions. Reactions such as $CH_4T^+ + CH_4 \rightarrow C_2H_6T^+ + H_2$ which may not be observable at mass spectrometer pressures may be among those which contribute to chain lengthening. The absence of a scavenger effect on the yield of tritiated parent indicates that the neutral stable molecule is formed by a single step such as $T^+ + CH_4 \rightarrow CH_3T + H^+$, or $T + CH_4 \rightarrow CH_3T + H$, or that its formation from a species such as CH_4T^+ is not altered by halogen.

Although it usually is not possible to differentiate hot radical reactions from ion-molecule reactions in condensed phases, it seems plausible that ion-molecule steps such as seem to be required above may also be involved in tritium labelling in condensed phases[2] and in a number of other unique processes recently reported. These include the reactions of tritons[10] and C^{14} ions[11] accelerated by electric fields, and the tritium labelling method of Wilzbach.[12,13] It is probable that such steps also account[9] for part, but not all, of the products of halogen recoil reactions in solution.

TABLE I

PRODUCTS OF THE $He^3(n,p)H^3$ REACTION IN GASEOUS CH_4, C_2H_6, AND C_3H_8[a]

	Alkane reactant						
Tritiated[b] product	CH_4	CH_4 (I_2 or Br_2)	C_2H_6	C_2H_6 (Br_2)	C_3H_8	C_3H_8 (I_2)	C_3H_8 (Br_2)
	Per cent. of total T in each product						
HT	46	40	43	42	43	42	50
CH_3T	31	50	5	2	4	4	3
C_2H_5T	6.8	Trace	28	37	2.5	1.5	1.5
C_3H_7T	5	Trace	9	0	36	47	39
C_4H_9T	1.5	0	7	0	3	1	0
C_4H_9T	1.7	0	0	0	2	1	0
$C_5H_{11}T$	1.2	0	4	0	5	1.5	0
$C_5H_{11}T$	1.9	0	0	0	0	0	0
$C_6H_{13}T$	1.9	0	3	0	4	1	0
$C_6H_{13}T$	1	0	0	0	0	1	0
Iodides or bromides	0	10	0	18	0	?	6

[a] The reaction mixtures contained about 1 atm. of alkane, 6 mm. of He^3 and either 6 mm. of H_2, 0.2 mm. of I_2 or 200 mm. of Br_2. [b] Duplicate formulas indicate isomers.

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(9) S. Aditya and J. E. Willard, THIS JOURNAL, **79**, 2680 (1957).

(10) R. Wolfgang, T. Pratt and F. S. Rowland, *ibid.*, **78**, 5132 (1956).

(11) R. M. Lemmon, F. Mazzetti, F. L. Reynolds and M. Calvin, *ibid.*, **78**, 6414 (1956).

(12) K. E. Wilzbach, *ibid.*, **79**, 1013 (1957).

(13) R. W. Ahrens, M. C. Sauer, Jr., and J. E. Willard, *ibid.*, **79**, 3285 (1957).

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RECEIVED APRIL 8, 1957

HYDROGEN LABELLING OF HYDROCARBONS USING IONIZING RADIATION

Sir:

Wilzbach has demonstrated that exposure to tritium gas is an effective method of labelling complex organic compounds.[1] It seems possible that such reactions are similar in mechanism to tritium recoil labelling by the $He^3(n,p)H^3$ [2] and Li^6 $(n, \alpha)H^3$ [2] processes and to recoil labelling by the halogens,[2] which appear to involve ion-molecule steps.[2]

Typical distributions of tritiated products which we have obtained by gas chromatographic analysis[2] of mixtures of hydrocarbons with T_2 or HT, activated by self irradiation with about 2×10^7 roentgens of tritium beta radiation or by doses of about 5×10^6 roentgens of Co^{60} gamma rays are shown in Table I. Both chain lengthening and chain degradation occur, as with activation by the $He^3(n,p)H^3$ process. Methane–HT mixtures irradiated with gamma radiation appear to show higher yields of tritiated pentanes and hexanes than of propane. The ratio of yields is changed by a change in the methane–H_2 ratio. Iodine scavenger causes a drop in the tritiated C_5H_{12} and C_6H_{14} components relative to the other components. In view of the chain lengthening observed, the conclusion seems nearly inescapable that these reactions are ion-molecule processes.[2] Quantitative studies on such systems should be rewarding by revealing the most probable stage of the chain lengthening process for reaction of the chain carrying species with hydrogen and with halogens.

