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THE PRODUCTION OF TRITIUM LABELED METHANE AND ETHANE IN THE CH_4-T_2 SYSTEM

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THE PRODUCTION OF TRITIUM LABELED METHANE AND ETHANE IN THE CH_4-T_2 SYSTEM

John B. Nash
(Ph. D. Thesis)

April 12, 1965

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THE PRODUCTION OF TRITIUM LABELED METHANE AND ETHANE IN THE CH_4-T_2 SYSTEM

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ABSTRACT

The rates of incorporation of tritium into labeled methane and ethane in the methane-tritium system has been investigated. The production of the tritiated products can be expressed by a sum of two terms. The first term of this expression is independent of time, and is the decay-induced labeling; the other, inversely proportional to time, is the radiation-induced labeling. The rate of incorporation of tritium into product as a result of the radiation field is shown to have a dependence on the absolute molecular concentration of tritium as well as its concentration as a source of radiation. The yields of labeled methane and ethane from the decay labeling is directly proportional to the rate of decay of the tritium. The rate of incorporation of tritium into labeled ethane is larger than that for incorporation into tritiated methane. A mechanism for both series consistent with the results is proposed The effect of additives was also determined. Addition of hydrogen elucidated the rate of labeling from the decay-induced series. Xenon was shown to enhance the product yield by 15 percent in concentrations up to 30 mole percent. Addition of ethylene in amounts less than 2 mole percent suppressed the labeling rate until the ethylene had disappeared by reaction with the radiolytic products. The effect on product formation of varying the pressure and the surface to volume ratio is also discussed.

I. INTRODUCTION

A. Wilzbach Labeling of Hydrocarbons

The method of labeling of organic compounds by exposure to tritium in the gas phase was initially proposed by Wilzbach.[1] The tritium atom decays by the emission of a β^- particle having a median energy of 5.57 to 5.70 keV.[2,3] The half-life of the decay is 12.26 to 12.36 years.[4]

The decay of the tritium molecule is represented by:

$$T_2 = HeT^+ + \beta^- . \qquad (1)$$

The HeT^+ ion is the predominant species existing following radioactive decay, being formed in 92% of the decays and having a bond energy of 40-46 kcal/mole.[5] This ion can then undergo reaction to ultimately stabilize the T in a labeled product. In addition to the reactions initiated by the HeT^+, there is an intense radiation field producing a mixture of radicals and ion-molecules which may react with the T_2 to produce labeled products of the radiolysis of the parent hydrocarbon.

The initial reactions in the radiolysis series, specifically for methane, are:

1) by ionization

$$CH_4 \rightsquigarrow \begin{cases} CH_4^+ + e^- \\ CH_3^+ + H + e^- \\ CH_2^+ + H_2 + e^- \end{cases} \qquad (2)$$

and 2) by excitation

$$CH_4 \rightsquigarrow \begin{cases} CH_3 + H \\ CH_2 + H_2 \end{cases} \qquad (3)$$

B. Other Labeling Methods

In addition to the gas exposure method described above, other methods for the labeling of hydrocarbons are addition of catalysts to the gas-exposure system, sparking the mixture with high voltage, and hot-atom reactions, as well as direct synthesis. The variations on the basic Wilzbach method as originally proposed yield specific labeling of the hydrocarbon present with less amounts of tagged radiolysis products. Of those mentioned above, the most recent approach is the one utilizing the hot-atom reactions. A hot-atom is described as any atom possessing kinetic energy greater than thermal energy. It is formed as a result of a nuclear reaction in which a neutron or charged particle is absorbed, or by recoil from beta- or gamma-decay.

The following reactions, specifically for tritium, illustrate the first method:

$$He^3 + n = T^* + p \qquad (4)$$

and

$$Li^6 + n = T^* + He^4 \qquad (5)$$

This tritium then replaces a hydrogen in the organic compound to be labeled. Reaction (4) is used for gas phase labeling; reaction (5) for solid and liquid phase. A comprehensive review of this and other methods of labeling of organic compounds with tritium, as well as specific applications is contained in the review article by Whisman and Eccleston.[7]

Labeling of other compounds with radioactive species, such as C^{14} (ref. 8) and S^{35} (Ref. 9) involve the method of excess kinetic energy atoms. When these atoms of high kinetic energy are formed by recoil as a result of a nuclear transformation, the process is referred to as the Szilard-Chalmers reaction.[10]

C. Radiolysis of Methane

The radiolysis of methane has been a subject of considerable study for many years. A review of this work prior to 1960 has been collected by both Swallow[6] and Chapiro.[11] Lind also includes a review in his book.[12] The effects of temperature, pressure, type of radiation and additive compounds have been established. The references at the end of this paper, in general, deal with all of these factors. As specific cases are cited, they will be individually designated.

G values for the production of hydrogen and higher hydrocarbons, up to C_5's have been tabulated. G values for methane destruction are also available. G values refer to the number of molecules of product formed or of substrate destroyed for every one hundred electron volts of energy absorbed. Ideally, this value should be independent of the type of radiation or of the rate of absorption by the system. Inspection of Refs. 6 and 11 will reveal that this is not the case.

The overall reactions depicting methane destruction at high conversions by radiation are:

$$2CH_4 = H_2 + C_2H_6 \qquad (6)$$

$$2CH_4 = 2H_2 + C_2H_4 \qquad (7)$$

These reactions are probably an oversimplification. The initial reactions in the series are given in reactions (2) and (3).

Radiolysis yields no pressure change. This is explained[12] by the formation of C_2H_4 initially having two free valences, as $-CH_2-CH_2-$. It is hypothesized that this double radical reacts rapidly to give a liquid-phase polymer. It may also react with hydrogen atoms and the other radicals formed under radiolysis.

Irradiations of methane at high conversions produces no unsaturates. Although, by freezing out a portion of the reactants while radiolysis is occurring,[13] or by low-pressure irradiations,[14] ethylene and acetylene have been observed and relative G values have been

inferred. At low conversions, that is less than 1% of the methane destroyed, ethylene and acetylene have been detected in relatively high concentrations.

Mechanisms have been proposed based on the mass spectra of the irradiated methane,[6] and, more recently, on more direct experimental evidence.[15,16] It is this series of reactions which leads to the radical and ion-molecule precursors of the stable products (see reactions (2) and (3)).

In the sections to follow, and in the discussion of the mechanisms involved, heats of reaction and heats of formation of proposed reaction sequences are given. These values are obtained from Field and Franklin[17] and Steacie.[18] They are also obtained from other publications concerned with the labeling of hydrocarbons. Such values are quoted to show which reactions are thermodynamically the most probable, and which will result in an excited decomposition product. Most of the experimental data are obtained with tritrium concentrations of one millicurie per cc. of sample volume. At this concentration, the complete mixture is being irradiated at a rate of 2000 Rads per hour, or 1.3×10^{16} e.v. per hour per gram of CH_4. This gaseous mixture is only slightly removed from thermal equilibrium for which most ΔH values are computed. Energies of activation of a few kcal. per mole may or may not be of consequence here. Additionally, the formation of products is governed by the random nature of the collisions of the reactants. Kandel[19] has stated that endothermicity of reaction is of little consideration in his study on the interactions of tritium and methane, but at 10^3 greater tritium to methane ratios than used here.

D. Kinetics of the Labeling Reaction

The kinetic evaluations of the labeling of hydrocarbons with tritium by the Wilzbach method has been the subject of recent investigations. Pratt and Wolfgang[20] and Wexler[21] explored the CH_4-T_2 system. Gant and Yang have examined a number of hydrocarbons and evaluated the rate expressions for the labeling with tritium. They studied the tritiation of ethane,[22] ethylene,[23] and propane.[24] Gant and Yang, as well as Pratt and Wolfgang, obtained results by the gas exposure method. Wexler induced his reactions in a high-pressure mass spectrometer and projected the results to the labeling of the methane system in the gas phase.

Each group of workers obtained an initial rate expression consisting of a sum of terms which explained the experimental results. Gant and Yang[22-24] analyzed their results in a two-term expression of the form:

$$L(X) = a + b(T_2) \qquad (8)$$

L(X) is the amount of labeled product formed per tritium decay. The (T_2) is the concentration of tritium in curies per bulb. The constant a is essentially a first-order rate constant, which relates to the rate of labeling directly as a result of tritium decay. In their terminology, this is the decay-induced labeling The constant b is the second-order constant, dependent on the square of the tritium concentration. This squared term gives the radiation-induced yield of the tritiated products.

Pratt and Wolfgang, in their investigation of the CH_4-T_2 system,[20] arrived at a three-term expression:

$$\frac{d(\text{prod})}{dt} = a(T_2) + b(T_2)^2 + c(T_2)^{3/2} \qquad (9)$$

Again, the constants a and b have the same significance as those in (8), although the absolute values are different. The additional

F. Effect of Other Additives

Ethylene has long been known to be an effective H atom scavenger. In addition to this, its ionization potential of 11.41 volts makes it an equally excellent inhibitor by virtue of charge exchange. Sieck and Johnson[32] observed that addition of low concentration of ethylene to methane under radiolysis decreased the G value for hydrogen formation, increased the G value of ethane and increased initial propane and butane production. It also increased polymer formation by a factor of 10 at 3.5 mol% concentration.

Addition of ethylene to the methane-tritium mixture should then clarify a portion of the reaction path, by providing an excellent menas for radical scavenging and charge exchange.

Pratt and Wolfgang[20] proposed a radiation-induced labeling mechanism based on excitation of the tritium molecule, fragmentation of it, and final stabilization of the tritium in a product by ion-molecule and radical reactions. On the other hand, Wexler[21] assumed ion attack on the tritium as T_2 followed by a reaction sequence to product. Addition of hydrogen to the system was proposed to choose between the two alternatives. It was initially assumed that Wexler's scheme was correct since the number of reactive species formed in the methane is many orders of magnitude larger than those which would be formed from tritium. Hydrogen, then, in small amounts, would not interfere with the decay labeling portion of the reaction, but should eliminate that portion induced by the radiation, if the assumption is correct.

It is the purpose of the present research to reinvestigate the tritium-methane labeling system to clarify the mechanism and to examine carefully the effects of various additives. The general method used was to expose gas mixtures of CH_4 and T_2, with and without additives, for varying times, and then to separate and count the labeled products by techniques involving gas chromatography and proportional counting.

II. EXPERIMENTAL

A. Reagents

The tritium was purchased in five curie ampoules of five cc. volume from the Oak Ridge National Laboratory. It was specified that the tritium be packaged just prior to shipment to reduce contamination. Analysis of the tritium revealed the presence of HT and CH_3T; no labeled ethane was seen. Of the six ampoules used the maximum amount of each was 0.1% methane-T and 1.0% HT. Since the amount of contamination was not large enough to mask product formation, no further purification was attempted.

The methane was obtained in ultra-high purity from Pacific Oxygen Company, distilled, and re-bottled by Aldo F. Sciamanna. Mass spectrographic analysis of the methane revealed the following purity limits: > 99.993 mol% CH_4, < 0.005 mol% C_2H_6, < 0.0015 mol% C_2H_4, and < 0.001 mol% N_2+CO_2.

Ethylene was obtained from Phillips Petroleum Company Special Products Division as Research Grade, guaranteed to be 99.99% pure.

Xenon was obtained from the Linde Company Special Products Division as Research Grade in one liter pyrex flasks.

Hydrogen was obtained by passing reagent grade gas through a heated palladium filter and then collecting the gas in a pyrex bulb prior to addition to the reaction flasks.

Helium for the gas chromatography unit was > 99% pure and passed through a six-foot silica gel column at room temperature prior to sample addition to the stream.

Propane, c.p. grade, was used as the quenching gas in the proportional counter. It was obtained from the Matheson Company.

All stopcocks were lubricated with Apiezon N grease.

B. Reaction Bulbs

The reaction vessels were made of pyrex glass and designed to have a volume of 200 ± 5 cc. They were spherical except for a 10-mm by 6-mm closed tube at the bottom which was opened to facilitate cleaning. They were constructed with a 2-mm capillary extending from the top into the center of the bulb to sample from the center of the mixture. The sampling tube also minimized small surface-to-volume effects from the constriction at the top of the bulb, as well as reaction of the gases with the stopcock grease. A calibrated volume was contained between two 2-mm stopcocks at the end of this tube. The actual sample volume varied from 0.30 to 0.45 cc. Calibration of this volume was done by weighing mercury trapped in it. Bulb volumes were obtained by weighing after completely filling them with water.

The bulbs for the measurements in which the surface was increased with respect to the gas volume were constructed with sampling volumes identical to those above. For a S/V ratio of 2:1, a tube of 2-cm diameter was made, having a total volume of 50 cc. For a ratio of 17:1, a bulb similar to those described above, but without the capillary tube, was filled with 6-mm glass beads. The gas space was 75 cc and determined by helium expansion from known volumes into the prepared vessel.

C. Preparation of Mixtures

The tritium was attached to and measured by a gas pipette. This is shown in Fig. 1.[33] The pipette was designed to minimize air leaks into the tritium and lessen contact with the stopcock grease. It also provides for excellent measurement and safe handling of the tritium. The pipette is a miniature Toepler pump containing a calibrated volume and a manometer tube for simultaneous pressure-volume measurements. Prior to the destruction of the break seal and after

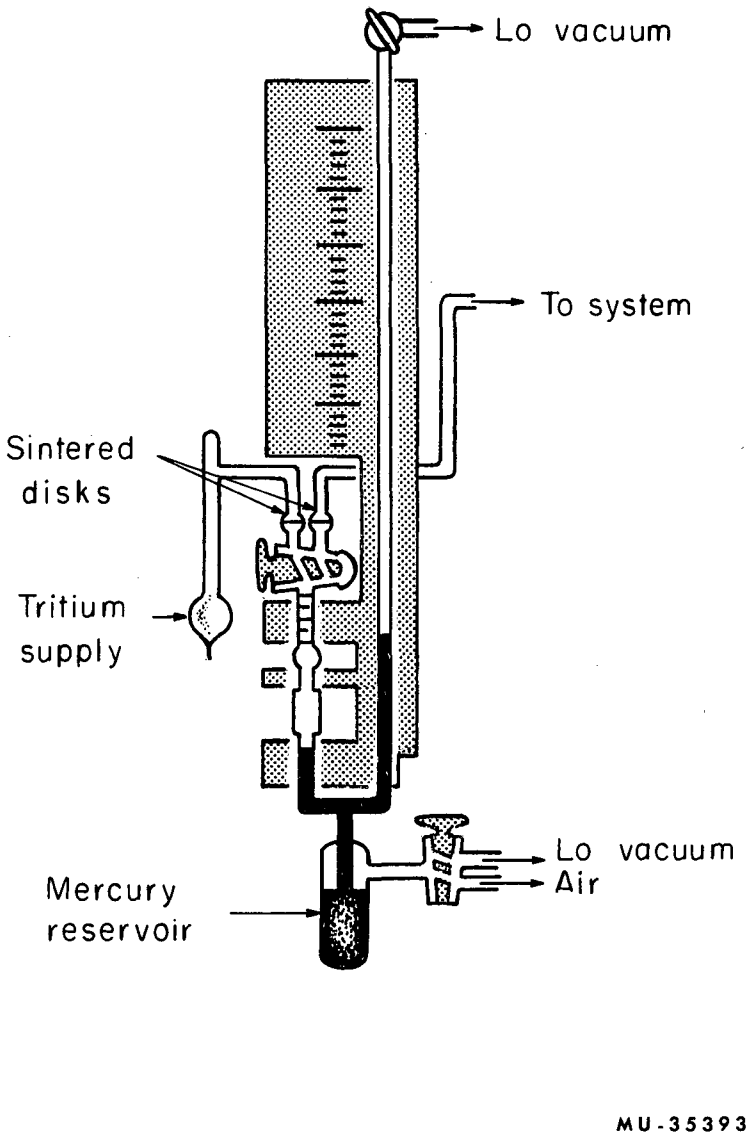

Fig. 1. Tritium metering pipette.

attaching the tritium ampoule to the pipette, the mercury was lowered into the reservoir. The pipette was then evacuated for a minimum of eighteen hours.

The mercury was then raised and the seal on the ampoule broken. Tritium was withdrawn in the desired amount by lowering the mercury and taking simultaneous pressure and volume measurements. One mm-cc of tritium at 24°C contains 3.148 mC.

The sintered discs above the three-way stopcock prevent accidental loss of mercury into the ampoule or into the vacuum system. After the desired amount of tritium had been measured, the ampoule may be sealed off by placing mercury between the stopcock and the sintered disc. This prevented unnecessary contact between the tritium and the stopcock grease as well as eliminated possible air leaks.

Addition of tritium to the reaction flasks takes place through a series of volumes known by the gas expansion method. The complete preparatory system is shown in Fig. 2.[33] A liquid nitrogen Dewar flask was placed around the U-tube between the pipette and the manifold to trap mercury vapors which may come from the pipette. Expansion of tritium was from the pipette into the known volume of the manifold, bulbs, and U-tube. After a time for equilibration, the bulbs were closed off, the Dewar removed, and the excess tritium was pumped through a copper oxide furnace kept at 400°C. Conversion of the tritium to the oxide took place and it was trapped in the liquid nitrogen trap preceding the fore pump.

Prior to the initiation of an experimental series, the bulbs were pumped on, five at a time, for a minimum of eighteen hours. They were allowed to stand, evacuated, for a period of from one to three days before filling with reactants. If, at the time of opening immediately before filling, a pressure was noted on the thermocouple gauge, the bulb was discarded and another substituted in its place.

After the tritium had been expanded into the bulb, additives were then expanded from the manifold of 33 cc volume at relatively high pressures. This was done to lessen the possibility of back diffusion of the tritium. (All gases were added to the bulbs by direct attachment to the manifold. The gas inlet in Fig. 2 was used only for

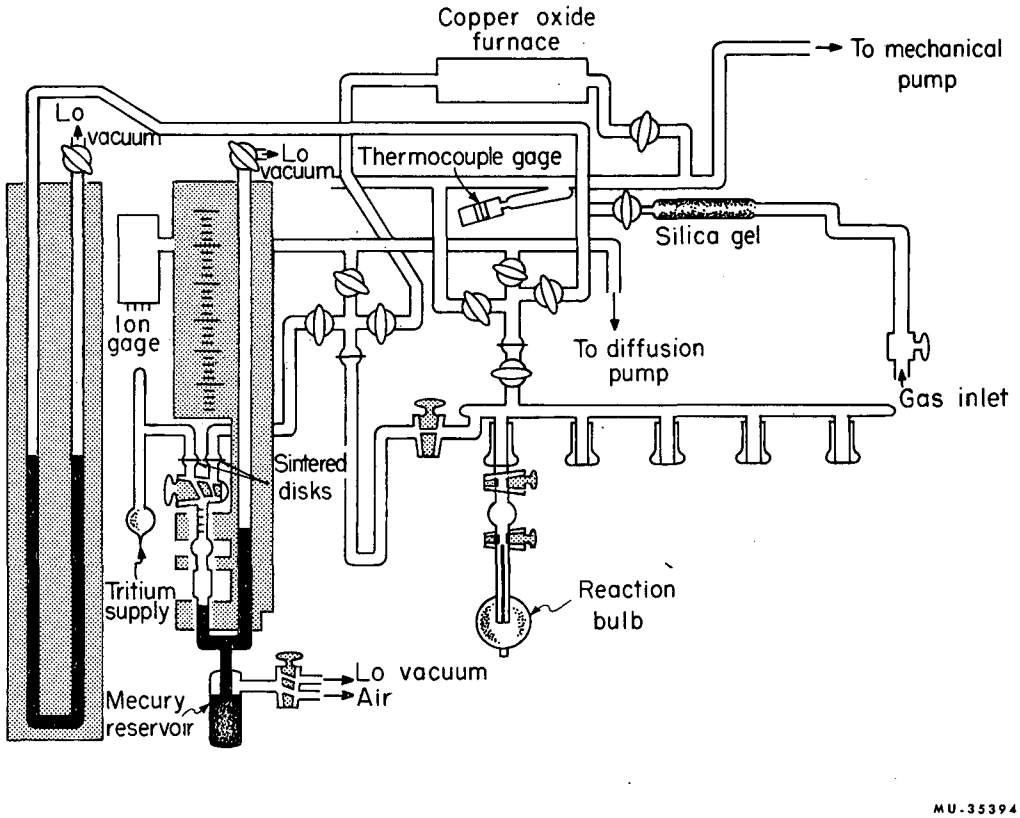

Fig. 2. Vacuum system for sample preparation.

on the Toepler pump are known by calibration with mercury. The remaining volume is known by gas expansion. The smaller volumes are 4.09 and 4.52 cc, while the larger one, described above and including those two, is 55.5 cc. In this manner, a sample of appropriate activity may be obtained by one or more dilutions.

