(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

	Irradiation conditions		
Chemical state	$10^{12.5}$ 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**, 2354 (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).