

The reduction of TPPO on the polarographic and voltammetric time scale probably proceeds by a one-electron reduction to the anion radical



The second wave represents further reduction probably followed by a fast chemical reaction. During large-scale electrolysis, a catalytic reaction is observed, and, since TPPO is recovered from the electrolyzed solution, this reaction probably involves a reaction of the anion radical to regenerate TPPO. The oxidation peaks found after coulometric reduction are probably caused by products of an undefined side reaction.

### Experimental Section

The general experimental methods and purification techniques are the same as those previously described.<sup>16</sup> A multipurpose

(16) K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **88**, 2669 (1966).

instrument employing operational amplifier circuitry with three-electrode configuration was used in voltammetric experiments. The reference electrode was an aqueous sce connected *via* an agar plug and sintered glass disk. All potentials quoted are with reference to this electrode.

Triphenylphosphine was obtained from Carlisle Chemical Works and triphenylphosphine oxide from Aldrich Chemical Co. TPP was recrystallized from diethyl ether to yield white plates with a melting point of 81°. The TPPO used had a melting point of 159°. The purity was further tested by thin layer chromatography. The TBAI was polarographic grade, obtained from Southwestern Analytical Chemicals (Austin, Texas).

The thin layer chromatography experiments were carried out on Eastman chromoplate activated at 100° for 30 min. The eluent was 70% pentane-methylene chloride. Iodine was used for developing the chromatogram.

A Chrom Alyser 100 (Dynatonic Instruments) was used for gas-liquid chromatography. The column used for identification purposes was 5% SE 30 on Chromosorb W, 30-60 mesh (1/8 in. × 6 ft) at 240°.

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## Reactions of He<sup>3</sup>H<sup>+</sup> Ions with Gaseous Hydrocarbons.

### II. Methane and Ethane

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**Abstract:** The reactions of the He<sup>3</sup>H<sup>+</sup> molecular ion, formed from the decay of gaseous tritium, with methane and ethane at atmospheric pressure were investigated under conditions ensuring that the labeled decay ions were the only source of the tritiated products, with no interference from radiolytic processes. The He<sup>3</sup>H<sup>+</sup> exothermically protonate the methane, giving excited CH<sub>4</sub><sup>3</sup>H<sup>+</sup> ions, that can be either collision stabilized at 760 torr or decompose into tritiated methyl ions and hydrogen. The stabilized ions react with CH<sub>4</sub> according to a thermoneutral proton-transfer process, which yields the observed tritiated methane, while the methyl ions react with CH<sub>4</sub> forming the highly unreactive ethyl ions, whose fate depends on the nature and the amount of the impurities contained in the system. The reaction of the He<sup>3</sup>H<sup>+</sup> ions with ethane yields excited C<sub>2</sub>H<sub>6</sub><sup>3</sup>H<sup>+</sup> ions, which appear to decompose into labeled ethyl ions, without any appreciable stabilization. The thermoneutral hydride ion transfer from the C<sub>2</sub>H<sub>6</sub> to the labeled ethyl ions leads to the formation of the observed tritiated ethane.

In recent years, a considerable amount of work was devoted to the study of the reactions of protonating agents, such as CH<sub>3</sub><sup>+</sup>,<sup>1-3</sup> H<sub>3</sub><sup>+</sup> and D<sub>3</sub><sup>+</sup>,<sup>4,5</sup> CHO<sup>+</sup>, etc.,<sup>6-9</sup> with a variety of gaseous hydrocarbons. All such investigations were carried out with mass spectrometric techniques, at pressures ranging from 10<sup>-4</sup> to 2 torr.

In the first paper of this series,<sup>10</sup> it was shown that, under suitable experimental conditions, the β decay of molecular tritium affords a convenient means of producing a very reactive protonating reagent, the He<sup>3</sup>H<sup>+</sup>

ion, within gaseous systems at any pressure, and of identifying, by tracer techniques, the labeled products formed from its interactions with the organic substrate.

The present paper describes the application of such a technique to the study of the reactions of the He<sup>3</sup>H<sup>+</sup> ions in the simpler alkanes, methane and ethane.

