A Tracer Study of the Reactions of Ionic Intermediates Formed by Nuclear Decay of Tritiated Molecules. I. Methane-t_4

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Abstract: A tracer technique has been employed to identify the stable products from the reactions of the ionic intermediates formed upon decay of a tritium atom contained in a methane molecule. Methane-t_4 has been allowed to decay in methane and in methane–propane mixtures, in the presence of oxygen, at atmospheric pressure and room temperature. Such a technique, combined with the available mass spectrometric data on the decay-induced fragmentation of monotritiated methane, and taking into account the ion–molecule reactions that occur in the systems investigated, has been employed to derive a detailed picture of the chemical fate of a methane molecule following the decay of a constituent tritium atom. The results suggest that the decay in systems at 760 torr produces a fragmentation pattern similar to that observed at low pressure in the mass spectrometer. In fact, taking into account the mass spectrometric data on the abundance of the organic ions from the decay of CH_3T and their known reactions in the systems investigated, it is possible to predict the nature and the yields of the observed final products and the dramatic changes caused by the addition of propane, in good agreement with the experimental data. The close correspondence of the results obtained with those expected from the current knowledge on the ion–molecule reactions in alkanes suggests that the decay of multilabeled molecules could afford a valuable tool to study such processes in systems at high pressure or even in the liquid state.

The β decay of a radioactive atom contained in a molecule produces characteristic chemical consequences. The electron emission causes the formation of a positively charged ion, that is often highly excited and eventually dissociates.

Theoretical models have been employed to calculate the momentum imparted in the nuclear event to the decayed atom, the probability of the bond rupture, the amount of excitation received by the molecule, its charge state, etc.[1–11]

In many cases, the stable products that arise from the decay of a radioactive atom in simple molecules have been analyzed, and the results used to substantiate theoretical calculations of the probability of the bond rupture.[12–20] Preparative applications of the nuclear decay have also been proposed.[21,22]

In all these investigations, the central chemical problem, *i.e.*, the determination of the reaction pathways leading from the original molecule to the final, stable products, was very difficult owing to the absolute lack of information concerning the primary fragments formed by nuclear decay.

Since 1958, however, mass spectrometric investigations[9,23–31] have provided detailed information on the low-pressure fragmentation pattern following the decay of radioactive atoms bound to organic or inorganic molecules. On the basis of the information made available by these mass spectrometric investigations, it was of interest to design experiments to follow by suitable tracer techniques the reactions of the intermediates produced by nuclear decay in systems at atmospheric pressure.

First of all, it was hoped that the mass spectrometric data could help to establish a detailed picture of the chemical reactions following the β decay, at least in a few simple cases.

In addition, the possibility to introduce by nuclear decay labeled ions in methane and other gases at atmospheric pressure could afford a valuable tool for the study of the ion–molecule reactions occurring in these systems. In fact, the use of such tracer techniques should allow one to identify the neutral, stable products of the ionic reactions that cannot be directly determined with the mass spectrometric techniques generally used in the study of these processes.

In order to meet the requirements for this kind of investigation it is necessary to know the primary fragments formed by the nuclear decay, the reactions of fragments of this kind in the systems considered and

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to determine the nature and yields of the final products formed.

As to the first requirement, the mass spectrometric[24] data on the decay-induced fragmentation of tritiated molecules were employed. It may be argued that there is no *a priori* reason why these data, obtained at pressures between 10^{-6} and 2×10^{-5} torr, should be valid for systems at 760 torr. In particular, the primary fragmentation process could be affected by such a large pressure increase.[32]

However, the relatively large excitation energy deposited by the nuclear decay into those primary ions that dissociate has led us to assume, at least as a working hypothesis to be verified by the experiments, that the decay-induced fragmentation is largely independent of the pressure.

The choice, as a source of decay fragments, of tritiated methane, a molecule giving upon β decay ions whose reactions have been studied in detail, was dictated by the necessity to fulfill the second requirement.