The sample, having been adequately diluted, is then forced into the by-pass unit, and by simultaneous turning of two three-way stopcocks, swept out by the helium stream into the gas chromatography-internal proportional counting system. The schematic of this is shown in Fig. 4. With slight modifications, it is essentially that described by Rowland, Lee, and White[34] and by Wolfgang and MacKay.[35] The chromatograph is a Perkin-Elmer Model 154D Vapor Fractometer with a thermal conductivity detector. Helium at a flow rate of 50 cc/min is used as the carrier gas.

The electronic arrangement is also shown in Fig. 4. The thermal conductivity response from the chromatograph is displayed on one pen of the dual pen recorder at a full scale response of one millivolt. The proportional counter response is amplified by a solid-state amplifier and the signal is fed to scalers No. 1 and No. 2. Scaler No. 1 is left on at all times and drives the ratemeter as well as the pipper. The pipper is a print-out register which is activated every twelve seconds to correspond to the marking on the recorder chart paper. The ratemeter response is shown by the other pen of the dual pen recorder at a sensitivity of ten millivolts. The response of the ratemeter is non-linear, and it is used only as an indication that activity is beginning to pass through the counter. Activity peak integrations were not attempted, but, rather, Scaler No. 2 is used to determine the actual number of counts in an activity peak. It is turned on at the beginning of a peak as indicated by the recorder response to the ratemeter and the characteristics of the separatory column, and turned off when the ratemeter response returns to zero. The printing register gives a check on this value.

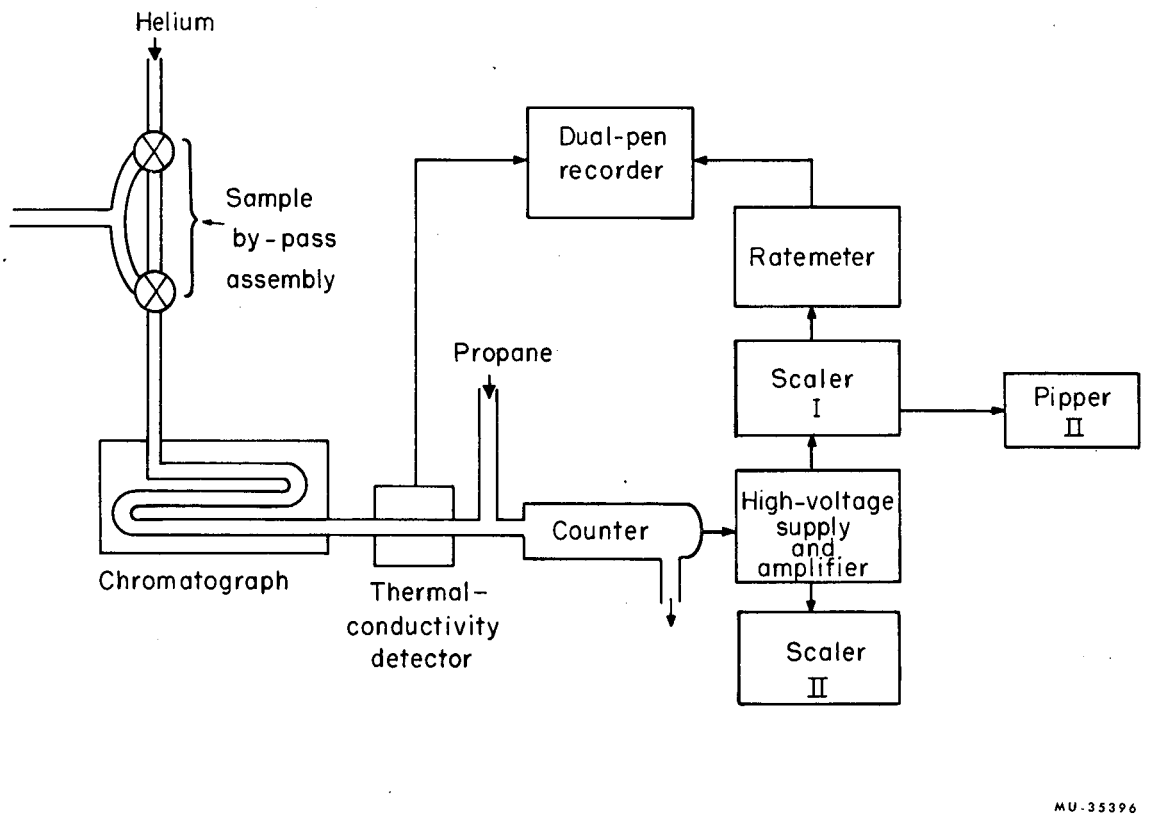

Fig. 4. Schematic of the gas chromatography and proportional counter part of the analytical system.

The proportional counting tube is a modification of one previously described[36] and is shown in Fig. 5.

In order to use the counter in the proportional region, a quenching gas must be added. Either methane or propane has proved satisfactory in the past. In this case, propane was chosen. It was reported that a propane-to-helium ratio of 1.8:1 was the most desirable.[37] Ratios between 1.5 and 2.0 were tested relative to plateau characteristics using an external Co^{60} source as a standard. Consistent with those values states, the ratio giving a stable plateau for minor gas flow fluctuations was 1.8:1. The plateau extended from 2.9 kv to 4.0 kv, and over a large range of discriminator settings. Normally the voltage used was 3.2 kv at a total gas flow of 140 cc/min. Turbulence did not cause reduction in observed counts until a flow of 250 cc/min was reached.

The flow of both helium and propane was regulated by flowmeters on each supply line and a soap-film bubble meter at the exit of the counting tube. It was felt that this arrangement allowed the rate of flow through the counter to be effectively controlled to ±3%. Since there is a definite pressure necessary to have flow through the chromatography column, this value was set and assumed to remain constant throughout a group of analyses. Flow measurements were taken before and after each activity peak and at intervals between. Appropriate corrections were made in the propane flow. The propane system had no ballast tank and the base pressure fluctuated for about three hours until a stable value was attained. During this period, continual adjustments were necessary, and were made accordingly. Adequate mixing of the two gas streams was accomplished by passing the propane into a bulb of about 10 cc volume in the center of which was a medium grade sintered disc. The effluent flow of the chromatograph was directed on the surface of the disc. Since the propane-to-helium flow ratio was 1.8:1, excellent mixing was obtained in this manner.

The effect of addition of large amounts of other hydrocarbons to the flowing gas mixture was also investigated. In was felt that

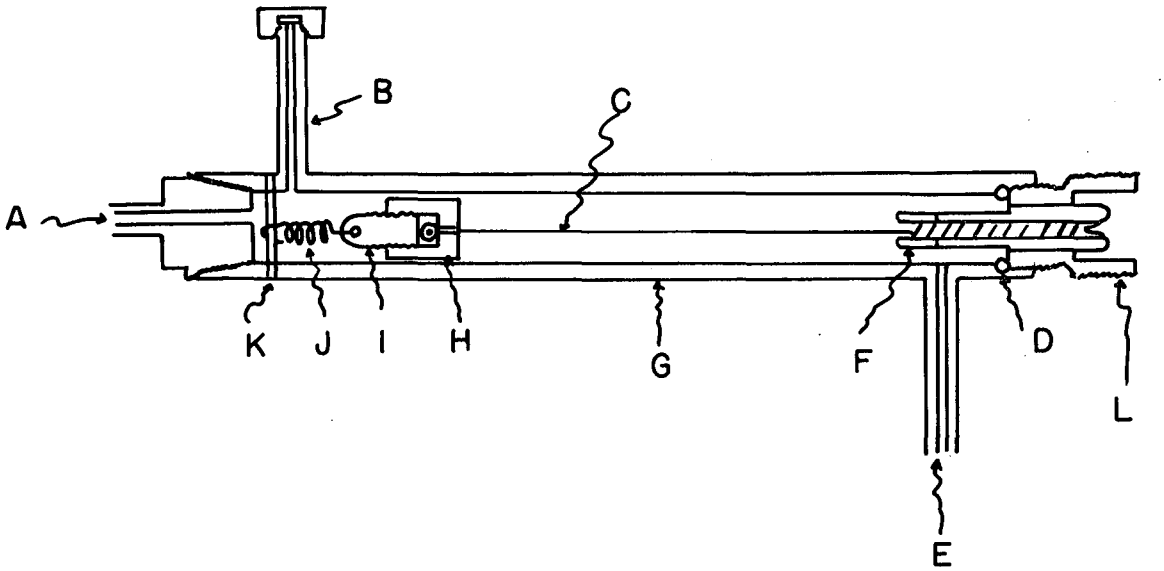

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Fig. 5. Cross section of the proportional counter
A = Connection to chromatography unit (T 7/15 inner taper)
B = Inlet for auxiliary counting gas (not used in this work)
C = 2-mil stainless steel wire soldered to receptical at one end and to washer at other
D = Teflon gasket
E = Gas outlet
F = Teflon sleeve
G = Brass counter tube
H = Grooved teflon
I = Nylon
J = Weak spring
K = Pin
L = UG-496/U recepticle (modified).

reduction in observed activity might happen in view of the variation in the electron affinities of other compounds added to the propane-helium mixture. With the Co^{60} source in place, 1 cc of methane at STP was added. During its passage, no reduction in counting rate was observed. Methane was chosen since it is the only hydrocarbon present in large amounts in the samples. In actual analyses, the largest amount of methane that passed through the counter was 100 mm-cc. For methane, no corrections were necessary. The other possible source of quenching was air, which could be introduced on sample injection. Addition of 1 cc of air to the column reduced the observed counts a maximum of 25% during its passage. Since air and methane are separated by only 0.5 min on the silica gel column, this could be a source of error. However, use of a closed system which could be evacuated solved the problem. Actually, air was not seen on the thermal conductivity tracing from this method of sampling. If an air peak was observed, it was assumed to come from contamination of the reaction mixture, and this bulb was then discarded.

No specific counter efficiency or active volume was obtained, but, rather a counter multiplication factor. This factor was found by analyzing known pressure-volume combinations of the He-T_2 mixture prepared as described earlier. The factor was determined by dividing the actual number of disintegrations per minute known to be present in the mixture by the counts observed. This was done at a flow rate identical to that used for analysis of the unknowns. In this manner, the observed counts were converted directly to disintegrations per minute. The HeT_2 analysis was done at the end of the day on which samples were taken from the reaction mixtures. This factor was further substantiated by dilution and actual analysis of the tritium content of two or three of the bulbs containing the lowest tritium concentration. In addition, the external Co^{60} standard was checked frequently during the day. As an example of the constancy of the counter multiplication factor, a value of 7.90 ± 0.12 disintegrations per minute per observed count was obtained for eight analyses of the He-T_2 mixture

during one experimental series. The total gas flow was always maintained at 140 cc/min, and the value of the factor was independent of the column being used.

The sample dilutions previously described were made to give 10,000 to 50,000 counts in the methane peak, preferrably toward the lower figure. This value was high enough to maintain reasonable counting statistics (less than 1% error), but low enough that coincidence losses were negligible.

In addition, no correction was made for observed activity in peaks with different column retention times. The average residence time of a molecule in the counter remained constant regardless of the time of emergence of the compound. The time of elution of a component after injection, t_e, had no effect on the amount of activity recorded. The He-T_2 mixture was examined on both the silica gel column (t_e=2 min) and the activated alumina column (t_e=28 min). In six samples so separated, the average difference was ±4%. This also gave an indication that all of the T_2 or HT activity was being counted. This was a point of initial concern since treated adsorbent columns of the alumina type will separate ortho and para isomers of the isotopic hydrogen mixtures.[38]

Actual component separations were made on three columns all operated at a helium flow of 50 cc per minute. All were made of 1/4-in. copper tubing. For the methane-ethane separation, a seven-foot silica gel, 60/70 mesh, column operated at 0° C was used. Excellent separation of methane and ethane was obtained, but more important, the tritium and methane midpeak-to-midpeak separation was three minutes. Figure 6 gives an example of this.

HT and T_2 were separated on a twelve-foot column of activated alumina, 110/120 mesh, uncoated and untreated, operated at 77°K. This is shown in Fig. 7.

Hydrocarbons up to C_5 were adequately separated at room temperature on a fifteen-foot column of β,β'-oxydipropionitrile coated 14% on activated alumina. Four standard hydrocarbon mixtures were

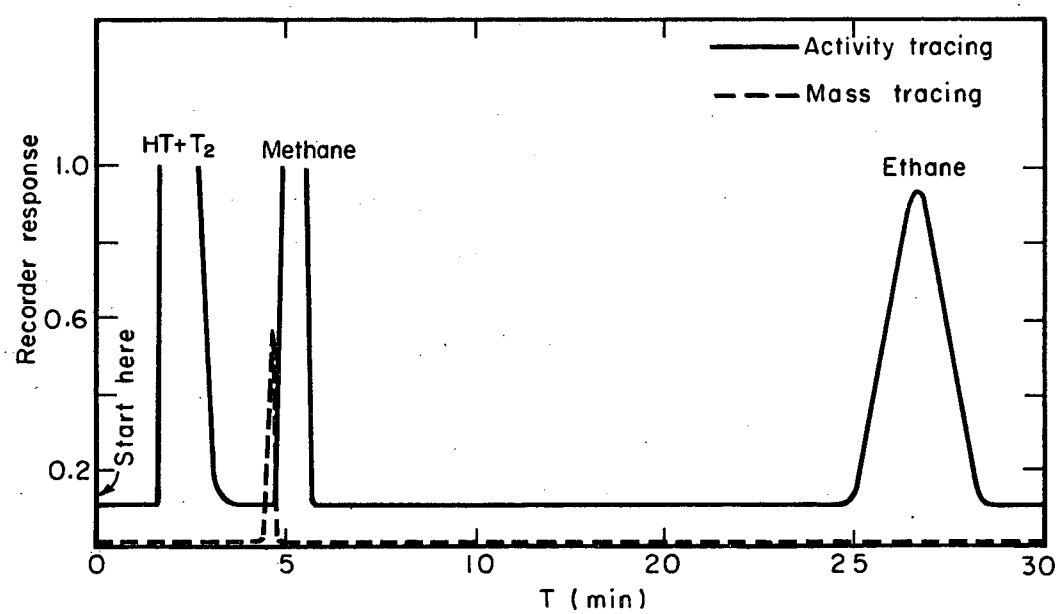

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Fig. 6. The separation of methane and ethane on Silica gel at 0° C.

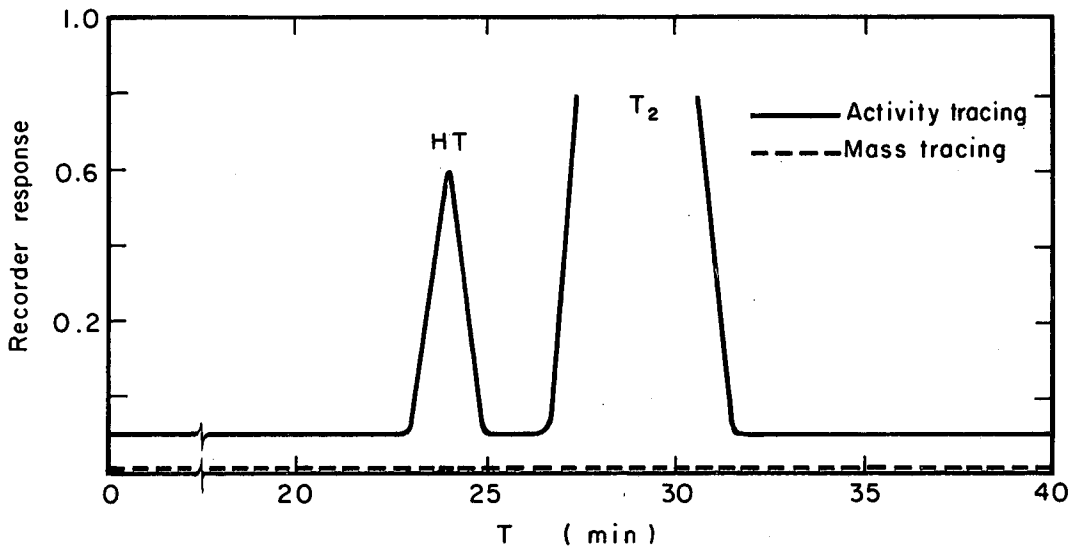

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Fig. 7. Separation of HT and T_2 on activated alumina at 77° K.

purchased from Phillips Petroleum Company and analyzed on this column. The composite results are shown in Fig. 8. Figure 9 is a plot of the reduced retention time, t_r, of the various hydrocarbons versus peak width at half-height. t_r is the retention time of the specific compound measured from the time of emergence of air which passes through the column unretarded. An efficient column will give a value ≤ 0.1 for peak-width at half-height divided by t_r. The slope of the line in Fig. 9 is 0.038. Figure 10 shows an analysis for labeled hydrocarbons up to C_4 for this column. Comparison with values obtained from Figs. 8 and 9 reveals that only saturated hydrocarbons are labeled; no labeled unsaturates are seen. This analysis is the last sample taken from the bulb, and is done only once.

As seen in Figs. 6 and 10, the only peak detected by the thermal conductivity cell is that of methane.

The sample for mass spectrographic analysis was prepared by vacuum distillation of the contents of six reaction bulbs into a trap at approximately 63°K, the freezing point of liquid nitrogen. The trap was surrounded with liquid nitrogen, and a lid sealed on the Dewar flask. The nitrogen was then pumped on at rapid speed to form the solid-liquid slurry and lower the temperature to the value above. Virtually 100% of each sample was collected in this way.

To ascertain whether the method for cleaning the reaction bulbs was adequate to remove hydrocarbons which may have been adsorbed on the walls, a reaction mixture was prepared in a bulb that had been used five times. It contained a tritium concentration of one millicurie per cc and 650 mm of helium. No observable increase in CH_3T above that present as contaminant in the tritium occurred. No tritiated ethane was formed.