### Experimental Section

**Materials.** The tritium gas, obtained from CEA (France), with a stated purity of 95%, was subjected to a careful radio gas chromatographic analysis, in order to establish the nature and the amount of any radioactive impurity.

The content of hydrogen tritide was measured using an 8-m silica gel column, cooled to liquid nitrogen temperature.<sup>11</sup> The outlet of the column was connected to a 25-ml flow ionization chamber, whose current was measured with an electrometer (Model

(1) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).

(2) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 4337 (1966).

(3) M. S. B. Munson and F. H. Field, *ibid.*, **89**, 1047 (1967).

(4) V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, **44**, 2307 (1966).

(5) V. Aquilanti and G. G. Volpi, *ibid.*, **44**, 3574 (1966).

(6) H. von Koch, *Arkiv Fysik*, **28**, 529 (1965).

(7) H. von Koch, *ibid.*, **28**, 559 (1965).

(8) E. Pettersson and E. Lindholm, *ibid.*, **24**, 49 (1963).

(9) E. Lindholm, I. Szabo, and P. Wilmenius, *ibid.*, **25**, 417 (1963).

(10) F. Cacace and S. Caronna, *J. Am. Chem. Soc.*, **89**, 6848 (1967).

(11) H. A. Smith and E. H. Carter, Jr., "Tritium in the Physical and Biological Sciences," Vol. I, International Atomic Energy Agency, Vienna, 1962, p 121.

**Table I.** Yields of Tritiated Products from the Reactions of He<sup>3</sup>H<sup>+</sup> Ions with Methane and Ethane

Run no. <sup>a</sup>	System compn (mole %)	—Activity, mcuries—		No. of independent detns	Yield, %		
		Tritium	Hydrogen tritide		CH <sub>3</sub> <sup>3</sup> H	C <sub>2</sub> H <sub>6</sub> <sup>3</sup> H	C <sub>2</sub> H <sub>5</sub> <sup>3</sup> H
1, 2, 3, 4	CH <sub>4</sub> <sup>b</sup>	1.70 <sup>c</sup>	...	24 <sup>d</sup>	38 ± 2.6 <sup>e</sup>	~2	13 ± 0.8
5, 6, 7, 8	CH <sub>4</sub> (98) + O <sub>2</sub> (2)	1.70	...	25	40 ± 2.8	~2	13 ± 0.9
9, 10	CH <sub>4</sub> (98) + O <sub>2</sub> (2)	...	2.00	16	...	...	...
11, 12	CH <sub>4</sub> (96) + C <sub>2</sub> H <sub>6</sub> (2) + O <sub>2</sub> (2)	1.70	...	16	35 ± 2.5	32 ± 1.9	...
13, 14	C <sub>2</sub> H <sub>6</sub>	1.70	...	20	14 ± 1.0	36 ± 2.2	...
15, 16	C <sub>2</sub> H <sub>6</sub> (98) + O <sub>2</sub> (2)	1.70	...	25	14 ± 1.0	34 ± 2.1	...

<sup>a</sup> All the runs carried out at 760 torr and room temperature; sample volume, 250 ml. <sup>b</sup> The methane contained ~10<sup>-2</sup> mole % oxygen. <sup>c</sup> The tritium contained 0.35% of hydrogen tritide and 0.105% of tritiated methane. <sup>d</sup> All the yields were determined using at least two different chromatographic columns. <sup>e</sup> The yields of tritiated methane are corrected for the small amount of CH<sub>3</sub><sup>3</sup>H contained in the molecular tritium. The detection limit of the radio gas chromatographic analysis corresponded to a yield of ca. 1%. The experimental error in the determination of the activity of a given peak was ±4%, and the standard deviation of the mean values tabulated 6%, except in the case of methane, where owing to the necessity of subtracting the CH<sub>3</sub><sup>3</sup>H impurity of <sup>3</sup>H<sub>2</sub> a somewhat higher standard deviation was observed. The absolute accuracy of the yields can be expected to be ±10%. The columns employed would have allowed the detection of the following hydrocarbons: methane, ethane, ethylene, acetylene, propane, propylene, cyclopropane, methylacetylene, allene, *n*-butane, isobutane, butene-1, butene-2, and isobutylene.