Finally, the identification of the stable reaction products was made possible by the use of multilabeled molecules, such as CT_4, as a source of the decay ions. In fact, the decay of one T atom in a given molecule leaves a tritiated ion that, reacting with the surrounding molecules, yields labeled products, whose nature and amount can be determined by radio gas chromatography.

In addition, the methane is one of the few cases where it is possible, through the use of recently developed chromatographic techniques,[33] to separate the isotopic molecules with different tritium contents, that represent possible reaction products. On the base of the above considerations, methane-T_4 was prepared, purified, and allowed to decay in the following systems: methane + 2% O_2, methane + 3% propane + 2% O_2, and propane + 14% methane + 2% O_2. All the systems were at 760 torr and room temperature.

Experimental Section

Materials. CT_4 was prepared from aluminum carbide and tritiated water,[34] which was obtained by oxidizing pure tritium gas over copper oxide. Immediately after the preparation, the labeled methane was diluted with a large excess of CH_4 and purified by preparative gas chromatography. The radiochemical purity of the labeled methane was assayed by radio gas chromatography, and its isotopic purity was assayed by mass spectrometry. It was deemed necessary to obtain additional information of the composition of the sample by a chromatographic separation of the isotopic methanes, using the capillary column described by Bruner and Cartoni.[33] The results of both the mass spectrometric and gas chromatographic method demonstrated that CT_4 represented more than 95% of the activity contained in the various methanes.

Full details concerning the preparation, purification, and analysis of CT_4 are given elsewhere.[35]

The inactive hydrocarbons and the oxygen used were research grade samples obtained from Soc. Rivoira, Turin.

Growing in and Analysis of the Decay Products. Samples of CT_4 in methane + 2% oxygen, having specific activity of about 0.2 mcurie per mmole, were stored in glass ampoules at atmospheric pressure and room temperature for different periods of time. The oxygen was added in order to suppress the reactions of thermal radicals that could superimpose on the ionic processes.

On the other hand, it would have been a difficult problem to reduce to a constant and very low level, corresponding to a few ppm, the oxygen concentration of the various samples of CT_4 in methane.

Similar procedures were employed for the samples containing propane. The radio gas chromatographic analysis of the reaction products other than methane was carried out with a Fractovap Model B of Soc. Carlo Erba, Milan, coupled to a 100-ml flow ionization chamber connected to a Cary Model 32 vibrating reed electrometer.[36]

The separation of HT, CT_4, $C_2H_6 + C_2H_4$, C_2H_2, C_3H_8, and C_3H_6 was obtained using a silica gel column operated at 100°.

A 5-A molecular sieve column was used at 175° for the separation of ethane and ethylene. The analysis of the higher hydrocarbons was performed at room temperature, with a column of activated alumina, containing 0.5% of D.C. 550 silicone oil from Burrel Co. The analysis of the isotopic methanes, before and after storage, was performed using a capillary column, 47 m long, 0.22 mm i.d., prepared and activated according to Bruner and Cartoni.[33]

The gases from the column, diluted with a stream of nitrogen up to a total flow rate of 15 l. min^{-1}, entered the 100-ml flow ionization chamber connected to the electrometer.

The static activity analyses were carried out with a 250-ml Borkowski-type ionization chamber and a Cary Model 32 electrometer.

Results

The analysis of samples where CT_4 was allowed to decay for different periods of time, ranging from 38 days to 2 months, showed that the formation rate of the labeled products was remarkably constant.

For all the systems investigated a simultaneous analysis of the products was carried out after a storage period of 30 days. Table I summarizes the composition of the various systems and the yields of tritiated products, calculated by dividing the activity found in each product by the total activity of the decay fragments formed during the experiment.