TABLE I

RELATIVE AMOUNTS OF TRITIATED PRODUCTS FROM THE IRRADIATION OF VARIOUS MIXTURES CONTAINING CH_4, C_3H_8, HT, H_2 AND I_2[a]

Sample	CH_4	C_2H_5	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
CH_4-HT-H_2[b]	[h]	2.5	1	2.8	2.7	4.1
CH_4-HT-H_2[c]	[h]	6.7	1	2.8	11.5	15.8
CH_4-HT-H_2-I_2[d]	5.4	1.4	1	2.7	1.3	0.4
CH_4-HT-H_2-I_2[e]	1.6	1.9	1	?.2	*ca.* 0.0	*ca.* 0.0
CH_4-T_2[f]	[h]	3.5	1	(12.8)	3.9	1.9
C_3H_8-T_2[g]	1.2	0.4	1	[h]	[h]	[h]

[a] CH_4, C_2H_6, C_3H_8, C_4H_{10} characterized with known samples: C_5H_{12} and C_6H_{14} identity assumed from position on gas chromatogram. [b] *ca.* 5×10^5 r. Co^{60} gamma radiation, 2.5 μc. tritium, 7 mm. H_2, 60.7 cm. CH_4. [c] *ca.* 6×10^6 r. Co^{60} gamma radiation, 2.5 μc. tritium, 57 mm. H_2, 52.4 cm. CH_4. [d] *ca.* 3.5×10^6 r. Co^{60} gamma radiation, 2.5 μc. tritium, 5 mm. H_2, 64.5 cm. CH_4, solid I_2. [e] *ca.* 3.0×10^6 r. Co^{60} gamma radiation, 2.5 μc. tritium, 6 mm. H_2, 61.0 cm. CH_4, solid I_2. [f] *ca.* 5 mc. T_2, 50 cm. CH_4, 72 days standing. [g] *ca.* 5 mc. T_2, 48 cm. C_3H_8, 49 days standing. [h] Relative abundance of this species not determined in this experiment.

Three possibilities must be considered for the primary step in these tritiation reactions: (1) the step $T\text{-}T \rightarrow T^+ + He^3$ (or, say, He^3T^+); (2) ionization of T_2 or HT by beta or gamma radiation; (3) ionization of the organic compound by beta or gamma radiation. The fact that reaction occurs in HT–CH_4 mixtures indicates that the molecule T_2 is not essential.

If reaction were initiated solely by ionization of H_2 and HT a *G* value of about 100 would be required to account for the yields of tritiated products obtained in Table I, assuming no isotope effect. Consequently it seems probable that much, if not all, of the reaction is due to ionization of the methane.

The ratios of tritiated C_4H_{10}, C_5H_{12} and C_6H_{14} to tritiated C_3H_8 produced from CH_4 are significantly higher when tritiation is induced by radiation

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(1) K. E. Wilzbach, THIS JOURNAL, **79**, 1013 (1957).

(2) A. A. Gordus, M. C. Sauer, Jr., and J. E. Willard, *ibid.*, **79**, 3784 (1957).

(Table I) than when it is induced by the $He^3(n,p)H^3$ process. This seems to indicate that the mechanisms are different. In the $He^3(n,p)H^3$ case the formation of each carbon chain presumably is initiated by attack of a tritium ion on a CH_4 molecule.

The many products formed in these reactions offer a valuable source of high specific activity labelled compounds when these non-parent "by-products" can be separated in carrier-free form by gas chromatography or otherwise.