610 B, Keithley Instruments, Inc., Cleveland, Ohio). The analysis indicated that the hydrogen tritide content of the <sup>3</sup>H<sub>2</sub> sample was 0.35%.

The tritium was further analyzed for the lower tritiated hydrocarbons with a 3-m molecular sieve column (Linde 5A), whose temperature was programmed in the range 80–240°, at a rate of 10°/min. The analysis showed that the only radioactive impurity detectable in the sample was a trace of tritiated methane.

Considerable difficulties were experienced by other workers in the attempt to free tritium samples from tritiated methane. The latter was easily removed by low-temperature absorption on molecular sieves, but rapidly reached the original concentration when the purified sample was allowed to stand in a Pyrex vessel for short periods of time.<sup>12</sup>

Since a number of determinations showed the methane content of the <sup>3</sup>H<sub>2</sub> sample used in the present work to be very low, and to remain constant over a long period of time, it was decided to use the tritium as such, without attempting to remove the tritiated methane. The activity of the latter measured by radio gas chromatography was found to be 0.105% of the tritium activity and was of course subtracted from the larger amount of labeled methane formed by the reaction of He<sup>3</sup>H<sup>+</sup> ions with methane and ethane.

Finally a radio gas chromatographic analysis, carried out with both a 6-m silica gel column heated at 100° and a 12-m dimethyl-sulfolane column held at room temperature, failed to detect any higher labeled hydrocarbon in the tritium sample.

Hydrogen tritide was prepared from high specific activity tritiated water by reaction with metallic sodium at room temperature. This procedure was preferred to the usual method of sparking a mixture of <sup>3</sup>H<sub>2</sub> and <sup>1</sup>H<sub>2</sub> at low pressure with a Tesla coil, since it was found that the latter technique produced a hydrogen tritide sample contaminated with traces of labeled methane.

The inactive methane, ethane, and the other gaseous hydrocarbons, used for the preparation of the reaction mixtures and for identification purposes, were research grade samples from Società Rivoira (Torino, Italy). Their minimum purity, checked with a Model 800 gas chromatograph, Perkin-Elmer Corp. (Norwalk, Conn.), equipped with a flame ionization detector, was higher than 99.95 mole %. The methane contained 0.01 mole % of oxygen.

**Procedure.** The samples were prepared by expanding the gaseous hydrocarbons into 250-ml Pyrex vessels evacuated to 10<sup>-4</sup> torr. Each vessel was equipped with a 10-ml side arm, containing 1.7 mcuries of <sup>3</sup>H<sub>2</sub> and closed with a break-seal. For the preparation of the ethane samples, the vessels, filled with C<sub>2</sub>H<sub>6</sub> at 760 torr, were frozen with liquid nitrogen and sealed off after their contents was thoroughly outgassed. The vessels containing the methane at 760 torr were closed with greaseless stopcocks, featuring a Teflon stem and a Viton O-ring. The break-seal of the side ampoule was then broken, and the contents was repeatedly frozen in liquid nitrogen in order to allow the <sup>3</sup>H<sub>2</sub> to mix with the gaseous alkanes. The samples were stored in the dark, at room temperature, for periods ranging from 1 to 4 months.

After the required storage period, the samples were opened and the contents were analyzed by radio gas chromatography, using the columns described in the previous section and monitoring the activity of the effluents with a 100-ml ionization chamber<sup>13</sup> whose current was measured with a Model 475A vibrating reed electrometer, Victoreen Instruments Co. (Oak Lawn, Ill.). The static activity measurements were carried out with a 250-ml ionization chamber of the Borkowsky type.

## Results and Discussion

The yields of the tritiated products from the reaction of the He<sup>3</sup>H<sup>+</sup> ions with methane and ethane at 760 torr are summarized in Table I. The yields represent the per cent of the total activity of the He<sup>3</sup>H<sup>+</sup> ions formed within the system found in each product. The total number of He<sup>3</sup>H<sup>+</sup> ions is calculated from the initial activity of the <sup>3</sup>H<sub>2</sub>, taking into account its half-life and the storage period.

Each decay event produces, in fact, an excited He<sup>3</sup>H<sup>+</sup> ion, which has a 94.5% probability to survive as such, according to the mass spectrometric measurements of Wexler.<sup>14</sup> Kinetic experiments indicated that the formation rate of the tritiated products was constant over an extended period of time, ranging from 1 to 4 months.