Table I. Radiochemical Yields of the Products from the Decay of CT_4

	Radiochemical yields[a]		
Products	CH_4 + 2% O_2[b]	CH_4 + 3% C_3H_8 + 2% O_2	84% C_3H_8 + 14% CH_4 + 2% O_2
CHT_3[c]	5.00	5.00	74.00
Hydrogen[d]	28.70	34.00	16.60
Ethylene	10.90	0.02	0.20
Ethane	1.00	49.00	7.00
Propane	0.80	0.02	0.20
Propylene	0.02	0.02	0.06
n-Butane	0.30	0.02	0.06

[a] Obtained by dividing the activity found in each product by the total activity of the $CT_3{}^3He^+$ fragments produced within the system during the experiment. [b] All the samples have been stored for 30 days at atmospheric pressure and room temperature. [c] Owing to the incomplete separation of CHT_3 from CT_4 the yields of CHT_3 are affected by a standard deviation of about 20%. [d] The standard deviation of the yields of the products other than CHT_3 has been found to be about 5%.

All the data tabulated represent the average value of at least three different analyses with the same column. In addition, it was often possible to determine the yield of a given product with analyses carried out on different columns.

In the first system studied, CH_4 + 2% O_2, the identified reaction products, including the CHT_3 account for less than 50% of the decay fragments activity, the major labeled products being hydrogen and ethylene.

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A search for labeled hydrocarbons in the C_4–C_6 range failed to detect any significant activity. No attempt was made to identify oxygenated species.

In methane containing 2% oxygen and 3% propane, as an ethyl ion interceptor, more than 80% of the decay fragments activity is accounted for. Again the activity of methane-T_3 is below the detection limit and only two labeled products, hydrogen and ethane, have been identified.

Finally, when an excess of propane is present, all the activity of the decay fragments is found in the products identified. Methane-T_3 is formed with a yield of 74%, while the yields of tritiated hydrogen and ethane drop to 16.6 and 7.0%, respectively.

It must be pointed out that the accuracy of the CHT_3 analysis is much lower than for the other products, owing to the lack of a complete resolution of the CT_4 and CHT_3 peaks, respectively.

Discussion

Effects of Self-Radiolysis of the Sample. Before discussing the mechanism of formation of the products listed in Table I, it is necessary to evaluate the possible effects of the radiation associated with the decay of the tritium atoms. Each nuclear event produces, together with a labeled decay fragment, a β particle with a mean energy of 5.6 kev. If the radiation destroys a significant fraction of the CT_4 contained in the system, labeled radiolytic products are formed that cannot be distinguished from the products of the decay-induced reactions.

In order to reduce the radiation damage, the specific activity of the stored samples was kept around 0.2 mcurie per mmole of gas. At this level, for storage periods of 30 days and assuming that the $G_{-\mathrm{M}}$ value is the same for the labeled and unlabeled methane, it can be shown that the activity of the radiolytic products is small in comparison with the activity of the decay fragments. This conclusion was experimentally verified by storing samples of monotritiated alkanes, having specific activities of about 0.2 mcurie per mmole, for the same period and under the same conditions as the samples of CT_4.

In monotritiated molecules, the fragments from nuclear decay are not labeled and radiolytic reactions are the only source of radioactive products other than the starting material. A gas chromatographic analysis of the samples after 30 days showed, as expected, no significant amount of labeled products.

It was therefore concluded that, under the conditions employed, radiolytic processes play no significant role in the formation of the products listed in Table I.

Primary Fragmentation Following Nuclear Decay. The fragmentation pattern from the decay of T in CH_3T was determined by Snell and Pleasonton[24] in the mass spectrometer at low pressure. The β decay produces the primary ion $CH_3{}^3He^+$ which invariably fragmentates with the loss of a neutral ^3He atom. Both the mass spectrometric evidence and the theoretical calculations[1] show that about 80% of the original ions have little or no excitation energy and give stable methyl ions after the loss of ^3He. The remaining 20%, or so, of the original ions are highly excited—up to about 20 ev—and fragment further, producing the secondary ions listed in Table II.

