pentane gave 0.2 g. of material, m.p. 74–76°, mixed m.p. with the *p*-nitrobenzoate of 1,1-dimethyl-2-*o*-anisylethanol, 74.5–76.5°.

In order to determine the amount of *o*-methoxyneophyl alcohol in the alcohol fraction, 0.40 g. of this material was treated with 1 g. of *p*-toluenesulfonyl chloride in dry pyridine at room temperature for 30 minutes. The sulfonate was isolated in the usual way and dissolved in 50 ml. of 0.0310 *M* sodium acetate in dry acetic acid. The acetolysis rate constant was $3.5 \pm 0.3 \times 10^{-4}$ sec.$^{-1}$ at 75°, the infinity titer being taken after 20 hr.

Formolysis of *o*-Methoxyneophyl *p*-Toluenesulfonate.—To a solution of 3.5 g. of sodium formate in 720 cc. of dry formic acid, heated to 50°, was added 12 g. of *o*-methoxyneophyl *p*-toluenesulfonate. After 2 hr. at 50°, the reaction mixture was cooled and worked up exactly as described for the acetolysis. The chromatography yielded 1.8 g. of benzofuran, b.p. 41–42° (2 mm.), $n^{25}D$ 1.5251, 1.2 g. of olefin, b.p. 60° (2 mm.), $n^{25}D$ 1.5458, and 2.5 g. of alcohol, b.p. 78–82° (2 mm.), $n^{25}D$ 1.5183.

The benzofuran fraction was redistilled to give material with $n^{25}D$ 1.5178. The infrared spectrum of this material was essentially the same as that of the ethanolysis product mentioned above. In ultraviolet absorption in methanol, λ_{max} 285 mμ, ϵ 2170; 279 mμ, ϵ 2700; and 224 mμ, ϵ 4720.

The olefin fraction reacted slowly with potassium permanganate in acetone.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.35; H, 8.71.

The alcohol fraction, 0.5 g., gave 0.2 g. of a *p*-nitrobenzoate of m.p. 76.5–77.5° after two crystallizations from ether-pentane. A mixed melting point with authentic material was 76.5–78°.

Kinetic Measurements.—Solvolysis rates were measured by the usual methods.[6,7] An attempt was made to follow the acetolysis of *o*-methoxyneophyl toluenesulfonate after the first infinity value. The solvolysis solution became yellow and difficult to titrate, a rough rate constant of *ca.* 6×10^{-7} sec.$^{-1}$ being obtained at 75°. A value of 8.5×10^{-7} sec.$^{-1}$ has been reported[8] for methyl *p*-toluenesulfonate at 75°.

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COMMUNICATIONS TO THE EDITOR

EVIDENCE ON MECHANISMS OF HALOGEN AND TRITIUM RECOIL LABELLING REACTIONS

Sir:

Displacement reactions very different from ordinary atom and radical reactions have been observed between gaseous alkanes and iodine,[1a,1b] bromine,[1c] and chlorine[1d,1e] activated by the (n,γ) process. Tritium activated by the $Li^6(n,\alpha)H^3$ process in the presence of liquid or solid organic compounds gives superficially similar reactions.[2] Tritium is of particular interest in this connection because of its chemical differences from the halogens and because a much larger fraction of its recoil kinetic energy is available for internal energy of the activated complex.

We have used the $He^3(n,p)H^3$ reaction to produce tritons in gaseous alkanes[3] under conditions[4] similar to those for which the halogen reactions have been studied. With a given target compound a multiplicity of tritium containing compounds is formed which cannot be explained by "conventional" reaction steps. In the absence of scavengers about 45% of the tritium appears as HT, 30% in the alkane target species and the remainder in four to ten other products. Halogen scavengers decrease or eliminate the yield of tritiated products with more carbons than the target but have relatively little effect on the HT, or the tritiated target compound or fragments thereof.

The only reaction steps which seem capable of explaining the extensive chain-lengthening are ion-molecule reactions[8] (such as, for example, $T^+ + CH_4 \rightarrow CH_2T^+ + H_2$ and $CH_2T^+ + CH_4 \rightarrow C_2H_4T^+ + H_2$, followed by similar steps leading to further chain lengthening). Ion-molecule steps

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(1) (a) J. F. Hornig, G. Levey and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952); (b) G. Levey and J. E. Willard, *J. Chem. Phys.*, **25**, 904 (1956); (c) A. Gordus and J. E. Willard, THIS JOURNAL, in press; (d) J. C. W. Chien and J. E. Willard, *ibid.*, **75**, 6160 (1953); (e) J. E. Quinlan and J. E. Willard, unpublished.

(2) (a) R. Wolfgang, F. S. Rowland and C. N. Turton, *Science*, **121**, 715 (1955); (b) R. Wolfgang, J. Eigner and F. S. Rowland, *J. Phys. Chem.*, **60**, 1137 (1956); (c) F. S. Rowland, C. N. Turton and R. Wolfgang, THIS JOURNAL, **78**, 2354 (1956); (d) F. S. Rowland and R. Wolfgang, *Nucleonics*, **14**, 58 (1956).

(3) While this work was in progress, we received word from R. Wolfgang that he had observed the production of CH_3T and higher hydrocarbons from the $He^3(n,p)H^3$ reaction in CH_4.

(4) A typical run consisted of irradiating a 5-ml., thin-walled, quartz bulb containing 6 mm. He^3, 6 mm. H_2, and 1 atm. of alkane in the isotope tube of the CP 5 reactor of the Argonne National Laboratory for one hour. The neutron flux[5] was 3×10^{12} n.cm.$^{-2}$ sec.$^{-1}$ The bulb was broken in a stream of methane at the inlet of a 12 ft. long, 4 mm. i.d. spiral Pyrex column containing 30–80 mesh silica gel. The general technique was the same as reported earlier,[6] the main difference being that a flow proportional counter[7] was used to detect the radioactive components. The fraction of the activity in each component was estimated from the peak area; the identification of the minor components is tentative.

(5) The accompanying gamma flux was about 5×10^5 r./hr. That the gamma radiation was not the cause of the chain lengthening or the large fraction of tritium in the target compound seems evident from the three CH_4-He^3-H_2 samples which received about 7×10^5 r. from a Co^{60} source after the usual pile irradiation. This did not change the percentage of CH_3T much, but raised the percentage of HT slightly and lowered the percentages of the higher hydrocarbons somewhat.

(6) J. B. Evans and J. E. Willard, THIS JOURNAL, **78**, 2908 (1956).

(7) A. Gordus, Ph.D. thesis, University of Wisconsin, 1956, available from University Microfilms, Inc., Ann Arbor, Michigan.

(8) (a) V. L. Tal'roze and A. K. Lyubimova, *Doklady Akad. Nauk S.S.S.R.*, **86**, 909 (1952) (*Chem. Abs.*, **47**, 2590 (1953)); (b) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **24**, 926 (1956); (c) D. P. Stevenson and D. O. Schissler, *ibid.*, **23**, 1353 (1955); (d) G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **25**, 790 (1957); (e) F. H. Field, J. L. Franklin and F. W. Lampe, THIS JOURNAL, **79**, 2419 (1957).

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]

Tritiated[b] product	Alkane reactant: 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).

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, α)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_6	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	2.2	*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.* 3.0×10^8 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).