**Effect of Radiation Damage to the System.** In order to ascertain whether radiolytic processes play any role in the formation of the labeled products, blank runs were carried out, replacing the molecular tritium with hydrogen tritide, which produces unlabeled HeH<sup>+</sup> ions upon β decay.

In these experiments, the formation of tritiated species through the reactions of the decay ions was suppressed, and any labeled product observed must necessarily arise from radiolytic processes. The failure to detect any such product (see Table I) provides direct evidence that, under the experimental conditions prevailing in the present work, at concentrations of tritium corresponding to about 7 μcuries/ml of gas, the radiolytic processes leading to the formation of the tritiated products are insignificant in comparison with those formed by the reactions of the He<sup>3</sup>H<sup>+</sup> ions. This finding is supported by several independent observations, including the lack of a significant effect on the yields of labeled products when using radical scavengers and the satis-

(12) K. Yang and P. L. Gant, *J. Phys. Chem.*, **66**, 1619 (1962).

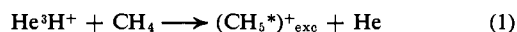
(13) F. Cacace, *Nucleonics*, **19** (5), 45 (1961).

(14) S. Wexler, *J. Inorg. Nucl. Chem.*, **10**, 8 (1959).

factory activity balance (the combined activity of the products is invariably smaller than the activity contained in the  $\text{He}^3\text{H}^+$  ions). Moreover, it can be shown that the dose received by the system during a storage period of 30 days is very low indeed, of the order of  $10^{-4}$  eV per molecule. Finally, it may be worth pointing out that even the empirical kinetic expression derived by Pratt and Wolfgang<sup>15</sup> from their experiments on Wilzbach labeling of methane, carried out at much higher tritium concentrations, would indicate that at the levels of tritium activity employed in the present work "decay labeling" is the only significant process.

**Reaction of  $\text{He}^3\text{H}^+$  Ions with Methane.** The major products formed from the reactions of the  $\text{He}^3\text{H}^+$  ions with methane were tritiated methane and ethylene, whose combined yields accounted for *ca.* 50% of the total activity initially as  $\text{He}^3\text{H}^+$ .

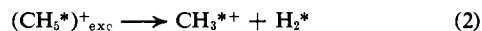
The product pattern was unaffected by the presence of 2 mole % of oxygen as radical scavenger, while a significant change was observed when  $\text{C}_3\text{H}_8$  (2 mole %) was introduced into the methane. Under such conditions, tritiated ethane was formed in a 32% yield, and the combined activity of the reaction products identified rose to *ca.* 70%. These results may be rationalized by assuming that the  $\text{He}^3\text{H}^+$  ions protonate the methane according to the process



where the asterisk indicates, as in the following equations, a tritiated species.

Reaction 1 is analogous to the gas-phase protonation of methane by ionic reagents, such as  $^3\text{H}^+$ ,  $^3\text{D}^+$ ,  $\text{CHO}^+$ ,  $\text{CH}_5^+$  ions, that has been well established by mass spectrometric techniques.<sup>1-9</sup>

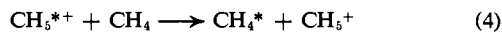
Owing to the large energy released in reaction 1 which is exothermic by 67 to 89 kcal/mole,<sup>15</sup> the  $\text{CH}_5^{*+}$  ions formed are in a state of high excitation and can decompose, according to the equation



or be stabilized by collision



The stabilized ions react with the inactive methane, according to the thermoneutral proton-transfer process



to form the observed tritiated methane.

It should be noted that this mechanism includes processes well established by current mass spectrometric investigations (for instance, reaction 4 was recently observed by Aquilanti and Volpi<sup>4</sup> with  $\text{CH}_4\text{D}^+$  ions), which are insensitive to the presence of low concentrations of radical scavengers and other impurities contained in the inactive methane.

The tritiated methyl ions from reaction 2 react<sup>16-21</sup> rapidly with methane, according to the fast process

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

(16) F. H. Field and M. S. B. Munson, *ibid.*, **85**, 3575 (1963).