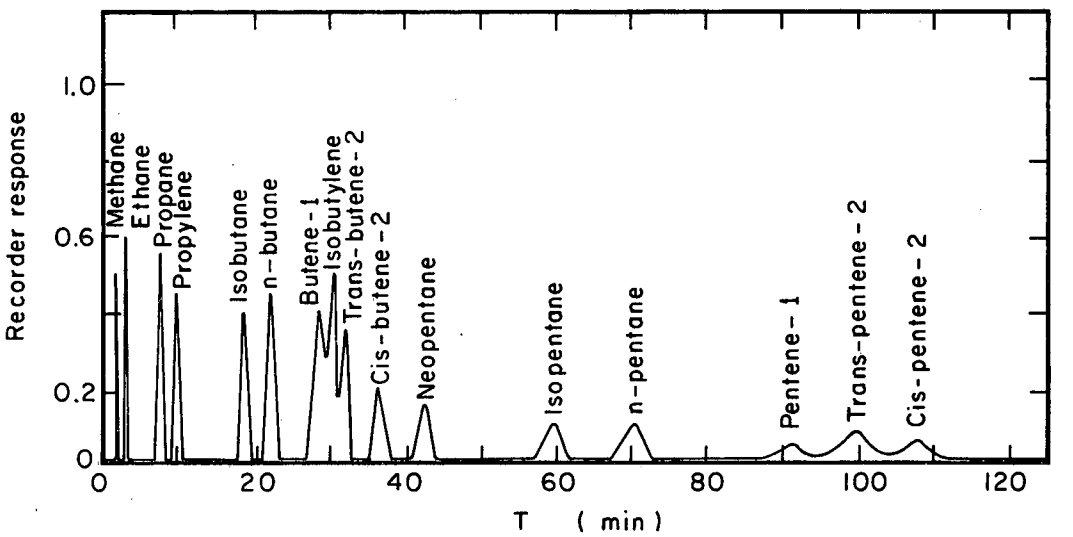

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Fig. 8. Separation of hydrocarbons on column containing β,β'-oxydipropionitrile coated 14% on activated alumina at room temperature.

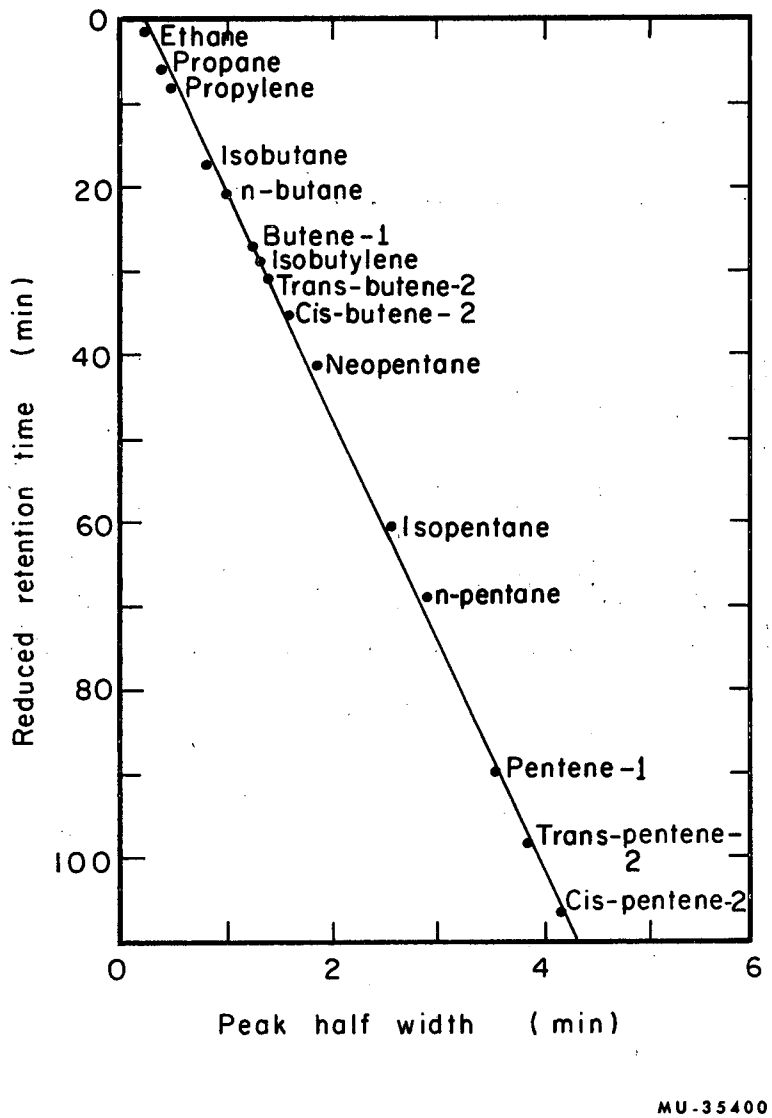
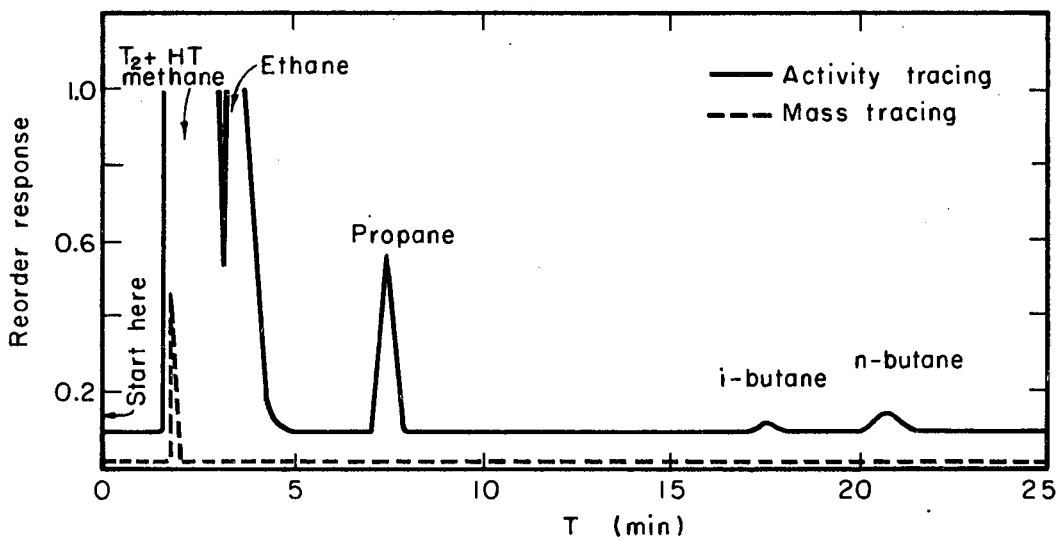


Fig. 9. Plot of peak half width vs reduced retention time for the column containing β,β'-oxydipropionitrile coated 14% on activated alumina operated at room temperature.



MU-35401

Fig. 10. Analysis of labeled hydrocarbons on column of 14% β,β'-oxydipropionitrile coated on activated alumina at room temperature.

E. Energy Absorption by Methane

There are two methods available to obtain the amount of energy absorbed by the methane. The first is that of Dorfman.[30] He states that if the product of the radius of the spherical container and the density of the gas is 0.08 mg/cm^2, energy absorption is 50% for the tritium beta. For this series, the radius is 3.6 cm, and the gas density is 0.61 mg/cm^3. The result is 27.5 times greater than the critical half absorption value.

The other method is that of Mueller.[3] The formula to calculate the percent energy absorption of the tritium beta particle for various gases is:

$$F = 1 - 1.26/\alpha$$
$$\text{and} \qquad \alpha = \mu d \tag{13}$$

The result, F, is the total amount of energy absorbed by a gas uniformly mixed with tritium in a spherical container. The value of F is the sum of the energy directly absorbed plus the energy absorbed if the beta particle is scattered back by the container walls. The constant, α, is the product of the linear absorption coefficient, μ, and the diameter of the spherical container, d. The formula for the calculation of F given in Eq. (13) is valid only for large values of α. At 650 mm, $\mu_{CH_4} = 7.2\ cm^{-1}$ and d=7.2 cm, for this specific reaction vessel. Then, α=51.8. This is large enough to use the approximation above. The result is 98% absorption of the beta particle energy. Thus, from both methods, assumption of complete energy absorption is reasonable.

Other additives, specifically hydrogen and ethylene, may decrease this slightly, but their concentrations never exceed 2%, so the effect is minimal.

The only gas which was added in greater amount than 2% was xenon. The linear absorption coefficient at 760 mm for xenon is 33.4 cm^{-1}, while that for methane at the same pressure is 8.4 cm^{-1}.[3] Corrections for energy absorption in this system are not necessary.

F. Decomposition Limits

In order to obtain meaningful results based on initial reaction kinetics, the limit of decomposotion of methane was set at 0.5%. However, this limit may be too high, since, as the concentration of labeled products increases, the methylene insertion reaction

$$(CH_2)^* + R - T = R - CH_2 - T \qquad (14)$$

builds up labeled hydrocarbons of higher molecular weight. This reaction begins to cover the initial products complicating the analysis. For an average tritium beta energy of 5.69 keV, assuming complete energy absorption, and $G(-CH_4)$ equals 9.6,[15] this limit is reached at 9.8×10^4 minutes for a concentration unit of one millicurie per cc. Above this value, the concentration of labeled ethane remains essentially constant. No doubt, this is the result of the formation of higher labeled products by reaction (14).

III. RESULTS

A. Discussion of Errors

The errors in volume assignments calibrated by weighing with mercury, such as the tritium pipette, the volumes on the Toepler pump in the analytical system, and the volumes on the reaction bulbs, are assumed negligible. Equally so are the ones assigned to the reaction bulbs themselves and found by weighing with water.

Other volumes found by the gas expansion method from bulbs calibrated as above are known to be ±3%. Helium was used as the expansion gas to minimize corrections for its deviation from ideality. Errors in the volume assignments in the preparatory system are cancelled by the preparation of the He-T_2 mixture for each series of samples. These errors are also compensated for by analysis of the actual amount of tritium present in two or three of the bulbs.

Counting errors are less than 1%. The statistics are intrinsically compensated for by the choice of peak activity. Counter background is of the order of 100 to 200 counts per minute. Correction

to a peak of long duration such as ethane would be 1% or less. The background was subtracted from all values obtained.

Errors in the flow systems controlling the helium and propane rates were ±3%, or less, since the rate was checked before and after each activity peak, and as often as possible between peaks.

The largest source of error is in the dilution of the samples to produce peak activities in the range previously specified. Obviously, those samples containing the lower tritium concentrations have the best confidence limits, cumulatively 3 to 4%. It is for this reason that much of the work with additives was done at tritium concentration of 1 mC/cc. The mixtures containing larger amounts, specifically 2 mC/cc and 4 mC/cc, have the highest errors, 8 to 10%. This is partly because multiple expansions were necessary to reduce the amount of activity in the methane peak to the desired level and partly because decomposition of the methane may have been great enough to convert initial products to higher hydrocarbons.

As successive samples were taken, an increase in observed activity of about 6 to 10% was anticipated over the previous result. Addition of this to the above results gives the error in concentration of 0.5 and 1.0 mC/cc as 10 to 15% and that for the 2.0 and 4.0 mC/cc samples as 20 to 30%. This is the absolute error that would be expected, and is encountered as each sample is taken.

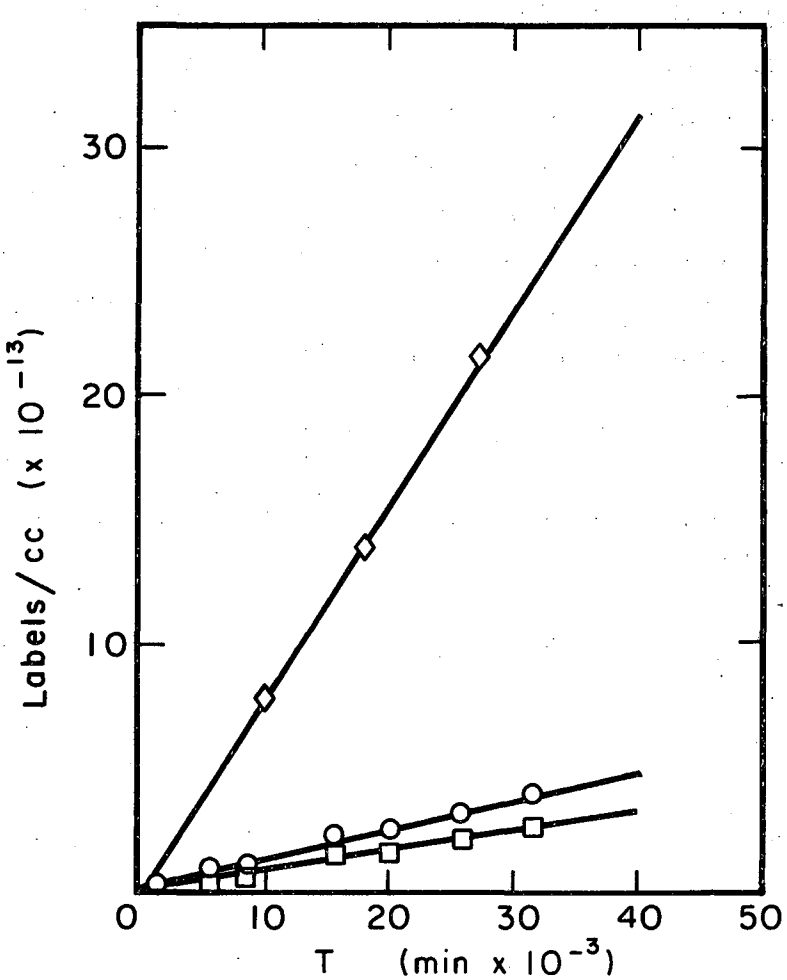
B. General

To establish the rate of production of labeled methane and ethane as a function of time, tritium in concentrations of 0.5, 1.0, 2.0, and 4.0 mC/cc were added to methane. At these tritium concentrations, the rate of production of both methane and ethane decreased as a function of time. This is observed in all samples containing no additives, as well as those containing xenon. Samples containing xenon showed an increase in product formation for concentrations of xenon up to 30 mol%, and then a decrease at higher concentrations.

Addition of ethylene caused a marked decrease in the rate. When hydrogen was added to the mixture, the rate decreased also, but not so greatly as when ethylene was added. Increasing the surface-to-volume ratio from 2:1 to 17:1 resulted in a decrease in the rate of production of tagged ethane and an increase in the labeled methane formed. In these systems, xenon exhibited a supressing effect. Finally, the effect of varying the pressure of the methane gave no marked results. These experimental results are shown in Figs. 11-40. Total hydrocarbon concentrations were evaluated at the completion of an experimental series and are given in Table I.

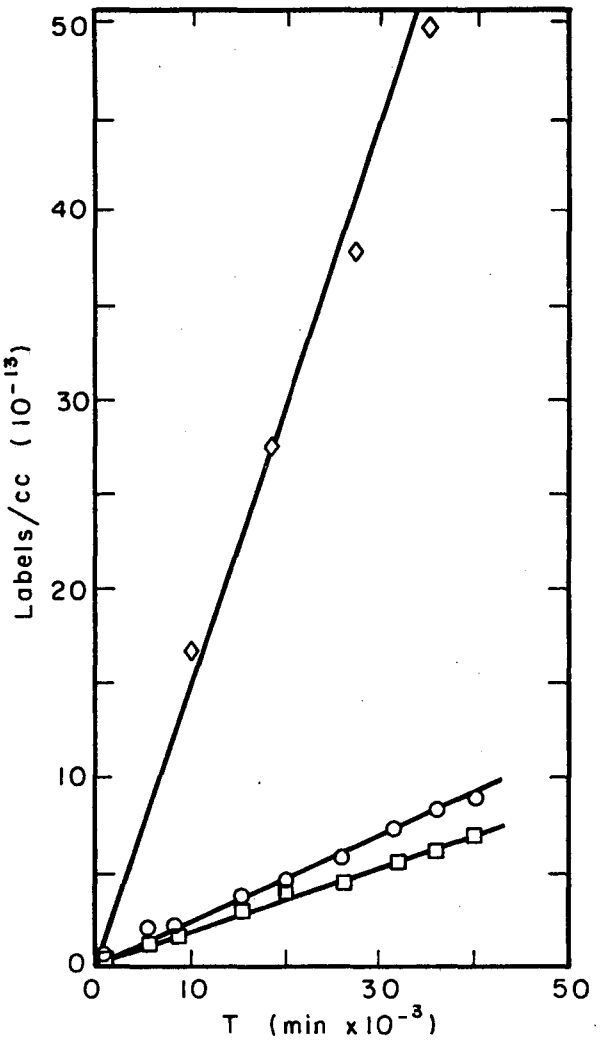
Table I. Total hydrocarbon analysis. Total activity observed is normalized to C_2H_6(labeled)=1.00 with no additives at a tritium concentration of 1 mC/cc.

Additive and T_2 conc. in mC/cc	CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}
None 0.5 mC/cc	0.28	0.52	0.08	0.01	0.02
None 1.0 mC/cc	0.55	1.00	0.14	0.04	0.06
None 2.0 mC/cc	1.11	1.84	0.30	0.07	0.11
None 4.0 mC/cc	2.30	3.56	0.64	0.17	0.25
15 mol% Xe 1.0 mC/cc	0.64	1.14	0.19	0.05	0.06
2 mol% H_2 1.0 mC/cc	0.16	0.12	0.02	<0.01	0.01
2 mol% C_2H_4 1.0 mC/cc	0.08	<0.01	<0.01	~0	<0.01
None, S/V=2:1 1.0 mC/cc	0.49	1.08	0.21	0.04	0.04



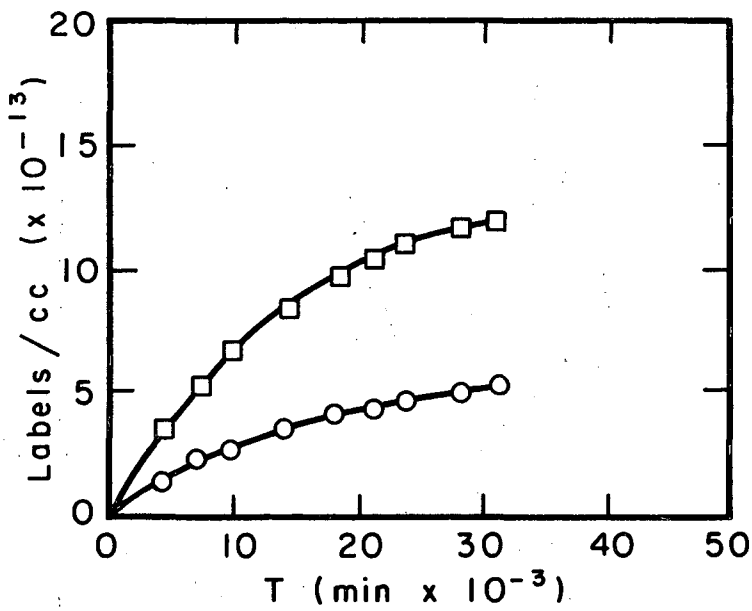
MU-35402

Fig. 11. Incorporation of tritium into labeled methane, ethane, and HT as a function of time. Tritium concentration is 1 mC/cc. The additive is 2 mol% H_2. The total pressure is 650 mm. ○ Methane. □ Ethane. ◇ HT.