Table II. Fragmentation of CH_3T by Nuclear Decay (According to Snell and Pleasonton[a])

Charged fragment	Abundance, %
H^+	2.40 ± 0.10
$H_2{}^+$	0.14 ± 0.01
$(He^3)^+$, $H_3{}^+$	0.12 ± 0.01
$(He^3H)^+$	0.15 ± 0.02
C^{12+}	4.90 ± 0.10
$C^{12}H^+$, $(^{13}C^+)$	4.00 ± 0.10
$CH_2{}^+$	4.90 ± 0.10
$CH_3{}^+$	82.00 ± 1.50

[a] See ref 24.

In the following discussion we will make use of the following assumptions. (i) The decay of a T atom in the CT_4 molecule produces a spectrum of tritiated ions corresponding to the protonated ions formed in the decay of CH_3T. (ii) The fragmentation following the decay of a tritiated methane molecule at 760 torr is similar to that found in the low-pressure mass spectrometric investigations.

The last assumption is plausible, since it is likely that the intrinsic weakness of the C–He bond[9,37] should cause the loss of ^3He from the primary ions even at high pressure, and of course it is to be expected that the ions escaping fragmentation at low pressure should not dissociate at 760 torr. It could be argued however that the fraction of the methyl ions that are excited by the nuclear decay enough to dissociate in the mass spectrometer could be stabilized in experiments carried out at 760 torr and therefore their fragmentation could be reduced or suppressed. The validity of the assumption made has therefore to be verified by the experimental results.

System CH_4 (14%) + C_3H_8 (84%) + O_2 (2%). The yields of the major products found in this system are consistent with the view that the dissociation of the organic molecule following the nuclear event in a system at 760 torr is similar to that found at low pressure.

Methyl ions are the predominant species (82%) formed during the decay of monotritiated methane in the mass spectrometer as shown in Table II. In the presence of an excess of propane, the methyl ions undergo[38,39] a hydride ion transfer. In addition, they

$$CT_3{}^+ + C_3H_8 \xrightarrow{k_1} CHT_3 + C_3H_7{}^+ \tag{1}$$

react with methane to give labeled ethyl ions, which in turn, undergo[40] hydride-ion transfer with propane. In these and in the following equations, the asterisk indicates labeled species containing an unknown number of T atoms.

$$CT_3{}^+ + CH_4 \xrightarrow{k_2} C_2H_5{}^{*+} + H_2{}^* \tag{2}$$

$$C_2H_5{}^{*+} + C_3H_8 \longrightarrow C_2H_6{}^* + C_3H_7{}^+ \tag{3}$$

The CHT_3 and the labeled ethane are actually found in this system, with a yield of *ca.* 74 and 7.0%, respectively.

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Since tritiated hydrogen is produced by a number of reactions, the yield of labeled hydrogen from reaction 2 cannot be measured directly. If, however, in the lack of more detailed information, we assume a statistical distribution of the tracer between the ethyl ions and the hydrogen, we can evaluate, from the yield of ethane, the contribution of reaction 2 to the total tritiated hydrogen yield. A simple calculation shows that the hydrogen from 2 represents $7.0 \times {}^2/_5 = 2.8\%$ of the total activity of the decay fragments.

We are now in a position to evaluate the fraction of nuclear events producing methyl ions from the total activity contained in their reaction products. The value obtained in this way

$$74\%(CHT_3) + 7.0\%(C_2H_6{}^*) + 2.8\%(H_2{}^*) = 83.8\%$$

compares favorably with the relative abundance (82%) of methyl ions from the decay of CH_3T at low pressure. If collisional deactivation processes, occurring at 760 torr, could prevent the dissociation of the ~20% of the methyl ions which are highly excited and dissociate at low pressure, then one should expect a higher yield of CH_3T and/or labeled ethane.

The other major product found in this system is tritiated hydrogen. Part of it originates from reaction 2, while the remaining fraction most probably arises from the primary fragmentation of the decay ions and the consecutive reactions of the fragments, as discussed below in detail. Taking into account the contribution from the fragmentation processes, a lower limit of 9.8% for the yield of labeled hydrogen has been calculated, while the experimental value is 16.6%.