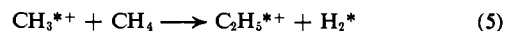
(17) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *J. Chem. Phys.*, **40**, 5 (1964).

(18) F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 3289 (1965).

(19) R. M. Haynes and P. Kebarle, *J. Chem. Phys.*, **45**, 3899 (1966).

(20) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 3294 (1965).

(21) M. S. B. Munson and F. H. Field, *ibid.*, **87**, 4242 (1965).

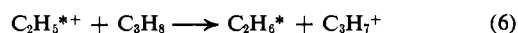


The resulting ethyl ions are quite unreactive toward methane. Field and Munson<sup>18</sup> calculated that the rate constant of any reaction with methane is smaller than  $10^{-12}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>, while Haynes and Kebarle<sup>19</sup> concluded from their experiments carried out at  $\text{CH}_4$  pressures up to 160 torr that the rate must be smaller than *ca.*  $10^{-15}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>.

Such a low reactivity of the  $\text{C}_2\text{H}_5^+$  ions toward methane, together with a remarkably high reactivity toward such compounds as propane, butanes, higher alkanes, water, etc., makes it likely that the fate of the tritiated ethyl ions from reaction 5 is determined to a critical extent by the nature and the concentration of the impurities contained in the system.

In this connection, it must be pointed out that Haynes and Kebarle<sup>19</sup> observed that 1 ppm of  $\text{C}_3\text{H}_8$  is already sufficient to considerably reduce the intensity of the ethyl ions in methane at 40 torr, through a fast<sup>20</sup> ( $K \approx 10^{-9}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>) hydride ion transfer. Moreover, the effect of even small concentrations of impurities can be expected to be further enhanced under the conditions prevailing in the present investigation, owing to the fact that the reaction time allowed to the ethyl ions is not restricted by instrumental limitations to a few milliseconds, but is only limited by the relatively slow process of neutralization.

In view of the above considerations, it appears that the analysis of the final tritiated products in "pure" methane can hardly provide reliable information on the abundance of the labeled ethyl ions formed from process 5 and subsequent reactions. In fact, the system is likely to contain various impurities at concentrations largely sufficient to intercept any labeled ethyl ions, to form different tritiated products through several poorly defined competitive processes. Therefore, in order to determine the yield of the ethyl ions from reaction 5, a relatively large concentration (2 mole %) of an efficient interceptor, propane, was added to the system. Since  $\text{C}_3\text{H}_8$  is known<sup>19,20,22</sup> to react with the  $\text{C}_2\text{H}_5^+$  ions according to the fast hydride ion transfer



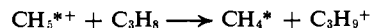
and the propane concentration becomes now orders of magnitude larger than those of the other impurities, one can expect that the activity contained in the labeled ethyl ions is quantitatively transferred into the tritiated ethane.

Under such conditions, it seems possible to use the distribution of the activity among the tritiated reaction products to estimate the relative weight of processes 2 and 3.

Owing to the lack of competitive processes,<sup>23</sup> and to the very large excess of inactive methane, reaction 4 causes the whole activity originally contained in the stabilized  $\text{CH}_5^{*+}$  ions to be incorporated in the triti-

(22) P. J. Ausloos, G. G. Lias, and R. Gorden, Jr., *J. Chem. Phys.*, **39**, 3341 (1963).

(23) Actually, Munson and Field<sup>20</sup> observed that the  $\text{CH}_5^+$  ions protonate propane readily. However, owing to the low concentration of  $\text{C}_3\text{H}_8$  and to the high probability that the  $^3\text{H}$  atom remains bound to the methane molecule in the process



the occurrence of this reaction should not affect the conclusion that the activity of the  $\text{CH}_5^{*+}$  ions is to be eventually found in the tritiated methane.

ated methane, whose yield reaches 35%. The remaining 65% of the activity must be contained in those excited  $\text{CH}_3^{*+}$  ions which dissociate. Assuming a statistical distribution of the tritium among the products of reactions 2 and 5, one can calculate that *ca.* 28% of the activity should be eventually found in the tritiated ethane. The agreement with the experimental yield (32%) is satisfactory, if one takes into account the rather crude assumptions made, *i.e.*, a statistical  $^3\text{H}$  distribution, the lack of isotope effects, etc.