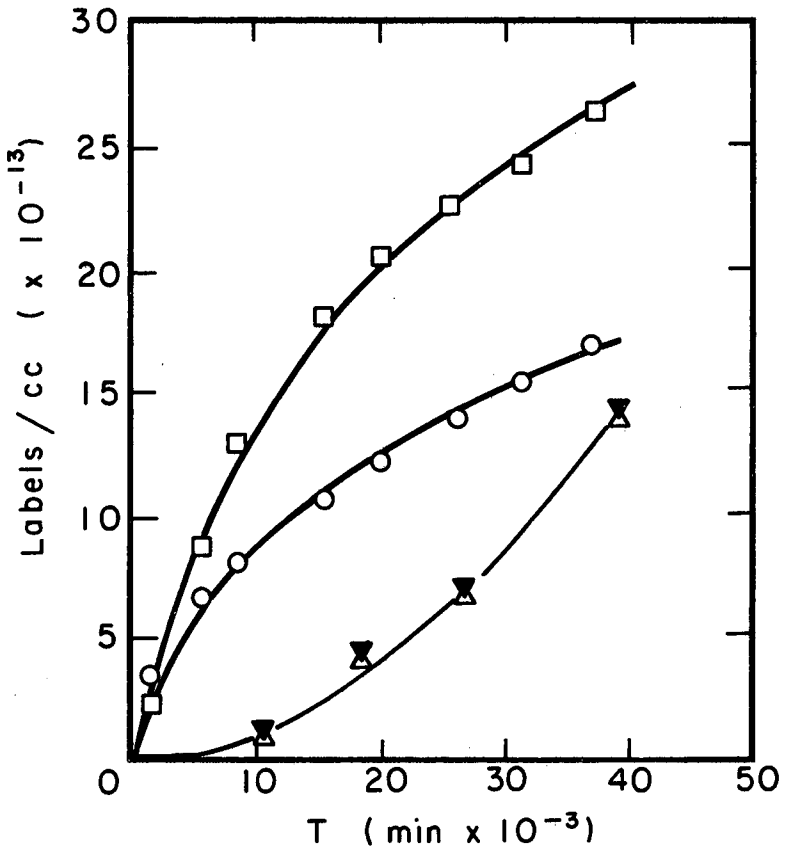
MU-35403

Fig. 12. Incorporation of tritium into labeled methane, ethane, and HT as a function of time. Tritium concentration is 2 mC/cc. The additive is 2 mol% H_2. The total pressure is 650 mm. ○ Methane. □ Ethane. ◇ HT.



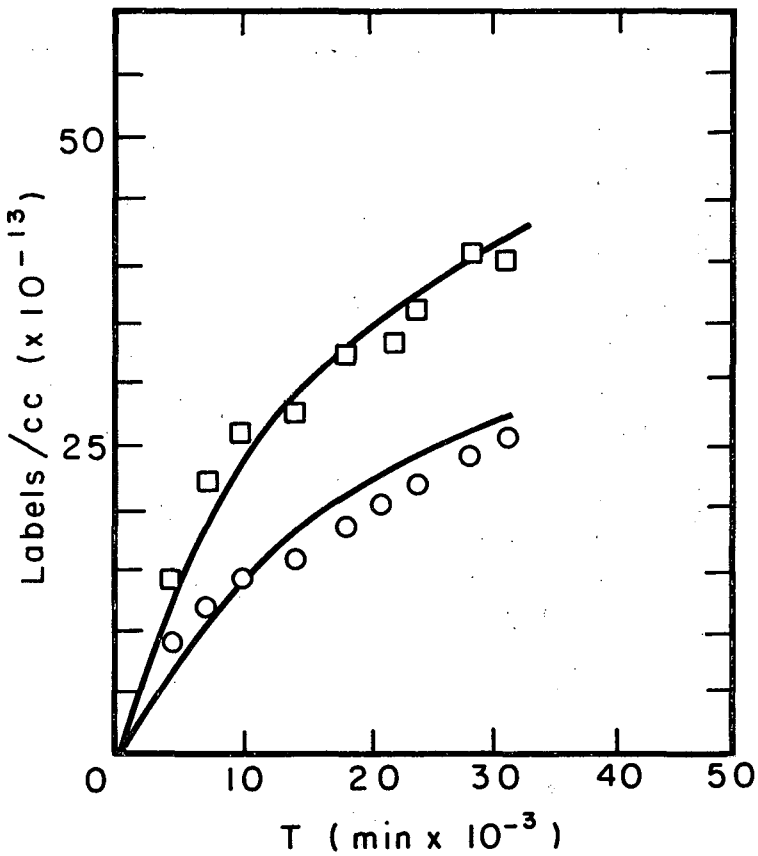
MU-35404

Fig. 13. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 0.5 mC/cc, with no additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



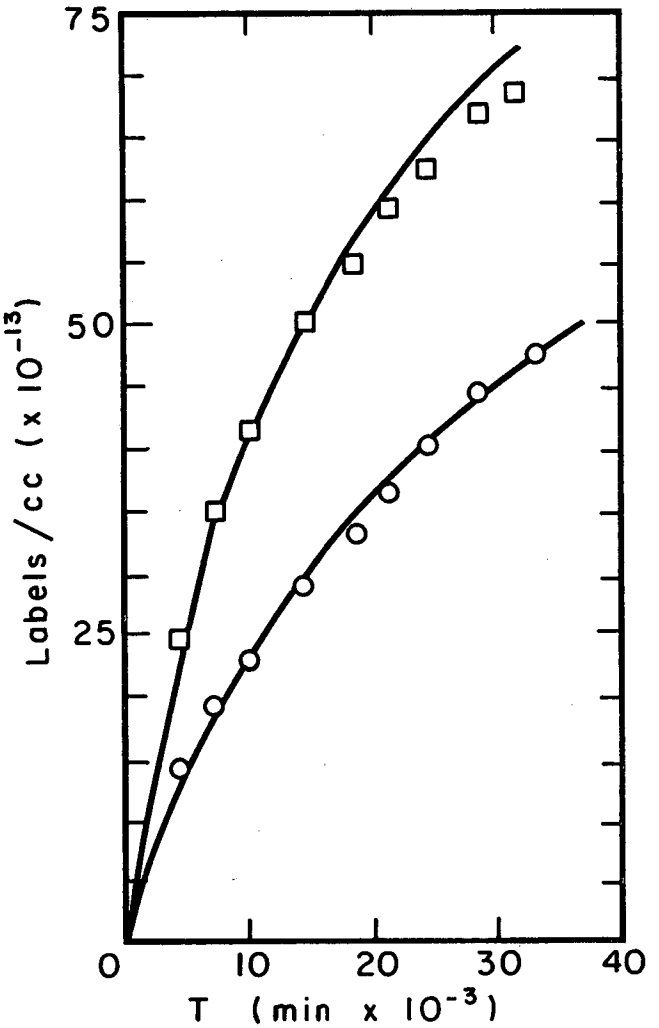
MU-35461

Fig. 14. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, with no additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



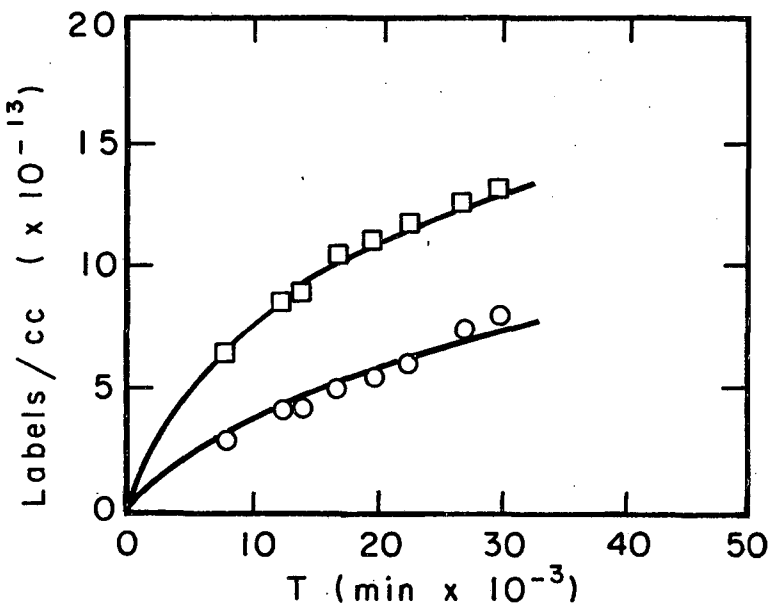
MU-35405

Fig. 15. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 2 mC/cc, with no additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



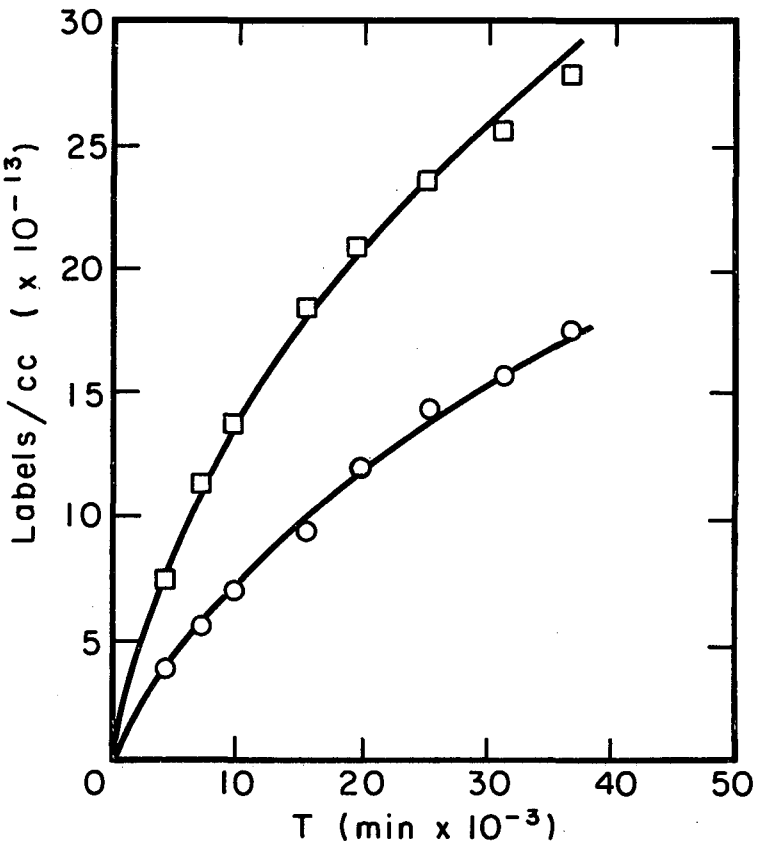
MU-35406

Fig. 16. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 4 mC/cc, with no additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



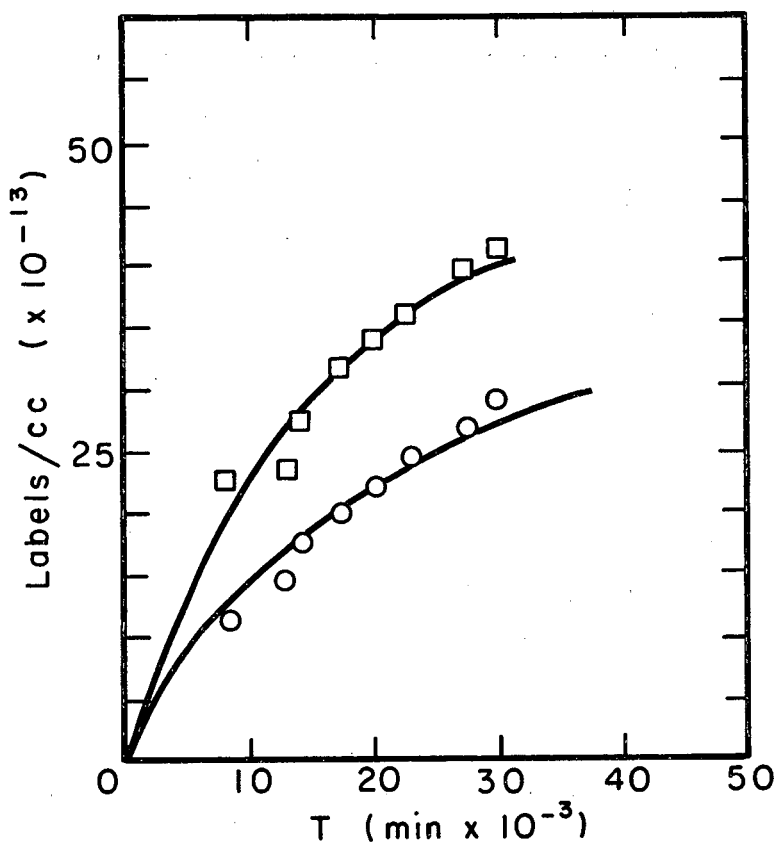
MU-35407

Fig. 17. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 0.5 mC/cc, 5 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



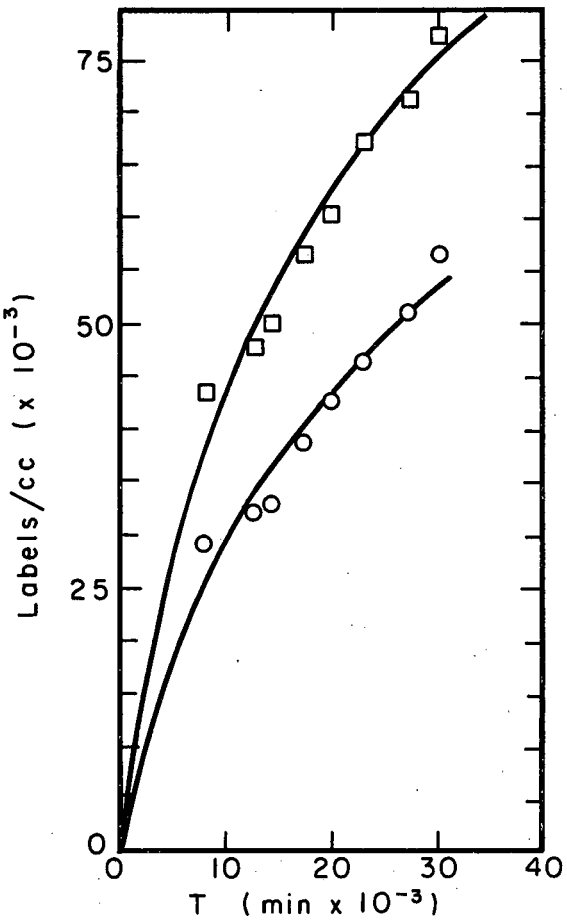
MU-35408

Fig. 18. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 5 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



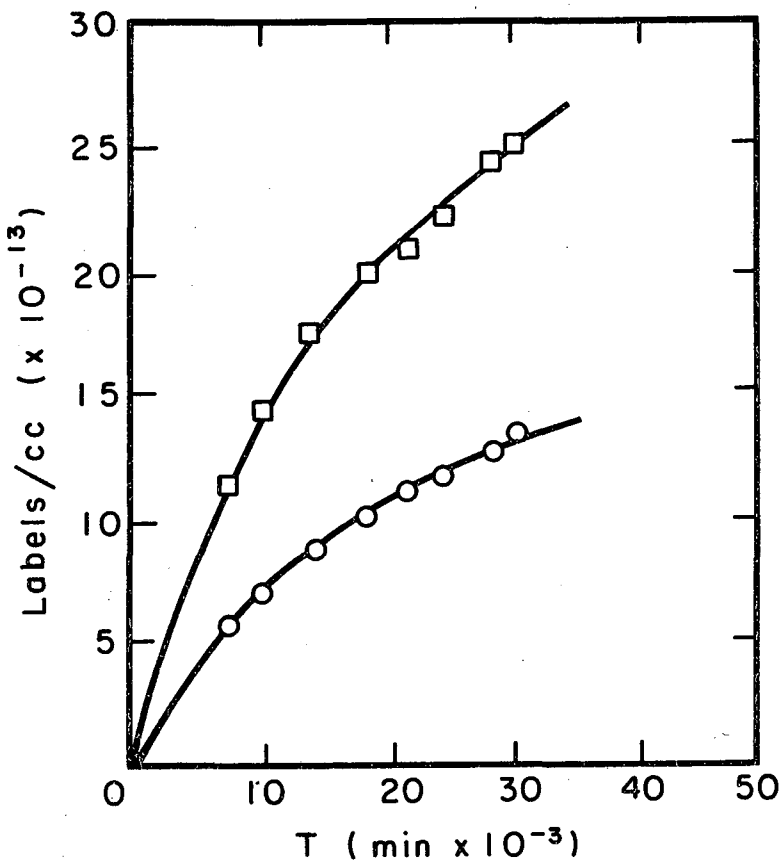
MU-35409

Fig. 19. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 2 mC/cc, 5 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



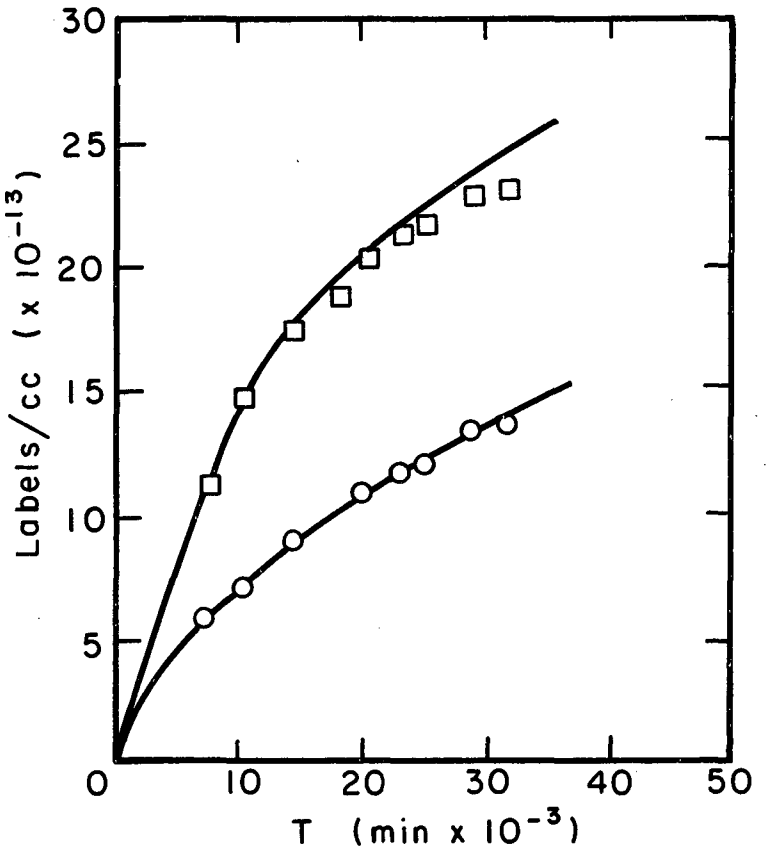
MU-35410

Fig. 20. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 4 mC/cc, 5 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



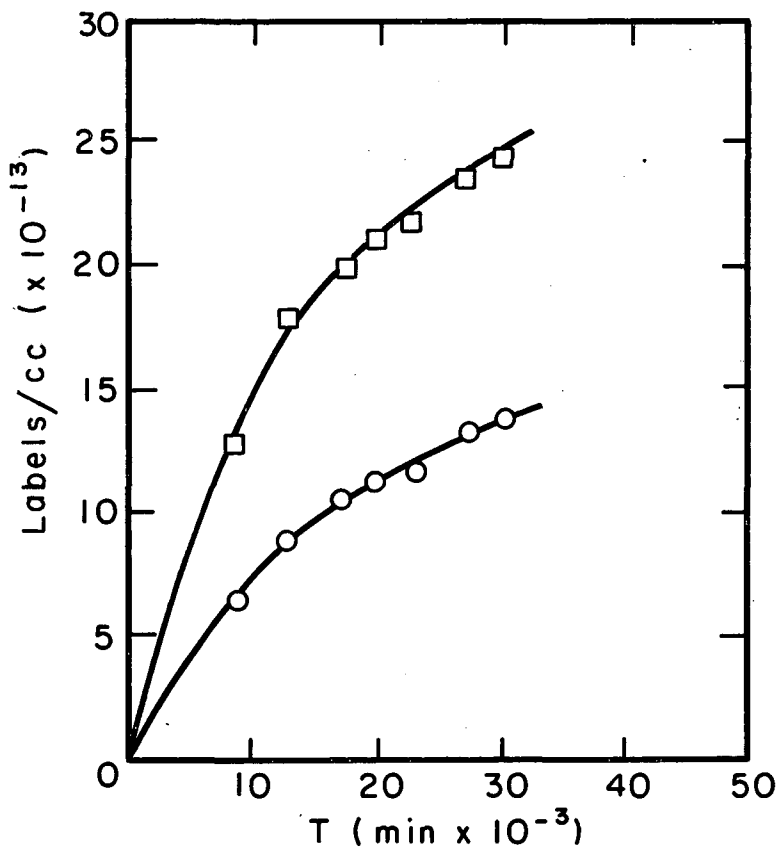
MU-35411

Fig. 21. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 2 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