It may be added that, from the yields of CHT_3 and labeled ethane, the constants k_1 and k_2 appear to be of the same order of magnitude, in agreement with mass spectrometric measurements[39,41] and that the methyl ions produced from the nuclear decay do not react appreciably with the oxygen contained in the system, in agreement with the findings of Munson, Field, and Franklin.[42]

System CH_4 (95%) + C_3H_8 (3%) + O_2 (2%). Only two major products arise from the decay of CT_4 in this system: tritiated hydrogen, with a yield of 34.0%, and ethane, with a yield of 49.0%. The formation of ethane can be explained by the equations 2 and 3. It must be pointed out that, owing to the large excess of methane, the hydride ion transfer 1 is no longer significant, as shown by the low yield of CHT_3. However, owing to the low reactivity of the ethyl ions in methane,[40] even the low concentration of propane present is sufficient to produce ethane by process 3.

The yield of ethane can be calculated from the abundance of methyl ions (Table II) and using the assumptions made in the previous section. The calculated yield is 58.6% as compared to an experimental yield of 49.0%.

The yield of labeled hydrogen from reaction 2, calculated from the abundance of methyl ions, amounts to 23.4%. Additional tritiated hydrogen probably arises from the fragmentation of the primary decay species, as shown in the next section. If we take into account these fragmentation processes, we obtain 30.4% as a lower limit for HT production, in fair agreement with the experimental yield (34%).

System CH_4 (98%) + O_2 (2%). In methane, containing 2% O_2 as a radical scavenger, the major products are tritiated hydrogen and ethylene. This can be expected, since the methyl ions react with methane according to eq 2 producing ethyl ions and hydrogen. Additional hydrogen is produced directly from the fragmentation of the primary ions.

The dissociation processes

$$CH_3{}^{*+} \longrightarrow C^+ + H_2{}^* + H^* \qquad (4)$$

$$CH_3{}^{*+} \longrightarrow CH^{*+} + H_2{}^* \qquad (5)$$

$$CH_3{}^{*+} \longrightarrow CH_2{}^{*+} + H^* \qquad (6)$$

that have been found to occur in the mass spectrometer, produce molecular and atomic hydrogen.

We will take into account only the former, since the oxygen contained in the system is supposed to scavenge the hydrogen atoms. However, even reaction 6 could contribute to the formation of molecular hydrogen through the consecutive reactions of the methylene ion.[40]

$$CH_2{}^{*+} + CH_4 \longrightarrow C_2H_4{}^{*+} + H_2{}^* \qquad (7)$$

$$CH_2{}^{*+} + CH_4 \longrightarrow C_2H_3{}^{*+} + H + H_2{}^* \qquad (8)$$

From the abundance of the fragment ions C^+, CH^+, and $CH_2{}^+$ as shown in Table II and again assuming a statistical distribution of the tracer among the products of the reactions 4–8, one can calculate the yield of molecular hydrogen produced in the fragmentation of the primary ions. The value obtained (7.0%) is, of course, a low limit, since other species, such as H^+ ions[43,44] could conceivably react with methane to produce tritiated hydrogen. When we add to the hydrogen from the primary fragmentation the hydrogen from reaction 2, whose yield has been shown in the previous section to be 23.4%, we calculate for the formation of labeled hydrogen a yield of 30.4%, in fair agreement with the experimental value of 28.7%.

As to the other product of reaction 2, the ethyl ion, it has been shown[40] to be unreactive in methane. In particular, it cannot undergo a hydride ion transfer reaction similar to reaction 3. The small yield of ethane found is likely to be due to the small percentages of higher hydrocarbons contained as impurities in the inactive methane. The fate of the ethyl ions is probably to be neutralized, partly forming ethylene, which has actually been found with a yield of 10.9%.

$$C_2H_5{}^{*+} + e \longrightarrow C_2H_4{}^* + H^* \qquad (9)$$

It is clear that if ethyl ions were to react quantitatively according to reaction 9, a much higher yield of tritiated ethylene (about 45%) should be obtained. The lower value observed suggests that under the conditions prevailing in the present experiments, *i.e.*, in methane at atmospheric pressure and in the presence of 2% oxygen, the ethyl ions either react with the scavenger or give, upon neutralization in the gas phase or on the walls, a species that reacts with the scavenger. According to Ausloos[45] and Field,[46] ethyl ions are scavenged

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

(44) E. Pettersson and E. Lindholm, *ibid.*, 24, 49 (1962).