The remaining fraction of the activity originally contained in the  $\text{He}^3\text{H}^+$  ions goes into the other product formed in reactions 2 and 5, *i.e.*, hydrogen tritide, whose yield could not be determined, since it is always contained as an impurity in the  $^3\text{H}_2$  used as a source of the  $\text{He}^3\text{H}^+$  ions.

According to the results of the present investigation, it therefore appears that about one-third of the excited  $\text{CH}_3^{*+}$  ions from the protonation of  $\text{CH}_4$  with  $\text{He}^3\text{H}^+$  are stabilized by collision in methane at 760 torr, while the remaining dissociate to produce methyl ions.

Independent evidence that only about one-third of the excited  $\text{CH}_3^{*+}$  ions from reaction 1 are stabilized by collision<sup>24</sup> is provided by the experiments carried out in methane containing no added propane, where a 38–40% yield of tritiated methane was again measured. Here in fact the stabilized ions react exactly as in the systems containing 2 mole %  $\text{C}_3\text{H}_8$  to form tritiated methane through the fast ion–molecule reaction (4), which was found, as expected, to be insensitive to small concentrations of additives such as  $\text{C}_3\text{H}_8$ . Also, the yield of tritiated methane appears to be insensitive to the presence of 2 mole %  $\text{O}_2$ , in agreement with the findings of Munson and Field<sup>21</sup> and Haynes and Kebarle,<sup>19</sup> who observed that the spectrum of organic ions in methane is not affected by the addition of small concentrations of  $\text{O}_2$ .

In the absence of added propane, the yield of tritiated ethane is reduced to *ca.* 2%, labeled ethylene is formed in a 13% yield, and the combined yield of all the identified products drops to about 50% of the activity contained in the  $\text{He}^3\text{H}^+$  reagent. There is little doubt that the small residual yield of labeled ethane arises from the reaction of the tritiated ethyl ions with the traces of  $\text{C}_3\text{H}_8$  or higher alkanes contained as an impurity in the  $\text{CH}_4$ . The source of labeled ethylene is rather uncertain. It could conceivably arise from the neutralization of the ethyl ions (either in the gas phase or on the walls), followed by the fast dissociation of the excited ethyl radicals into ethylene and hydrogen atoms. Such a possibility, however, appears unlikely, since the neutralization process is known to be very slow in gases at 1 atm pressure,<sup>25</sup> in comparison with efficient ion–molecule reactions. The recent investigation by Munson and Field<sup>21</sup> on the influence of additives on the ionic processes in methane suggests that the reaction of the labeled ethyl ions with the small concentrations of water contained as an impurity in the methane could represent a likely source of the tritiated ethylene observed.

(24) It is interesting to note that a few experiments, involving the decay of 1.7 mcuries of  $^3\text{H}_2$  in 6 l. of methane at a pressure of 20 torr, failed to detect a decrease in the tritiated methane yield. This suggests the possibility that part of the protonated ions from reaction 1 are produced in a form which cannot be stabilized by collision, even by a 40-fold increase of the pressure; *cf.* V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, **47**, 831 (1967).

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



Such proton transfer was shown<sup>21</sup> to be remarkably fast ( $k_7 \approx 6 \times 10^{-9}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>), and according to Haynes and Kebarle<sup>19</sup> even 10 ppm of water has a profound effect on the ionic spectrum of methane at 5 torr.

Again, owing to the much longer time available in our experiments for ionic reactions, a still lower concentration of water, possibly below 1 ppm, should effectively intercept the tritiated ethyl ions.

Since the water content of the methane samples employed in the present investigation almost certainly exceeded this extremely low value, we regard reaction 7 as the most likely source of the tritiated ethylene observed in systems containing no added  $\text{C}_3\text{H}_8$ .

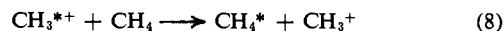
It is interesting to compare the results of the present investigation with those obtained by Pratt and Wolfgang<sup>15</sup> and by Wexler<sup>26</sup> in their study of the self-induced isotopic exchange of gaseous tritium with methane. Owing to the relatively high  $^3\text{H}_2$  concentration employed in their experiments, Pratt and Wolfgang found that two radiation-induced mechanisms, in addition to the reactions of the decay  $\text{He}^3\text{H}^+$  ions, were responsible for the formation of the tritiated products.