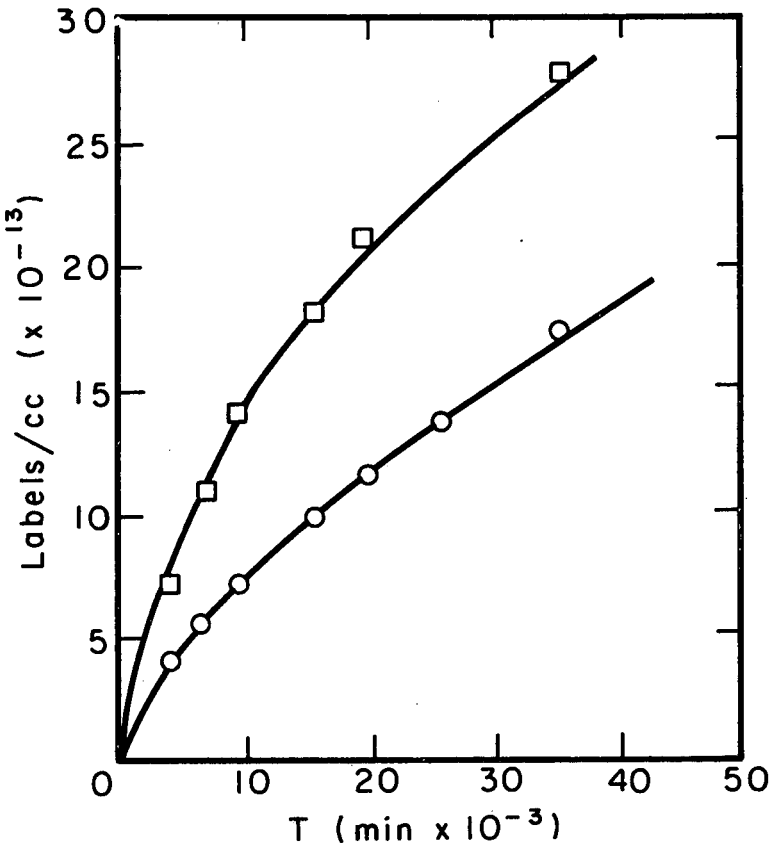
MU-35412

Fig. 22. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 4 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



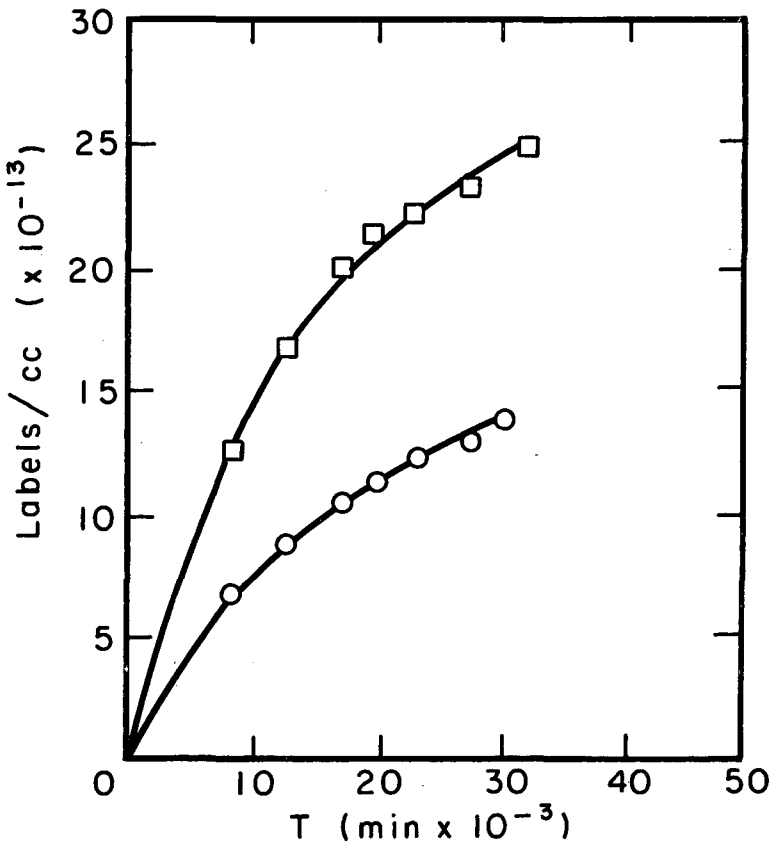
MU-35413

Fig. 23. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 7 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



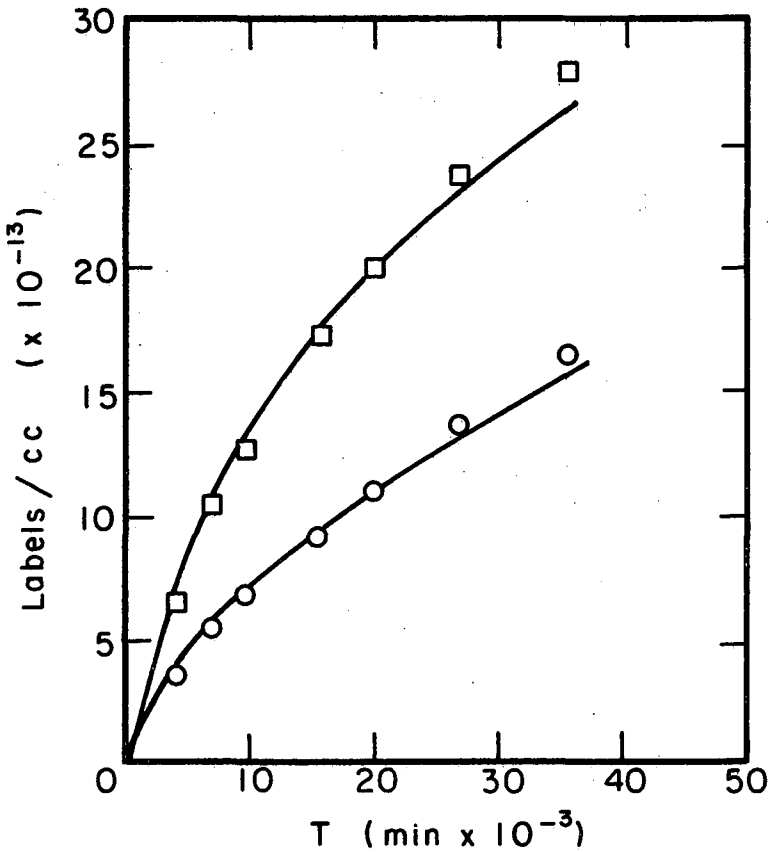
MU-35414

Fig. 24. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 10 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



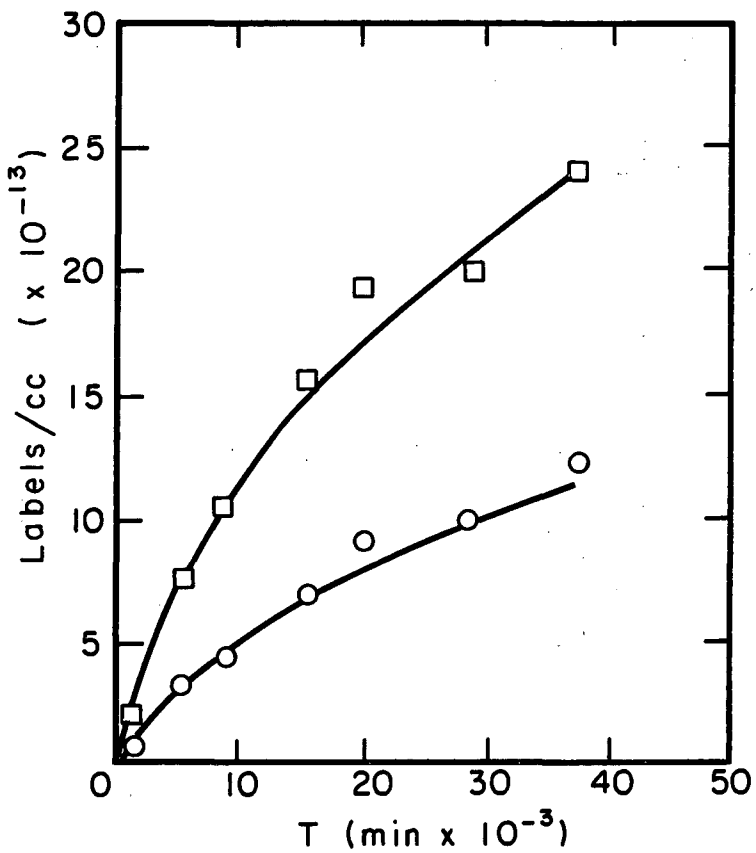
MU-35415

Fig. 25. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 15 mol% xenon is the additive. The total pressure is 650 mm.
○ Methane. □ Ethane.



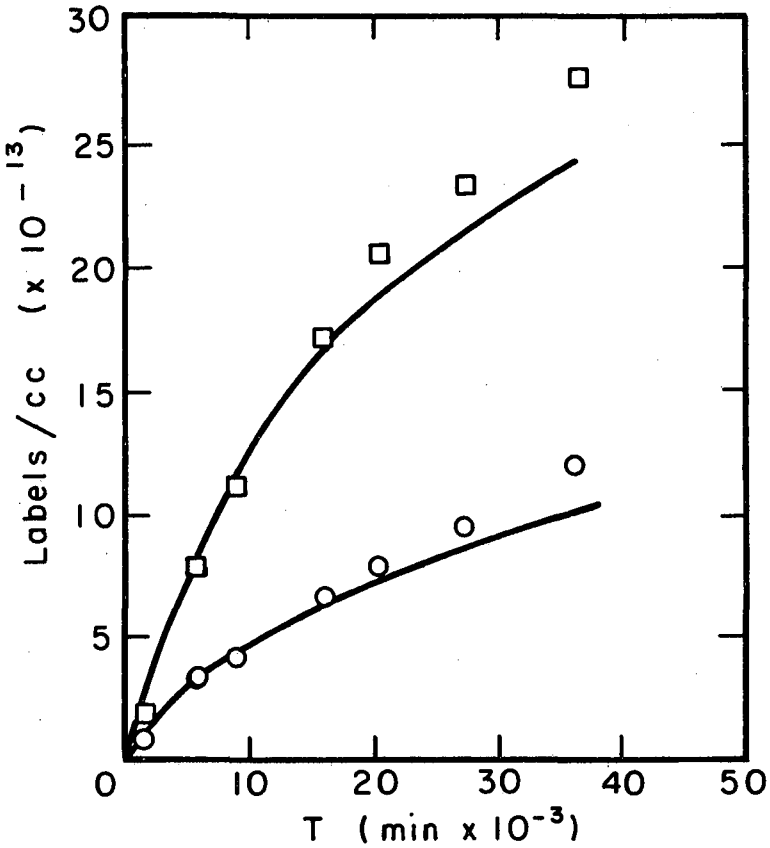
MU-35416

Fig. 26. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 20 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



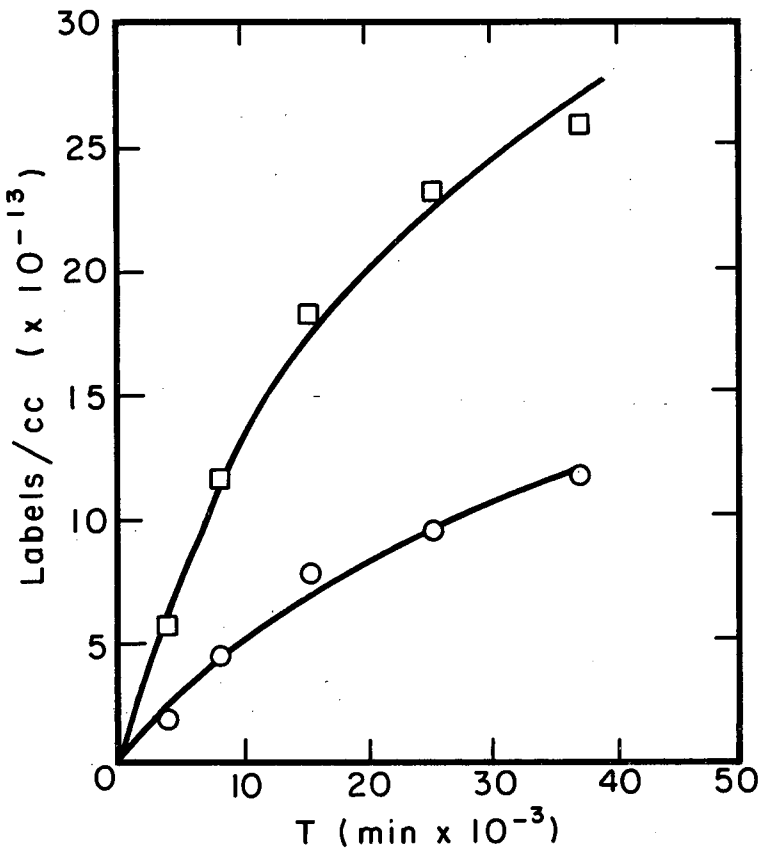
MU-35417

Fig. 27. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 40 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



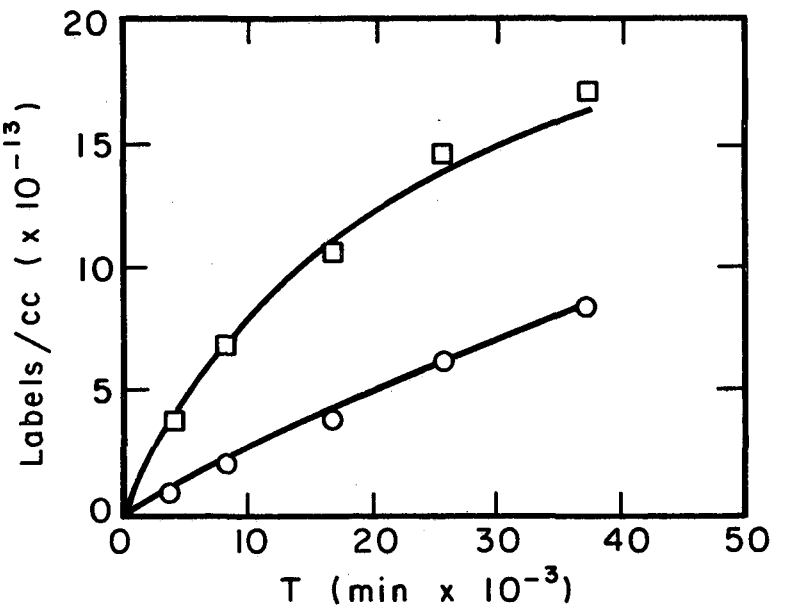
MU-35462

Fig. 28. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 60 mol% xenon is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



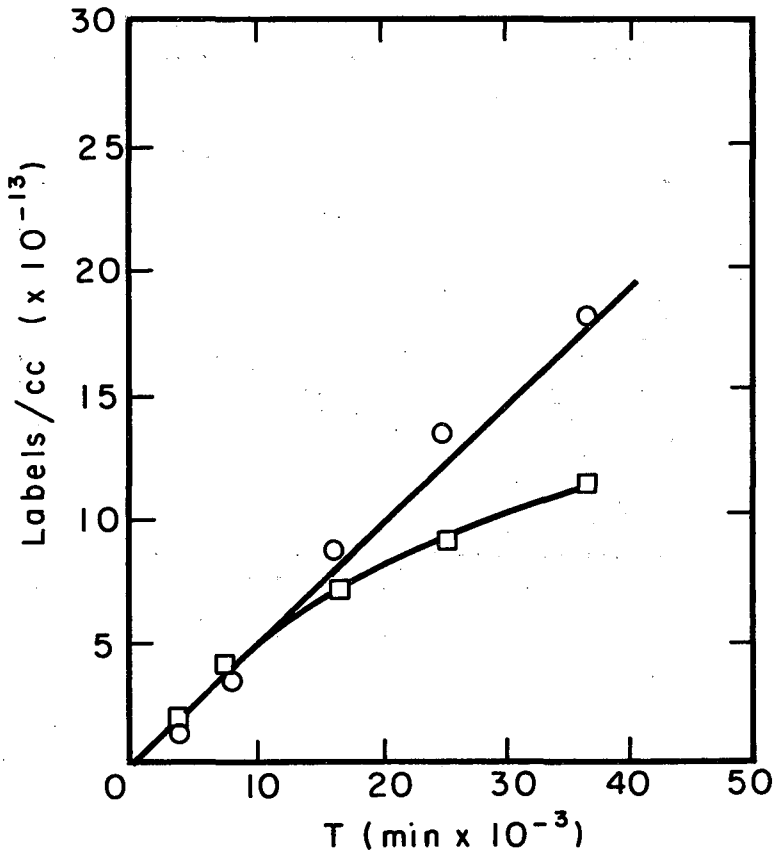
MU-35418

Fig. 29. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, with no additive. S/V ratio is 2:1. The total pressure is 650 mm. ○ Methane. □ Ethane.



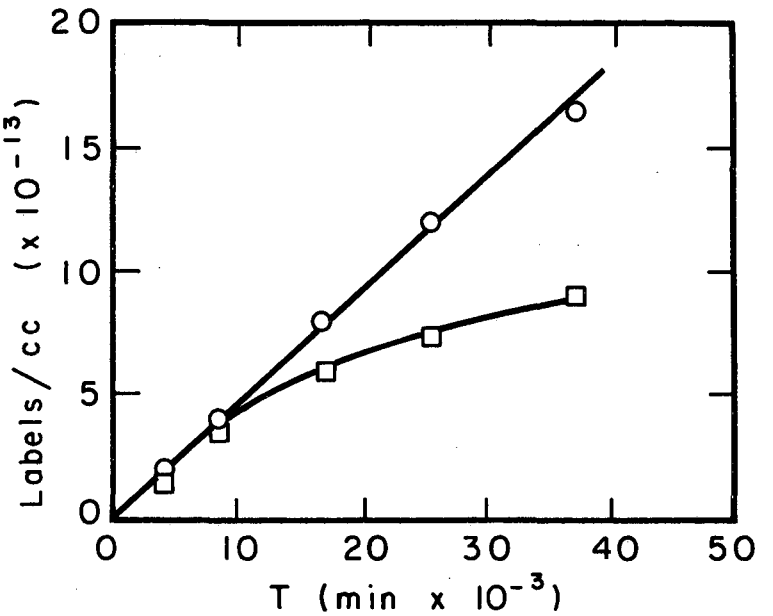
MU-35419

Fig. 30. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 5 mol% xenon is the additive. S/V ratio is 2:1. The total pressure is 650 mm. ○ Methane. □ Ethane.