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

(46) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 4242 (1965).

by the oxygen when the methane does not contain interceptors such as propane or higher alkanes. As to the latter possibility, it may be interesting to point out that, according to Wolfgang and Pratt[47] and Wexler[48] the labeled ethyl ions give, upon neutralization, methyl and methylene radicals, according to the equation

$$C_2H_5^{*+} + e \longrightarrow CH_3^* + CH_2^* \qquad (10)$$

Both these labeled radicals could be scavenged by the oxygen present in our experiments.

It is not possible to establish the fate of the ethyl ions from our experiments. The latter indicate, however, that in presence of oxygen only a minor fraction of the ethyl ions form ethylene upon neutralization.

It is also interesting to note that the yield of CHT_3 is low in methane. This indicates that the hydride ion transfer

$$CT_3^+ + CH_4 \longrightarrow CHT_3 + CH_3^+ \qquad (11)$$

which has been found by von Koch[43] to occur in the mass spectrometer, is slow in comparison with reaction 2. This is not the case with other alkanes; in ethane, for instance, the reaction

$$C_2H_5^{*+} + C_2H_6 \longrightarrow C_2H_6^* + C_2H_5^+ \qquad (12)$$

has been shown to occur with high efficiency, owing to the lack of effective competitive processes.[32,49,50]

Conclusion

The chemical effects of the decay of a constituent atom of a tritiated methane molecule in systems at atmospheric pressure have been interpreted using the available mass spectrometric data concerning the decay-induced fragmentation of CH_3T, and taking into account the reaction of the resulting ions.

The model obtained in this way allows one to predict, with reasonable accuracy, the nature and the yields of the products formed by the decay of CT_4 in systems at 760 torr.

The results indicate that the fragmentation following the β decay of a tritium atom in a methane molecule is largely independent of the pressure and suggest that a technique based on the decay of multilabeled molecules is a valuable means to introduce into systems at high pressure, or even in the liquid state, a known amount of ions of defined nature, whose reactions can be followed through the radioactivity of the final products.

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Relative Reaction Rates of Hydrated Electrons with Krebs Cycle and Other Anions

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Abstract: Using the e_{aq}^-–chloroacetate reaction as a reference, competition kinetics have been employed to obtain relative reaction rates of e_{aq}^- with a number of organic anions including the di- and tricarboxylates of the Krebs citric acid cycle. The latter, arranged in the order of oxidation recognized as obtaining in mitochondria, show alternately high and low rates of reaction with e_{aq}^- over a major part and possibly the whole of the cycle, in agreement with observations in the gas phase by Lovelock. Relative rate measurements throughout the work are in general agreement with the available pulse-radiolysis data.

The hydrated electron e_{aq}^- is the simplest reducing agent. The reaction of a given compound with e_{aq}^- can unambiguously be considered as an ideal charge-transfer process whose rate is determined by the availability of a molecular orbital of sufficiently low energy to react with the hydrated electron in solution.[1] The basic chemical properties of a compound can therefore be examined by studying its reactivity with e_{aq}^-. Since hydrated electrons represent one of the chief links between the purely physical and the slower chemical processes involved in the absorption of the energy of ionizing radiation in living matter, it is also important to know both the rate at which they react with biochemicals and the nature of the products formed. Further, a knowledge of e_{aq}^- reactions may yield information which will help to explain certain biological processes in which free electrons are thought to play an important part (photosynthesis,[2,3] transfer of energy in mitochondria[4–6]).

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