A careful kinetic analysis and the use of radical scavengers, however, enabled these authors to separate the various labeling mechanisms and to determine their relative contribution to the total yield of tritiated products. In the presence of  $\text{I}_2$  as a scavenger, despite the occurrence of radiolytic processes, the spectrum of labeled hydrocarbons, comprising methane, ethane, and ethylene as the major products, with smaller amounts of propane and butanes, corresponds qualitatively to that found in the present investigation, carried out at a  $^3\text{H}_2$  concentration some 150-fold lower. The major quantitative discrepancy arises from the much higher yield of tritiated ethane obtained by Pratt and Wolfgang.

The results of the present investigation support the conclusion of Pratt and Wolfgang that the exothermic protonation of  $\text{CH}_4$  by the  $\text{He}^3\text{H}^+$  ion is the first step in the formation of tritiated methane.

On the other hand, the details of the two mechanisms proposed by Pratt and Wolfgang for the subsequent reactions of the protonated methane, both based on the dissociation of the excited  $\text{CH}_3^{*+}$  ions into methyl ions, differ somewhat from ours.

The first mechanism (IA) postulates the reaction of the labeled  $\text{CH}_3^+$  ions with  $\text{CH}_4$ , according to eq 5, followed by the neutralization of the resulting ethyl ions, which produces in turn hot methyl radicals. The latter abstract hydrogen from  $\text{CH}_4$  to yield the observed tritiated methane. The second mechanism (IB) postulates the direct formation of labeled methane through the reaction



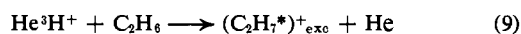
In the light of the results now available on the reactivity of the ethyl ions in methane, it appears that the neutralization process is too slow to compete with fast ion–molecule reactions such as process 6. The observed (Table I) insensitivity of the yield of tritiated methane to the addition of 2 mole %  $\text{C}_3\text{H}_8$  would therefore suggest that the neutralization of ethyl ions is not involved in the formation of tritiated methane.

(26) S. Wexler, *J. Am. Chem. Soc.*, **83**, 10 (1961).

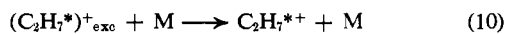
As to mechanism IB, the information now available on the ion-molecule reactions in methane, and especially the data of von Koch,<sup>6</sup> indicates that the exothermic reaction 5 is considerably faster than the thermoneutral process 8.

The results of the mass spectrometric investigation carried out by Wexler<sup>26</sup> on the system  $\text{CH}_4\text{-}^3\text{H}_2$  seem entirely compatible with the mechanisms proposed in the present paper for the formation of the tritiated products. In particular, Wexler's observation that at least a fraction of the  $\text{C}_2\text{H}_3^{*+}$  ions do not arise from radiolytic processes provides direct, even if qualitative, evidence for reaction 5.

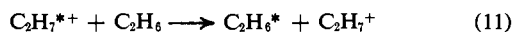
**Reactions of  $\text{He}^3\text{H}^+$  Ions with Ethane.** In ethane (both neat and containing 2 mole % of oxygen), the major products identified are tritiated methane and ethane, with yields of 14 and 34–36% respectively. In the samples containing  $\text{O}_2$ , a small (5%) yield of labeled ethylene was also observed. There is little doubt that the  $\text{He}^3\text{H}^+$  can protonate the ethane, with a reaction similar to those observed in "high-pressure" mass spectrometry, for reagents such as  $\text{CH}_5^+$ ,<sup>1</sup>  $\text{H}_3^+$  and  $\text{D}_3^+$ ,<sup>4</sup>  $\text{CHO}^+$ ,<sup>7</sup> etc.