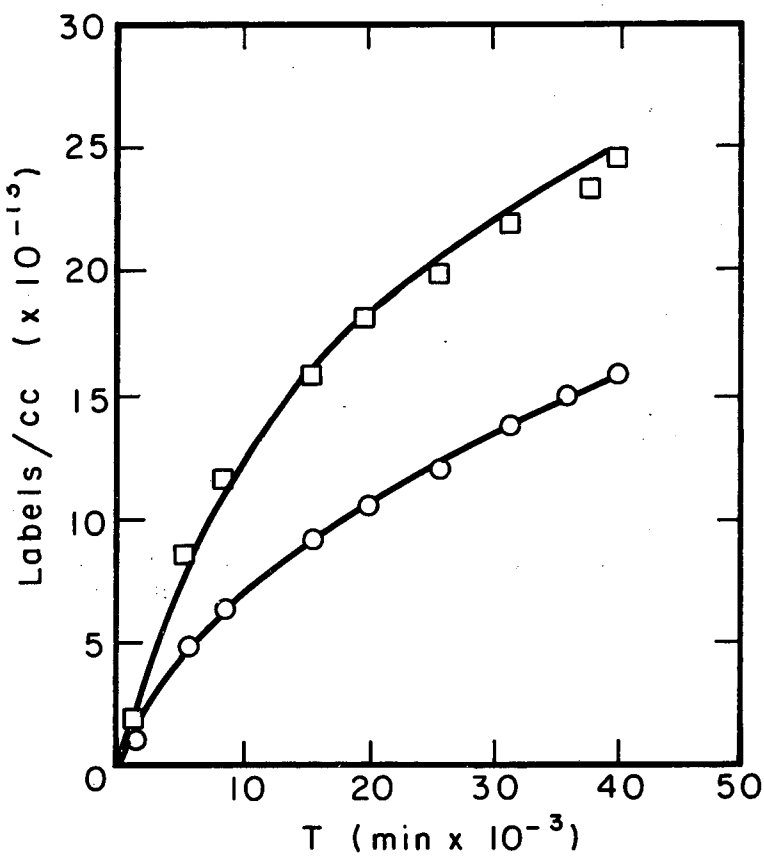
MU-35420

Fig. 31. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, with no additive. S/V ratio is 17:1. The total pressure is 650 mm. ○ Methane. □ Ethane.



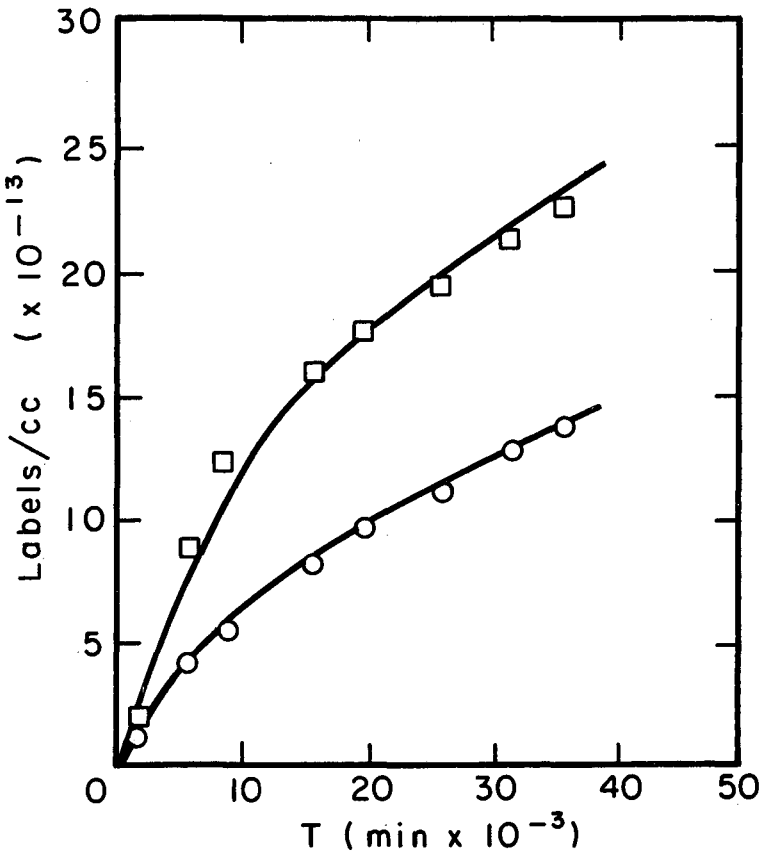
MU-35421

Fig. 32. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 5 mol% xenon is the additive. S/V ratio is 17:1. The total pressure is 650 mm. ○ Methane. □ Ethane.



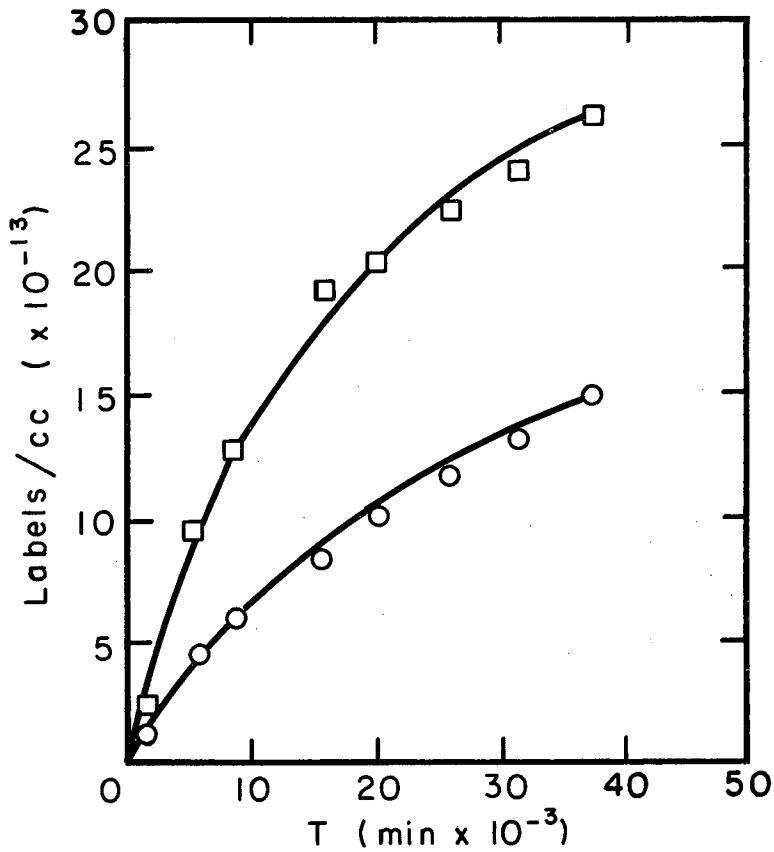
MU-35422

Fig. 33. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, with no additive. The total pressure is 300 mm. ○ Methane. □ Ethane.



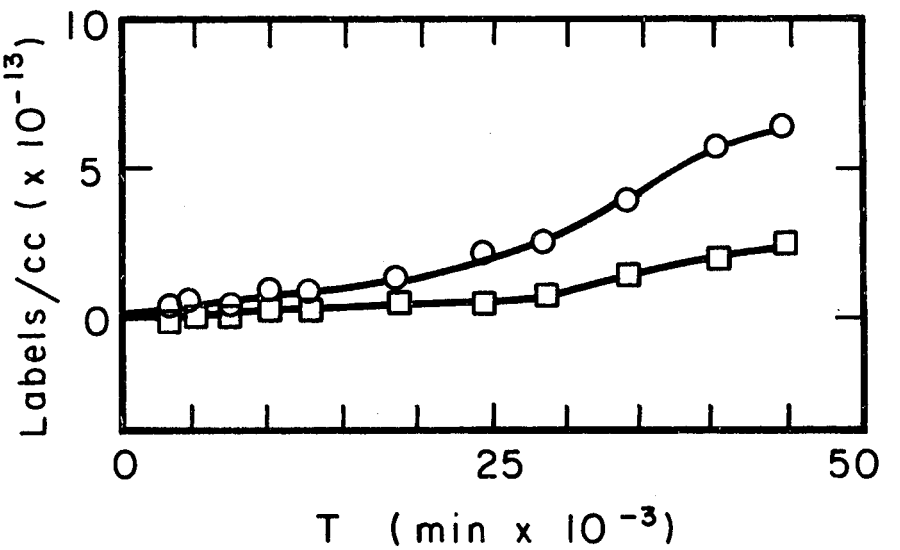
MU-35423

Fig. 34. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, with no additive. The total pressure is 500 mm. ○ Methane. □ Ethane.



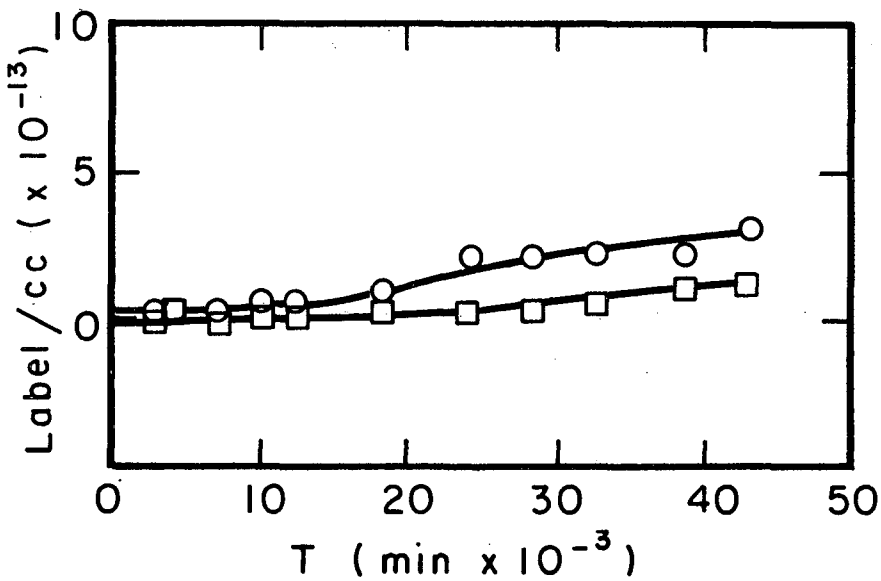
MU-35424

Fig. 35. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, with no additive. The total pressure is 700 mm. ○ Methane. □ Ethane.



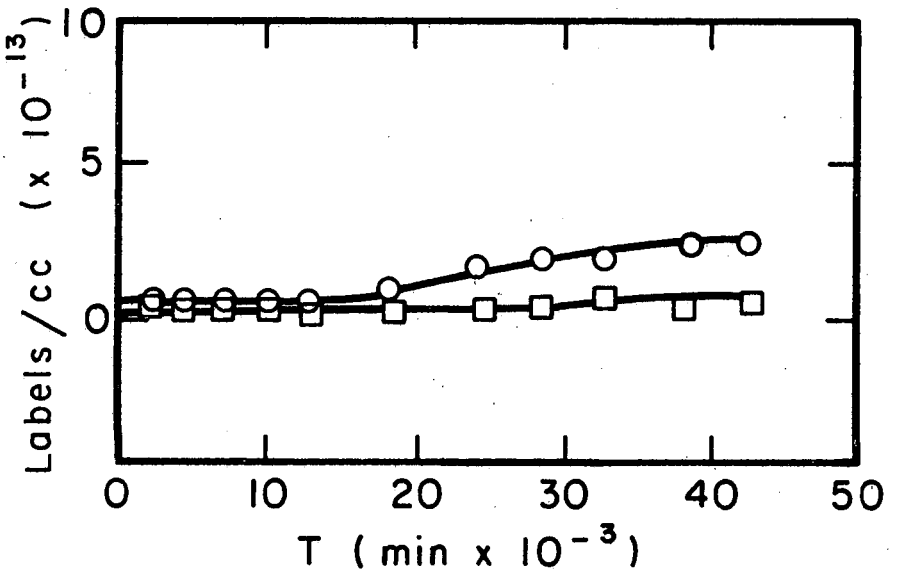
MU-35425

Fig. 36. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 0.1 mol% C_2H_4 is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



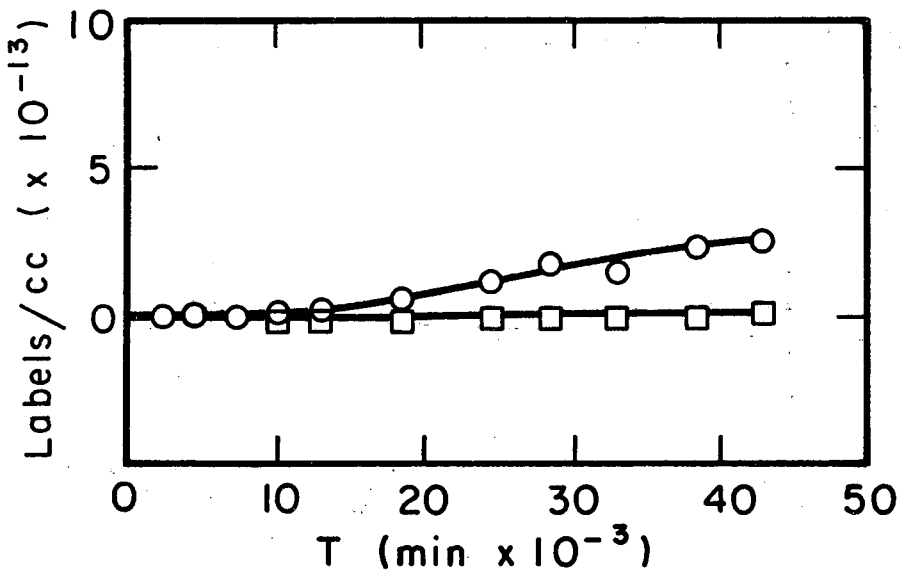
MU-35426

Fig. 37. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 0.2 mol% C_2H_4 is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



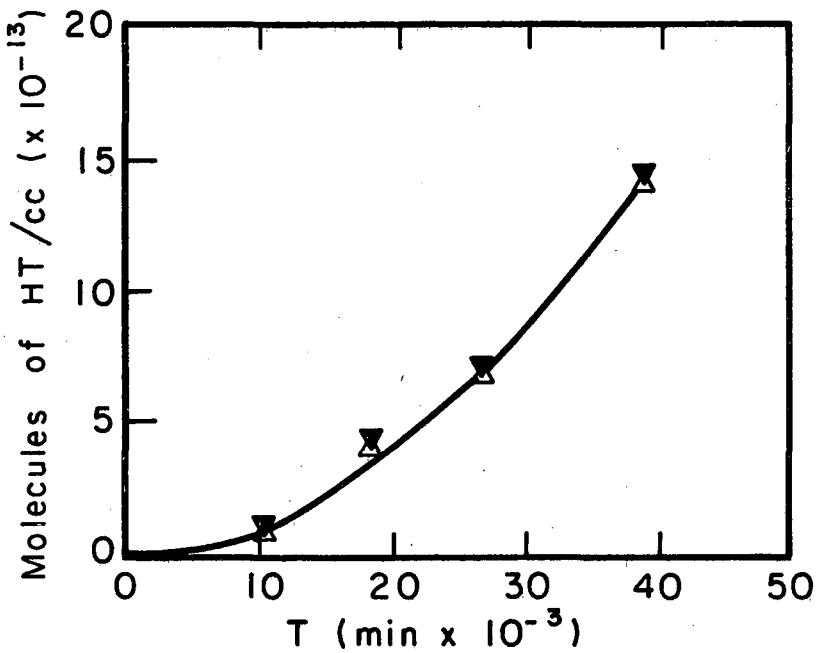
MU-35427

Fig. 38. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 0.5 mol% C_2H_4 is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



MU-35428

Fig. 39. Incorporation of tritium into labeled methane and ethane as a function of time. Tritium concentration is 1 mC/cc, 2.0 mol% C_2H_4 is the additive. The total pressure is 650 mm. ○ Methane. □ Ethane.



MU-35463

Fig. 40. Formation of HT as a function of time in the CH_4-T_2 system. Tritium concentration is 1 mC/cc, with no additive. ∇ Total pressure is 500 mm. △ Total pressure is 700 mm.

C. Kinetic Expression

Addition of hydrogen to the reaction mixture yielded a value for the term in the kinetic expression indicative of the decay-induced labeling. A concentration of 2 mol% hydrogen was thought to be negligible compared to the concentration of methane present and large relative to that of tritium. In actuality, owing to the magnitude of the radiation-labeling term in the ethane formation, a correction to the observed values was necessary. The results are:

$$\begin{aligned} &\text{For labeled methane,} \quad a = 1.17 \times 10^9 \\ &\text{For labeled ethane,} \quad a = 0.85 \times 10^9 \end{aligned} \qquad (15)$$

The units are T atoms incorporated in labeled product per millicurie-minute.

Having identified the first term, the second term was evaluated by plotting the experimental data less the constant first term as a function of the tritium concentration. The initial assumption that the radiation labeling was produced by attack of a radical or ion from the destruction of methane on a tritium molecule led to consideration of a function of the form:

$$\frac{d(\text{radiation labeled product})}{dt} = b\left[\frac{(T_2)}{(H_2) + (T_2)}\right](T_2)_a \qquad (16)$$

$(T_2)_a$ is the concentration of tritium expressed in mC/cc. (T_2) and (H_2) are the concentrations of tritium and hydrogen, respectively, expressed in molecules per cc. (H_2) is a function of time increasing at a rate of 7.0×10^{11} molecules/mC-min, assuming that $G(H_2)$ is 5.6. This value can be separately computed for each data point, if necessary.

This form of the term has essentially a second-order dependence on the tritium concentration. First of all, it is proportional to the decay rate of tritium as a source of energy to produce ions and radicals from radiolysis. Secondly, the actual molecular concentration

of tritium is considered. It is this molecule that is acted upon by the radiolytic intermediates to produce those tritiated compounds formed by radiation labeling.

Table II gives the results for the constants a and b experimentally determined and derived from Figs. 11 to 40. The solid lines in these figures are those corresponding to the results of a and b substituted in the complete rate expression.

To evaluate the order of the second term of the expression from the experimental values of b, these values must be corrected by a factor indicative of the amount of higher molecular weight products formed from labeled ethane as a result of reactions such as the methylene insertion. Table I is the source of this factor. Using the normalized data, $(C_3 + C_4)/C_2$ (labeled) is obtained for each concentration of tritium. Assuming the factor for a concentration of tritium of 0.5 mC/cc is equal to one, all ratios are found relative to this specific concentration. For 0.5 mC/cc, this normalizing factor equals 0.091/0.523, or 0.203. Then, for other concentrations,

$$F = \frac{(C_3)+(C_4)}{(C_2)} \times \frac{1}{0.203} \qquad (17)$$

The values obtained by this method are given in Table III and the results are plotted as the logarithm against the logarithm of the tritium concentration. The values of b found by this method are given in the complete expressions:

$$\frac{d(\text{Methane})}{dt} = 1.17 \times 10^9 \, (T_2)_a + 9.36 \times 10^9 \, \frac{(T_2)}{(H_2) + (T_2)} \, (T_2)_a$$

$$(18)$$

$$\frac{d(\text{Ethane})}{dt} = 0.85 \times 10^9 \, (T_2)_a + 2.18 \times 10^{10} \, \frac{(T_2)}{(H_2) + (T_2)} \, (T_2)_a$$

The corresponding slopes for the b term are 1.04 for methane and 0.96 for ethane in Fig. 41. The units are the same as those given for

Table II. Values of the constants a and b for Figs. 11 to 36. The solid lines in the figures are drawn from these values. Total pressure is 650 mm and the S/V ratio is 0.85:1 unless otherwise stated.