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RECEIVED APRIL 8, 1957

CHEMICAL REACTION OF RECOIL TRITIUM WITH GASEOUS ALKANES[1]

Sir:

We have studied the reaction of high energy tritium, as produced by nuclear reaction, with gaseous methane and ethane. The reactions $He^3(n,p)H^3$ (0.78 Mev.) and Li^6 $(n,\alpha)H^3$ (4.7 Mev.) were used to supply the "hot" tritium. In the He^3 runs about 0.1 cm. He^3 was sealed with 10–60 cm. CH_4 in a $\sim$ 7 ml. quartz ampoule. In the Li^6 runs a film of normal lithium nitrate formed the inside coating of similar vessels. After irradiation in the Brookhaven reactor, carriers were added and the various tritium labeled species separated and counted, largely as described elsewhere.[2]

A summary of some of our results on the chemical state of the tritium following interaction with methane is shown in Table I. This distribution of activity is independent of the source of the tritium, the pressure and the temperature (range 30–200°). However, a drastic reduction of neutron flux, with accompanying decrease in radiation density, although having little effect on the production of CH_3T, seems to reduce significantly the yields of labeled higher hydrocarbons while increasing the amount of HT. The addition of 0.2 mm. of iodine as a radical scavenger has little effect on the yield of CH_3T but virtually eliminates the yield of higher labeled hydrocarbons and reduces the yield of HT.

TABLE I

CHEMICAL STATE OF RECOIL TRITIUM STOPPED IN METHANE
Expressed as % of total gaseous activity in absence of I_2

Chemical state	Irradiation conditions		
	$10^{12.6}$ neutrons cm. $^{-2}$ sec. $^{-1}$, no I_2 present	$10^{9.3}$ neutrons cm. $^{-2}$ sec. $^{-1}$, no I_2 present	$10^{9.3}$ neutrons cm. $^{-2}$ sec. $^{-1}$, I_2 present
HT	50.6	61.9	29.8
CH_3T	30.9	29.1	26.0
$C_2H_5T + C_2H_3T$	8.2	2.9	0.1
$C_3(T)$ hydrocarbons	5.0	2.4	0.2
Higher tritiated hydrocarbons and iodides	5.3	3.7	43.9

Studies on the slowing of charged particles passing through matter[3] indicate that the tritium is uncharged on reaching its final reaction site. Taking this into account, our observations suggest two distinct modes of reaction of the tritium atom: (A) Most tritium combines by direct hot replacement reaction. For methane

$$T^* + CH_4 \longrightarrow CH_3T + H$$

$$T^* + CH_4 \longrightarrow HT + CH_3$$

Radical intermediates are definitely ruled out and Walden inversion probably is involved. (B) Some tritium escapes incorporation in stable molecules by hot reaction and becomes thermalized. Its reactions then become sensitive to radical scavengers, such as I_2. In their absence the tritium can react competitively to (1) abstract H to form part of the HT observed, or (2) combine with radiation produced radicals or ions to form the higher labeled hydrocarbons. (Production of the latter probably involves hydrocarbon chains lengthened by ion molecule reactions.[4])

The results observed with ethane are consistent with this picture. Most of the activity appears in HT and C_2H_5T with smaller amounts in CH_3T and higher hydrocarbons. Only C_3 and higher hydrocarbons are eliminated by I_2. This means that degradation products such as CH_3T from ethane are largely formed by direct hot replacement reactions (type A).

It has been demonstrated that neither radical intermediates nor a solvent cage, the central concepts of earlier theories of hot-atom reactions,[5] are necessary for hot reaction of hydrogen. Whether the reaction model postulated here holds also for recoil tritium reactions in the condensed phase remains to be seen. The similar product distributions in gaseous and liquid[2] alkanes are suggestive. But the retention of configuration observed in the solid phase[6] would require further explanation.

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(1) Research supported by the Atomic Energy Commission. See also accompanying communication by Gordus, Sauer and Willard, p. 3284.

(2) Wolfgang, Eigner and Rowland, *J. Phys. Chem.*, **60**, 1137 (1956).

(3) S. K. Allison and S. D. Warshaw, *Rev. Mod. Phys.*, **25**, 779 (1953).

(4) Meisels, Hamill and Williams, *J. Chem. Phys.*, **25**, 790 (1957).

(5) J. Willard, *Ann. Rev. Nuc. Sci.*, **3**, 193 (1953).

(6) Rowland, Turton and Wolfgang, THIS JOURNAL, **78**, 2351 (1956); F. S. Rowland, private communication.

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DEGRADATION OF BRAIN GANGLIOSIDE TO GLUCOCEREBROSIDE

Sir:

Since Klenk first described the brain gangliosides,[1] evidence has been presented that they are

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(1) E. Klenk, *Z. physiol. Chem.*, **273**, 76 (1942).