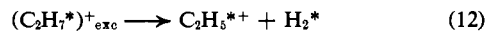
Assuming the occurrence of reaction 9, there are two major routes to the formation of labeled ethane. One involves the stabilization of the excited protonated ions



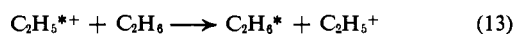
followed by thermoneutral proton transfer



The other possibility involves the decomposition of the excited  $\text{C}_2\text{H}_7^{*+}$  ions into ethyl ions



and the well-established<sup>4,7,27</sup> thermoneutral hydride ion transfer



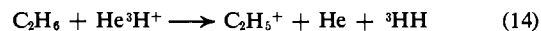
It is interesting to note that the latter mechanism may provide an explanation for the rather low yield of tritiated ethane observed (34–36%). In fact, according to Aquilanti and Volpi,<sup>4</sup> the elimination of  $\text{H}_2$  and HD from excited  $\text{C}_2\text{H}_6\text{D}^+$  ions, formed from the protonation of  $\text{C}_2\text{H}_6$  with  $\text{D}_3^+$  ions, occurs with about the same probability. If such result can be applied to reaction 12, it follows that the upper limit for the yield of ethyl ions, and therefore of the ethane they eventually form, is only about 50%.

Since a yield of 34–36% was actually observed, the mechanism based on the formation of ethyl ions (eq 12 and 13) seems to be preferred to the mechanism involving the stabilization of the  $\text{C}_2\text{H}_7^{*+}$  ions, where no activity is lost as hydrogen tritide. Moreover, this interpretation fits the trend observed in the protonation

(27) B. Aliprandi, F. Cacace, and A. Guarino, "Chemical Effects of Nuclear Transformations," Vol. II, International Atomic Energy Agency, Vienna, 1965, p 471.

of the lower alkanes with  $\text{H}_3^+$  and  $\text{D}_3^+$ , where it was found<sup>4</sup> that the relative stability of the protonated ions markedly decreases going from the  $\text{CH}_5^+$  to the  $\text{C}_2\text{H}_7^+$  ion.

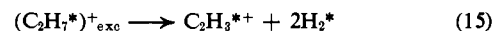
Another possible explanation of the low yield of tritiated products observed in this system is of course the exothermic hydride ion transfer



which could compete with the protonation of ethane.

There are several routes to the tritiated methane, which was isolated with a yield of 14% from the reactions of  $\text{He}^3\text{H}^+$  ions with ethane.

The ions from process 9 possess enough excitation energy to dissociate according to reaction pathways energetically less favorable than reaction 12. For instance, the excited protonated ions could undergo the loss of two hydrogen molecules, according to the reaction

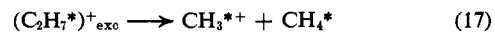


Such extensive fragmentation has been frequently observed in mass spectrometric investigation; for instance, the  $\text{C}_2\text{H}_3^+$  fragment is one of the most abundant ions in the highly exothermic charge exchange of  $\text{C}_2\text{H}_6$  with positive ions such as  $\text{He}^+$ ,  $\text{Ne}^+$ ,  $\text{Ar}^+$ ,  $\text{N}_2^+$ , etc.<sup>7</sup> The  $\text{C}_2\text{H}_3^{*+}$  ions could react with ethane according to the well-established<sup>17</sup> process

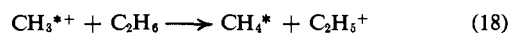


to yield the observed tritiated methane.

Another, admittedly unattractive, possibility is the dissociation



of the excited protonated ions, which could produce the tritiated methane, either directly or through the following hydride ion transfer process<sup>7</sup>



It is interesting to compare the results of the present investigations with those obtained by Gant and Yang<sup>28</sup> in a preliminary investigation on Wilzbach labeling of ethane. The major products identified were tritiated ethane, propane, and *n*-butane in the ratio 1:1.1:0.60. Owing to the large activity of tritium employed (2.0 curies), the  $\beta$  radiolysis of the tritium-ethane mixture contributed substantially to the formation of the labeled products. It appears that the main purpose of the investigation was the determination of the contribution of the different modes of labeling to the formation of the tritiated hydrocarbons, while no mechanism for the reactions of  $\text{He}^3\text{H}^+$  ions was provided.

**Acknowledgments.** The continued interest and the helpful discussions of Professor G. Giacomello are gratefully acknowledged. The authors are indebted to D. Carrara for his skillful assistance.

(28) P. L. Gant and K. Yang, *J. Chem. Phys.*, **30**, 1108 (1959).