Tritium conc.	Additive	Labeled compound	$a(T_2)_a$ T atoms incorp/min	$b(T_2)_a$ T atoms incorp/min	Figure
1 mC/cc	2 mol% H_2	Methane	1.20×10^9	0	11
		Ethane	0.85×10^9	0	
		HT	7.90×10^9	0	
2 mC/cc	2 mol% H_2	Methane	2.28×10^9	0	12
		Ethane	1.70×10^9	0	
		HT	1.49×10^{10}	0	
0.5 mC/cc	None	Methane	0.59×10^9	3.68×10^9	13
		Ethane	4.30×10^8	1.09×10^{10}	
1 mC/cc	None	Methane	1.17×10^9	9.1×10^9	14
		Ethane	0.85×10^9	2.00×10^{10}	
2 mC/cc	None	Methane	2.35×10^9	2.02×10^{10}	15
		Ethane	1.70×10^9	3.64×10^{10}	
4 mC/cc	None	Methane	4.70×10^9	3.21×10^{10}	16
		Ethane	3.40×10^9	6.20×10^{10}	
0.5 mC/cc	5 mol% Xe	Methane	0.58×10^9	4.86×10^9	17
		Ethane	4.30×10^8	1.18×10^{10}	
1 mC/cc	5 mol% Xe	Methane	1.17×10^9	1.08×10^{10}	18
		Ethane	0.85×10^9	2.22×10^{10}	
2 mC/cc	5 mol% Xe	Methane	2.34×10^9	2.07×10^{10}	19
		Ethane	1.70×10^9	3.58×10^{10}	
4 mC/cc	5 mol% Xe	Methane	4.68×10^9	4.06×10^{10}	20
		Ethane	3.40×10^9	6.65×10^{10}	
1 mC/cc	2 mol% Xe	Methane	1.17×10^9	9.8×10^9	21
		Ethane	0.85×10^9	2.23×10^{10}	
1 mC/cc	4 mol% Xe	Methane	1.17×10^9	9.90×10^9	22
		Ethane	0.85×10^9	2.20×10^{10}	
1 mC/cc	7 mol% Xe	Methane	1.17×10^9	1.04×10^{10}	23
		Ethane	0.85×10^9	2.27×10^{10}	
1 mC/cc	10 mol% Xe	Methane	1.17×10^9	1.10×10^{10}	24
		Ethane	0.85×10^9	2.25×10^{10}	

Table II. (Cont.)

Tritium conc.	Additive	Labeled compound	$a(T_2)_a$ T atoms incorp/min	$a(T_2)_a$ T atoms incorp/min	Figure
1 mC/cc	15 mol% Xe	Methane Ethane	1.17×10^9 0.85×10^9	1.05×10^{10} 2.28×10^{10}	25
1 mC/cc	20 mol% Xe	Methane Ethane	1.17×10^9 0.85×10^9	1.06×10^{10} 2.16×10^{10}	26
1 mC/cc	40 mol% Xe	Methane Ethane	1.17×10^9 0.85×10^9	6.77×10^9 1.86×10^{10}	27
1 mC/cc	60 mol% Xe	Methane Ethane	1.17×10^9 0.85×10^9	6.14×10^9 1.97×10^{10}	28
1 mC/cc	None S/V = 2:1	Methane Ethane	1.17×10^9 0.85×10^9	6.68×10^9 2.20×10^{10}	29
1 mC/cc	5 mol% Xe S/V = 2:1	Methane Ethane	1.17×10^9 0.85×10^9	2.65×10^9 1.21×10^{10}	30
1 mC/cc	None S/V = 17:1	Methane Ethane	4.69×10^9 0.85×10^9	--- 4.36×10^9	31
1 mC/cc	5 mol% Xe S/V = 17:1	Methane Ethane	4.58×10^9 0.85×10^9	--- 3.27×10^9	32
1 mC/cc	300 mm pressure	Methane Ethane	1.17×10^9 0.85×10^9	1.01×10^{10} 1.97×10^{10}	33
1 mC/cc	500 mm pressure	Methane Ethane	1.17×10^9 0.85×10^9	8.92×10^9 1.86×10^{10}	34
1 mC/cc	700 mm pressure	Methane Ethane	1.17×10^9 0.85×10^9	9.53×10^9 2.14×10^{10}	35
1 mC/cc	0.1 mol% Ethylene	Methane Ethane	--- ---	--- ---	36
1 mC/cc	0.2 mol% Ethylene	Methane Ethane	--- ---	--- ---	37
1 mC/cc	0.5 mol% Ethylene	Methane Ethane	--- ---	--- ---	38
1 mC/cc	2.0 mol% Ethylene	Methane Ethane	--- ---	--- ---	39
1 mC/cc	650 and 700	HT	---	---	40

Table III. Experimental values for the second-order constant, b. The observed values are corrected for the amount of higher hydrocarbons formed in the case of ethane. These values are used in Fig. 41.

Tritium conc.	Compound	$b(T_2)_a$ (T atoms per mc-min)	Correction f	Corrected $b(T_2)_a$
0.5 mC/cc	Methane	3.68×10^9	-	3.68×10^9
	Ethane	1.09×10^{10}	1.00	1.09×10^{10}
0.56 mC/cc	Methane	6.33×10^9	-	6.33×10^9
	Ethane	1.30×10^{10}	1.00	1.30×10^{10}
1.0 mC/cc	Methane	8.80×10^9	-	8.80×10^9
	Ethane	1.95×10^{10}	1.07	2.08×10^{10}
1.0 mC/cc	Methane	9.55×10^9	-	9.55×10^9
	Ethane	2.11×10^{10}	1.07	2.25×10^{10}
1.0 mC/cc	Methane	9.30×10^9	-	9.30×10^9
	Ethane	2.00×10^{10}	1.07	2.14×10^{10}
2.0 mC/cc	Methane	2.02×10^{10}	-	2.02×10^{10}
	Ethane	3.82×10^{10}	1.16	4.43×10^{10}
2.0 mC/cc	Methane	2.00×10^{10}	-	2.00×10^{10}
	Ethane	3.64×10^{10}	1.16	4.22×10^{10}
4.0 mC/cc	Methane	3.21×10^{10}	-	3.21×10^{10}
	Ethane	6.82×10^{10}	1.26	8.59×10^{10}
4.0 mC/cc	Methane	4.83×10^{10}	-	4.83×10^{10}
	Ethane	6.20×10^{10}	1.26	7.81×10^{10}

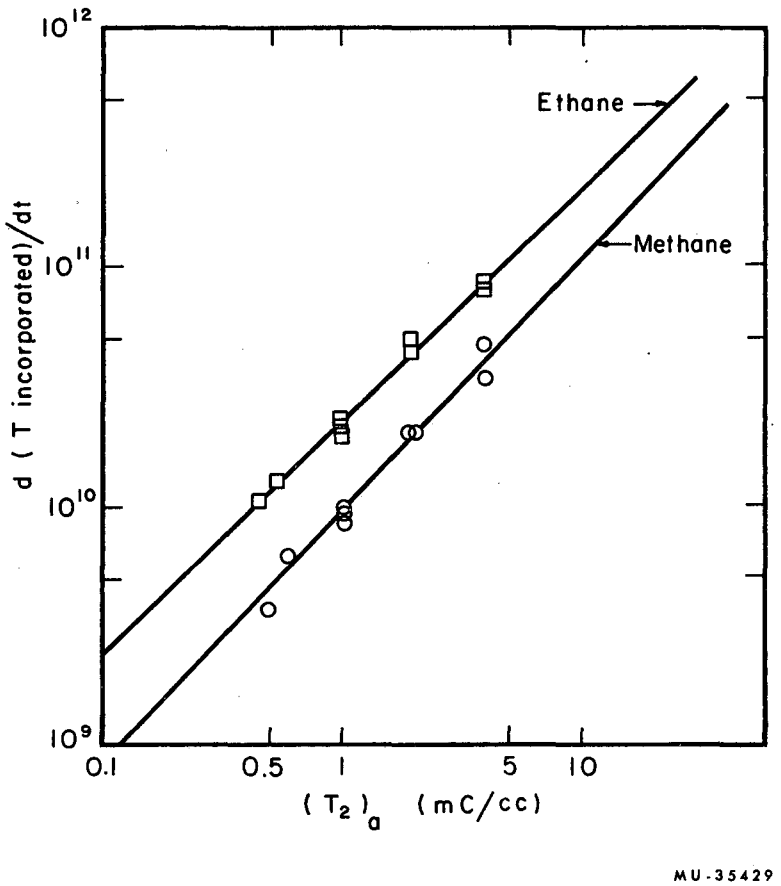


Fig. 41. Log-log plot of the rate of incorporation of tritium into labeled methane and ethane as a function of tritium concentration in mC/cc for the radiation induced labeling. ○ Methane. □ Ethane.

Eq. (16). d(Methane)/dt and d(Ethane)/dt are in units of atoms of T incorporated in the hydrocarbon per minute. The empirical expressions may be expressed better by substitution of the following two identities:

$$(T_2) = c(T_2)_a$$
$$(H_2) = k_1 t(T_2)_a \qquad (19)$$

The constant c is 1.03×10^{16} molecules of T_2 per mC and k_1 is the rate of production of H_2, 7.0×10^{11} molecules per mC-min. Substituting these values as well as the constant $(H_2)_o$ for the amount of hydrogen present in the initial mixture, if any, the results are:

$$\frac{d(\text{Methane})}{dt} = 1.17\times10^9(T_2)_a + 9.36\times10^9 \frac{c(T_2)_a^2}{k_1 t(T_2)_a + (H_2)_0 + c(T_2)_a} \qquad (20a)$$

$$\frac{d(\text{Ethane})}{dt} = 0.85\times10^9(T_2)_a + 2.18\times10^{10} \frac{c(T_2)_a^2}{k_1 t(T_2)_a + (H_2)_0 + c(T_2)_a} \qquad (20b)$$

With no initial hydrogen, the term $(H_2)_0$ is equal to zero, and the fractional part of the second term reduces to:

$$\frac{d(\text{Methane})}{dt} = 1.17 \times 10^9 (T_2)_a + 9.36 \times 10^9 \frac{c(T_2)_a}{k_1 t + c} \qquad (21a)$$

$$\frac{d(\text{Ethane})}{dt} = 0.85 \times 10^9 (T_2)_a + 2.18 \times 10^{10} \frac{c(T_2)_a}{k_1 t + c} \qquad (21b)$$

Earlier, it was stated that the labeled ethane produced in the mixtures with 2% hydrogen had to be corrected for the amount of ethane produced the the radiation labeling. Typical values for the fractional part of the second term with hydrogen initially present are, at t=0

and tritium concentration of 1 mC/cc:

$$\frac{c(T_2)_a}{(H_2)_0 + c(T_2)_a} = \frac{1.03 \times 10^{16}}{4.65 \times 10^{17}} = 0.022 \qquad (22)$$

Because of the relative magnitudes of the first and second terms in Eq. (20b), the correction for this was made to the data for the rate of production of ethane as a result of the tritium decay. Now, the necessity of this adjustment can be seen.

D. Xenon Addition

Xenon was added to the CH_4-T_2 mixtures in varying amounts from 2 to 60 mol% with particular emphasis on the range from 2 to 20 mol%. The experimental results are shown in Figs. 17 through 28. Analysis of these results in terms of Eqs. (21a) and (21b) revealed that the xenon effect could be explained by enhancement in the second term. The increased values of $b(T_2)_a$ are given in Table II. A plot of the second term vs mol% of xenon is shown in Fig. 42. The values plotted are the experimental ones, uncorrected for the amount of tritiated propane and butane formed from labeled ethane.

E. Ethylene Addition

Addition of ethylene in the amounts of 0.1, 0.2, 0.5, and 2.0 mol% suppressed the labeling rate of both methane and ethane to such an extent that analysis was not possible. Both terms of the expression were decreased to nearly zero with concentrations of 0.2 mol% and above. The results with ethylene are shown in Figs. 36 to 39. With the contamination present, there is an induction period. When ethane and methane finally appear, ethane seems to follow that rate which would be expected at that time from the first term only (compare Fig. 36 to Fig. 14). Methane production is slightly less than that which would be expected from the complete kinetic expression.

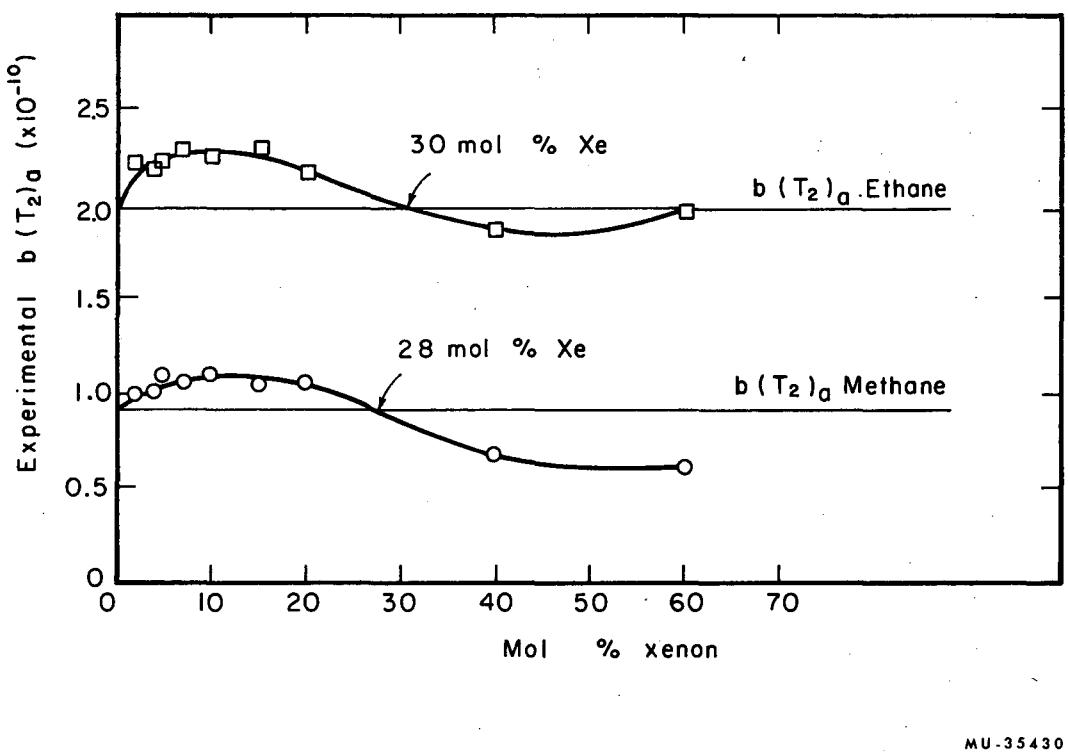


Fig. 42. Plot of the value of the second term coefficient, $b(T_2)_a$, vs the mol% of xenon added. The lines are the observed experimental values and are not corrected for the higher labeled products formed from previously labeled ethane. The tritium concentration in all samples is 1 mC/cc. ○ Methane. □ Ethane.

F. Other Considerations

Product formation as a function of pressure yielded data indicating no significant changes. The product of the pressure and the volume is still large enough that essentially all of the radiation is absorbed by the system.[39] The results are shown in Figs 33 to 36 and are included in Table II.

Surface-to-volume experiments indicated a change in value of the coefficients in the kinetic expression for production of the labeled compounds. The results are shown in Figs. 29 through 32, and are given in Table II. At a ratio of 2:1, methane production was decreased and ethane production increased, although the amount of ethane produced still exceeded that of the labeled methane. At a S/V ratio of 17:1, the initial rate of formation of labeled methane decreased, but more important, could be expressed independently of the hydrogen produced by the radiolysis. The ethane could still be expressed by a two term formula. In addition, labeled methane was formed at a faster rate than labeled ethane. At both S/V ratios, xenon at 5 mol% concentration, acted as an inhibitor. The surface-to-volume ratio for the normal reaction flasks was 0.85:1.

The rate of formation of HT increases with time. This is shown in Fig. 40. In the systems with added hydrogen, the rate of production of HT was linear, and to a good approximation, first order with a rate constant of 7.7×10^9 molecules/mC-min.

Mass spectrographic analysis of the products of the reaction, collected at 7×10^4 minutes, showed a peak at m/e equal to 34. This would be the parent peak of $C_2H_4T_2$. By comparison with the mass spectrum of normal ethane, it was noted that the 34 to 32 peak ratios were the same as the 30 to 28 ratios. Doubly-labeled ethane was calculated to be 0.34% of the unlabeled ethane present. The accuracy of the measurement is ±3% of the absolute value. The unlabeled ethane is formed by the radiolysis of the methane. No doubly-labeled methane was found.

The G values for ethane production vary from 0.95 to 2.2 (see Refs. 6, 11, 12, 14-16, 32,40) for various particles, rates of energy absorption, and pressures. An average value, between the extremes in which the system under investigation was considered, was 1.8 ± 0.3. The concentration range of the di-tritiated ethane, calculated from this value, is $4.7 \pm 0.8 \times 10^{13}$ molecules per cc at the time that the combined samples were collected. The value from the second term of the kinetic expression for ethane labeling is 2.38×10^{14} tritium atoms incorporated into ethane per cc. The percent of doubly-labeled ethane on a molecules basis is 24.6 ± 4.4%. On the basis of total labels, the percent of tritium incorporated into doubly-labeled ethane is 39.5 ± 7.1%. The number of singly-labeled ethane molecules is 1.44×10^{14} molecules per cc.

IV. DISCUSSION

The expression for the rate of formation of labeled methane and ethane in the CH_4-T_2 system is considered to consist of a first-order and a second-order term. The first-order term is that dependent only on the decay of tritium, the decay-induced labeling. The second-order term is dependent, first of all, on the concentration of tritium in mC/cc, as a source of radiation to produce ions and radicals, and, secondly, as being present in a definite concentration, to react with these radiolytic intermediates. This is the radiation-induced labeling.

A. Decay-Induced Labeling

The initiating species for the decay-induced series is the HeT^+ ion formed from the decay of tritium:

$$T_2 = HeT^+ + \beta^- \qquad (23)$$

The series of reactions initiated by this ion must be that which gives rise to the first term in the expression, being unaffected by the presence of hydrogen or xenon. This molecule-ion must go through a series of reactions in which neutralization of the charge takes place followed by free radical reactions to stabilization. The series must account for the scavenging effect of ethylene.

The reactions proposed in the following series are those considered to be the most probably thermodynamically.

The HeT^+ rapidly undergoes reaction with methane:

$$HeT^+ + CH_4 = CH_4T^+ + He \qquad (24)$$

CH_4 is reported to have a proton affinity of -115 kcal/mol.[41,42,43]

The ΔH_f of CH_5^+ has an upper limit of -235 kcal/mole,[41] and a more recent value of -196 kcal/mole;[48] the higher value assumes formation of a C-H bond of normal energy in the ion. For reaction (24) then,

$$\begin{array}{lcll} CH_4 + T^+ & = & CH_4T^+ & \Delta H = -196 \text{ kcal/mole} \\ HeT^+ & = & He + T^+ & \Delta H = +46 \text{ kcal/mole} \\ \hline CH_4 + HeT^+ & = & CH_4T^+ + He & \Delta H_r = -150 \text{ kcal/mole} \end{array}$$

The CH_4T^+ ion is formed in a highly excited state, and its lifetime against neutralization is unknown.[21] Then, there are two alternatives, breakup or reaction.

If breakup occurs,

$$(CH_4T^+) = \begin{cases} CH_2T^+ + H_2 \\ CH_3^+ + HT \end{cases} \qquad (25)$$

The CH_2T^+ will react immediately with methane:

$$CH_2T^+ + CH_4 = \begin{cases} C_2H_4T^+ + H_2 \\ C_2H_5^+ + HT \end{cases} \qquad (26)$$

Reaction (26) has been observed in the mass spectrometer[21] and is said to occur at the first collision. It must be thermodynamically possible since the requirement for observation of reactions in the mass spectrometer is that $\Delta H \leq 0$.

CH_5^+ is seen in relatively high concentrations in the mass spectrum of methane at pressures less than 0.5 mm.[44] As the pressure is increased, the concentration of CH_5^+ reaches a limiting value[16,44] and that of $C_2H_5^+$ increases, indicating that a reaction might be taking place. Since CH_5^+ is observed at low pressures, the probability of disintegration is low. If reaction with methane were not possible, the concentration of CH_5^+ would increase with pressure. In view of the excitation energy present and the observations in the mass

spectrometer that the concentration of CH_5^+ has a limiting value, the following reaction seems more probable:

$$CH_4T^+ + CH_4 = \begin{cases} C_2H_4T^+ + 2H_2 \\ C_2H_5^+ + HT + H_2 \end{cases} \qquad (27)$$

The thermodynamics of the reaction are : 1) scission of 4 C-H bonds +412 kcal/mole; 2) formation of a C-C bond = -80 kcal/mole; and 3) formation of 2 H-H bonds = -212 kcal/mole. Then, ΔH_r = +120 kcal/mole. The CH_4T^+ ion has -150 kcal/mole as excitation energy, more than enough to promote the reaction. The result for reaction (27) is ΔH_r = -30 kcal/mole.

Either reaction path to the formation of the $C_2H_4T^+$ ion may take place since both are possible, and both give the probability of 5/9 that the tritium remain with the major fragment.

Neutralization gives an excited species:

$$C_2H_4T^+ + e^- = (C_2H_4T)^* \qquad (28)$$

This radical is excited by virtue of the neutralization energy, and not by excitation from the radiation. Assuming the reaction takes place while the $C_2H_4T^+$ is in the ground state, ΔH = -134 kcal/mole.[17,47,48]

Decomposition of the excited radical occurs:

$$(C_2H_4T)^* = \begin{cases} (CH_2T)^* + (CH_2)^* \\ (CH_3)^* + (CHT)^* \end{cases} \qquad (29)$$

The two fragments may now go on to be stabilized as product methane or ethane. The methane is formed by hydrogen abstraction, or reaction with hydrogen atoms produced from the radiation field:

$$(CH_2T)^* + CH_4 = CH_3T + CH_3$$
$$(CH_2T)^* + H + M = CH_3T + M^* \qquad (30)$$

The reaction involving hydrogen abstraction is endothermic by the difference in bond energy between C-T and C-H, and has an energy of activation of 14.8 kcal/mole.[54] The CH_2T fragment has sufficient energy to promote the reaction. The reaction with a hydrogen atom is exothermic to such an extent that a third body is needed to de-excite the CH_3T.

The labeled ethane is formed by methylene insertion:[53]

$$(CHT)^* + CH_4 + M = C_2H_5T + M^* \qquad (31)$$

For this reaction, $\Delta H = -61$ kcal/mole.

This mechanism is consistent with all the experimental observations. It should be unaffected by the presence of hydrogen or xenon. However, the ions produced in the series should be scavenged by ethylene, leading to formation of polymer.

A further verification of the series may be seen when analyzed in terms of isotopic reaction rate theory at the high temperature limit. This does not seem unlikely in view of the amount of exothermicity of the proposed reactions. The reactions postulated are either those of excited species or those having a negative heat of reaction. The molecule-ions and radicals are identical to those of normal hydrocarbons, with the exception of a tritium atom replacing one of the hydrogens. That is, the rotational and electronic corrections to the partition functions of the activated complex are not necessary. (For a more complete treatment, see the Appendix.) The unimolecular decompositions should be governed by the differences in the zero-point energy of the normal and isotopically substituted radicals and ions in the series as they move along the reaction

coordinate to decomposition. This simply reduces to the square roots of the masses of the hydrogen and of the tritium. Thus, the relative bond strengths of C-H and C-T would be the ratio of the square roots of their masses, 1.000 and 1.732, respectively. The probability that a C-H bond is broken in reactions (25), (26), and (27) is 1.732; that a C-T bond is broken is 1.000. Reaction (29) is not considered since it involves scission of the C-C bond, as well as reactions (30) and (31) which involve stable product formation. The determining rate of formation of the HeT^+ ion is the decay rate of tritium, 2.22×10^9 per minute-millicurie. Together with the probability that the tritium remain with the major fragment or form HT in reactions (25), (26), (27), and (29), the results are:

$$\frac{d(\text{Methane})}{dt} = (5/9)(1.732)(3/5)(2.22 \times 10^9) = 1.28 \times 10^9 \text{ molecules/mC-min}$$

$$\frac{d(\text{Ethane})}{dt} = (5/9)(1.732)(2/5)(2.22 \times 10^9) = 0.85 \times 10^9 \text{ molecules/mC-min} \qquad (32)$$

These compare very well with the observed values for the first-order constant, 1.17×10^9 molecules/mC-min for decay-labeled methane and 0.85×10^9 molecules/mC-min for labeled ethane.

B. Radiation-Induced Labeling

Elucidation of a mechanism for this portion is not as clear as that for the previous section. Owing to the very nature of the second-order term, formation of labeled methane and ethane depend on radical and ion production as a result of the absorption of radiation. This may be interpreted in two ways. First, radicals and ions from radiolysis of the methane attack the tritium and, from this point, react further to produce stable tritiated products. Secondly, the tritium may be ionized to form a T_2^+ ion which goes through a series to yield product.

The second of the two alternatives above is dependent on attack of methane by activated tritium, to form CH_2T^+ from:

$$T_2^+ + CH_4 = CH_2T^+ + HT \qquad (33)$$

Reaction would then proceed as in the decay-induced series. If this were the case, a decrease in the yield of the tritiated products by virtue of charge exchange would be expected when xenon were present in large amounts. However, in concentrations up to 30%, xenon has the opposite effect, that to enhance the yield obtained from the radiation-induced term of the empirical expression. From the ratio of tritium to tritium plus hydrogen, $(T_2)/(H_2+T_2)$, and the large amount of tagged ethane produced by this process relative to labeled methane, radical attack on tritium would be the preferred mechanism. Were tritium the activated species initiating the series, a constant rate of radiation-induced labeling of both methane and ethane would be observed. The concentration of tritium is essentially constant, as well as the radiation field and the number of electrons per cc.

In addition, the rate of production of T_2^+ ions by the radiation field is three orders of magnitude less than the observed second-order values. The decay of tritium is releasing energy to the system at a rate of 1.26×10^{13} eV/mC-min. The concentration ratio of tritium to methane is 5×10^{-4}. The linear absorption coefficient of tritium

is $\mu_{T_2} = 1.81$ and, for methane, $\mu_{CH_4} = 8.40$.[3] The ratio is 0.22. The energy absorbed by the tritium is 1.39×10^9 eV/mC-min. Dividing by 15 eV, the ionization potential of tritium, there are 9.3×10^7 ions formed per mC/-min. If the T_2^+ ion were to react as postulated in reaction (33), the concentration would not be sufficient to initiate reactions to produce labeled methane and ethane at a total initial rate of 3.12×10^{10} T atoms incorporated in labeled product per mC-min.

The observance of doubly-labeled ethane in the mass spectrum of the products, and the exclusion of methane of this type can be satisfactorily explained by the following reaction sequence. Since the general reaction series are essentially the same as those previously discussed, the ΔH_r values will be given only for those that are new.

In a recent discussion of the radiation chemistry of methane, Fayard[15] divides the series into two parts, one dependent on the ionization of the methane:

$$CH_4 \rightsquigarrow \begin{cases} CH_4^+ + e^- & (51\%) \\ CH_3^+ + H + e^- & (40\%) \\ CH_2^+ + H_2 + e^- & (4\%) \end{cases} \qquad (34)$$

and the other on the excitation of methane:

$$CH_4 \rightsquigarrow \begin{cases} CH_3 + H & (50\%) \\ CH_2 + H_2 & (50\%) \end{cases} \qquad (35)$$

A total initial G value for ionization and excitation is given as 6.37, 3.66 for ionization and 2.71 for excitation. Decomposition of the methane occurs 57% by ionization and 43% by excitation. The proposed reactions in the series are given below.

The ionization series yields various charged species as given initially in reaction (34). The reactions of the CH_4^+ ion are:

$$CH_4 \rightsquigarrow CH_4^+ + e^- \qquad (36)$$

After formation of the CH_4^+, there are two possible sequences to yield the $C_2H_5^+$ precursor of the radicals. One is:

$$CH_4^+ + CH_4 = CH_5^+ + CH_3 \quad -89 \text{ kcal} < \Delta H_r < -132 \text{ kcal} \qquad (37)$$

The variation in ΔH values was previously discussed in terms of the decay labeling series, but the formation of the CH_5^+ ion is accomplished by proton abstraction from methane, rather than breaking the lower-energy bond. A more complete discussion is now necessary. The range quoted above is found from reported values for the heat of formation of CH_5^+. The limits, $-218 \text{ kcal} < \Delta H_r < -235$ kcal were reported by Lampe and Field.[42] Kevan[46] gives a value for the proton affinity of CH_4 as 180 kcal/mole. Hoyland and Lampe[47] calculate the value to be 7.26 eV, or 167 kcal/mole. More recently, Lampe and Fturell[48] reported a calculated value of $\Delta H_f(CH_5^+) = -186$ kcal/mole. The calculated C-H distance, consistent with this value, is less than that experimentally reported and may indicate a more negative value for the heat of formation. Values for the proton affinity of methane range from an estimate of greater than 5.0 eV[43] to a reported range of valuesof 113-129 kcal/mole.[41,42] Reaction (37) has been observed in the mass spectrometer by Stevenson and Schissler,[43] so the degree of exothermicity is the question.

The next reaction in the series is:

$$CH_5^+ + CH_4 = C_2H_5^+ + 2H_2 \qquad (38)$$

This reaction depends critically on the amount of energy in the CH_5^+. ΔH_r for reaction (38) is +120 kcal/mole. Including the energy of the CH_5^+, Wexler and Jesse[44] state that it is endothermic by 14 kcal/mole, however, the value of $\Delta H_f(CH_5^+)$ that gave this result was not stated.

In view of the range of ΔH values quoted for reaction (37), it is possible that the heat of reaction (38) is zero or negative within the errors resulting from appearance potential measurements.[44] Wexler and Jesse[44] further state that if reaction (38) is accepted, then the molecular yield of hydrogen per ion pair becomes 1.4, larger than the experimental value of 0.9. The concentration of CH_5^+ as a function of pressure in the mass spectrometer source chamber is seen to reach a maximum at approximately 0.15 mm and then drops to a limiting value at 0.5-mm pressure.[44] At this same time, the concentration of $C_2H_5^+$ is seen to rise steeply as a function of pressure, although not as steeply as would be expected. This is most likely due to scattering in the source chamber at the relatively higher pressures. The results were not corrected for this.

The variation in the molecular hydrogen yield per ion pair can be easily explained. Discussions of the radiolysis of methane at low conversions[32] reveal that hydrogen formation, or $G(H_2)$ decreases from 6.47 to a limiting value of 5.6 to 5.7. In addition, calculations, such as are on page 79 regarding this system, show that the tritium molecule is the reactant in the radiation-induced labeling, rather than the T atom or the T^+ ion. Relating this to a system of methane under radiolysis, it is clear that initial yields of hydrogen disappear by reaction with radicals from CH_4 radiolysis. Further, on radiolysis of CH_4-CD_4 mixtures, Spittler, Jordan, Dorfman, and Sauer[49] observed a certain percentage of HD was formed which could not be scavenged by NO or C_2D_2. They concluded that the HD was the product of a bimolecular process involving four possibilities, one of which is discussed in the following section concerning the reactions of CH_3^+. Another was based on CH_4D^+ (or CD_4H^+), formed analogous to reaction (37). These investigators then state that there are two series by which HD could be formed from CH_4D^+ (or CD_4H^+). The first of these is reaction (38), and the other is:

$$CH_4D^+ + e^- = CH_3 + HD$$
$$CD_4H^+ + e^- = CD_3 + HD \qquad (38a)$$

Of the two alternatives reaction (38) is chosen by this group.[49]

Thus, in view of the mass spectrometric evidence,[44] the hydrogen yields in the radiolysis of methane at low conversions,[32] and the observance of a bimolecular process in methane radiolysis to produce unscavengeable hydrogen,[49] reaction (38) does occur.

An alternative to the scheme involving reactions (37) and (38) would be:

$$(CH_4^+)^* + CH_4 = C_2H_5^+ + H_2 + H \qquad (39)$$

Fayard[15] states that this reaction is exothermic if the excitation energy of the CH_4^+ ion is greater than 9 kcal/mole.

The $C_2H_5^+$ ion is then neutralized and decomposes:

$$C_2H_5^+ + e^- = (C_2H_5)^*$$
$$(C_2H_5)^* = (CH_3)^* + (CH_2)^* \qquad (40)$$

The series based on the CH_3^+ ion begins with the formation of the ion:

$$CH_4 = CH_3^+ + H + e^- \qquad (41)$$

then

$$CH_3^+ + CH_4 = C_2H_5^+ + H_2 \qquad (42)$$

$\Delta H_r = -20$ kcal/mole, and is observed to occur at every collision in the mass spectrometer.[6,45] Next, neutralization and breakup occur:

$$C_2H_5^+ + e^- = (C_2H_5)^* = (CH_3)^* + (CH_2)^* \qquad (43)$$

For ionization to form CH_2^+ and subsequent reactions, the scheme is:

$$CH_4 \rightsquigarrow CH_2^+ + H_2 + e^- \qquad (44)$$

then

$$CH_2^+ + CH_4 = C_2H_5^+ + H \qquad (45)$$

Reaction (45) has a value of $\Delta H_r = -41$ kcal/mole. It is one of several that may happen.[15] Others are:

$$CH_2^+ + CH_4 = CH_3^+ + CH_3 \quad \Delta H_r = -21 \text{ kcal} \qquad (45a)$$

and

$$CH_2^+ + CH_4 = C_2H_4^+ + H_2 \quad \Delta H_r = -12 \text{ kcal} \qquad (45b)$$

Reactions (45) and (45a) are the most probable. Reaction (45) is followed by neutralization and decomposition,

$$C_2H_5^+ + e^- = (C_2H_5)^* = (CH_3)^* + (CH_2)^* \qquad (46)$$

Reaction (45a) results in a two-step process:

$$CH_3^+ + CH_4 = C_2H_5^+ + H_2 \qquad (47)$$

$$C_2H_5^+ + e^- = (C_2H_5)^* = (CH_3)^* + (CH_2)^* \qquad (48)$$

The processes involving CH^+ and C^+ as products of the ionization of CH_4 are neglected.

The series following the excitation of methane is not so involved and is simply the two reaction previously stated:

$$CH_4 \rightsquigarrow CH_3 + H \tag{49}$$

and

$$CH_4 \rightsquigarrow CH_2 + H_2 \tag{50}$$

The overall $G(-CH_4)$ is 9.6 with 57% loss occurring by ionization and 43% by excitation. The initial yields for ionization and excitation reported gave a total of 6.37. No estimate for recombination of methyl radicals and hydrogen atoms to yield initial compound can be made. Then, use of 9.6, rather than 6.37 is of little consequence. The yields of radicals from the above reactions are much greater than 9.6. Subsequent reactions by the radicals from the ionization series may involve recombination to form methane by

$$CH_3 + H + M = CH_4 + M^* \tag{51}$$

$$CH_2 + H_2 + M = CH_4 + M^* \tag{52}$$

Reaction (51) is well-known and reaction (52) has been shown to be the predominant methylene reaction once the radical has been thermalized.[53] Above 100°C, the reaction of methylene with hydrogen is[53]

$$CH_2 + H_2 = CH_3 + H \tag{53}$$

which can then give back methane by reaction (51).

Ionization consumes 5.47 molecules of CH_4 per 100 eV of energy absorbed; excitation, 4.13. The total $G(-CH_4)$ of 9.6 gives the rate of destruction of methane as

$$\frac{-d(CH_4)}{dt} = 1.21 \times 10^{12} \text{ molecules } CH_4 \text{ destroyed/mC-min} \qquad (54)$$

From the ionization series, $G(-CH_4)=5.47$. Formation of CH_4^+, 51% abundance, gives 3 methyl and 1 methylene radicals. CH_3^+, formed in 40% abundance, yields 1 methyl and 1 methylene radical. From CH_2^+ as the initial ion, in 4% abundance, 2 methyl and 1 methylene radical are obtained if one considers the reaction that gives the largest radical yield, reaction (45a) and those following. Excitation gives 50% methyl radicals and 50% methylene radicals based on a $G(-CH_4)_{ex}=4.13$. The results are shown in Table IV. Then, G(radicals)=17.5. As a result, the rate of production of radicals is:

$$\frac{d(\text{radicals})}{dt} = 2.21 \times 10^{12} \text{ radicals/mC-min} \qquad (55)$$

The excited methyl and methylene radicals then may react with tritium:

$$(CH_3)^* + T_2 = CH_3T + T \qquad (56)$$

$$(CH_2)^* + T_2 = CH_2T + T \qquad (57)$$

On the basis of bond energies, both reaction (56) and reaction (57) are endothermic by an energy of approximately 15-20 kcal/mole. This is found by comparing the hydrogen abstraction reaction of methyl radicals from methane giving a reported value for the energy of activation of 14.8 kcal/mole[54] and including the difference in the binding energy for C-H and C-T.

Table IV. Initial radical yields from radiolytic decomposition of methane.

Precursor	%	Methyl radicals	Methylene radicals
A. Ionization			
CH_4^+	51	(2)(0.51)(5.47)=5.58	(1)(0.51)(5.47)=2.79
CH_3^+	40	(1)(0.40)(5.47)=2.19	(1)(0.40)(5.47)=2.19
CH_2^+	4	(2)(0.04)(5.47)=0.44	(1)(0.04)(5.47)=0.22
B. Excitation			
CH_3	50	(1)(0.50)(4.13)=2.06	
CH_2	50		(1)(0.50)(4.13)=2.06
Total		10.27	7.26

The methyl and methylene radicals are formed in excited states, most probably translationally excited, each having an energy of 65 kcal/mole (the ΔH for neutralization of $C_2H_5^+$ is -131 kcal/mole). Three non-reactive collisions would be necessary to degrade these radicals below the energy of activation to react with tritium, reaction (56) and (57).

In addition, reaction of these species with T_2 gives a T radical which may combine with CH_3, CH_2, or H to give product or product precursor. Abstraction of H atoms from methane

$$T + CH_4 = HT + CH_3 \qquad (58)$$

is not an important reaction to remove the T atom. Reference to Figs. 11, 12, and 40 reveal this. Were H atom abstraction from methane by the T atom an important reaction, the rate of production of HT shown in Fig. 40 would follow the same shape as that for production of labeled methane and ethane. Also, the rate of production of HT in Figs. 11 and 12 would not be as large since the radiation labeling has been suppressed. H atoms formed from the radiolysis of both methane and hydrogen would react with the methane present in a concentration ratio of 2×10^3 greater than that of T_2. Finally, Firestone et al.[55] investigating the tritium beta-ray sensitized exchange of deuterium with methane observed no evidence to indicate H atom abstraction as a primary process.

These radicals formed can react with themselves, with the methane present, or with ions as well as the tritium. In order to substantiate reactions (56) and (57) as the primary ones in the radiation series, a radical concentration within an order of magnitude of the sum of the coefficients of the observed second-order constants, $9.36 \times 10^9 + 2.18 \times 10^{10} = 3.12 \times 10^{10}$ T incorporated/mC-min is necessary. This must be modified by the ratio of methane to tritium, 2×10^3. Then, the necessary radical concentrations are $\simeq 6.2 \times 10^{13}$ per mC-min.

The calculated radical concentrations are 2.2×10^{12}/mC-min. On the average, this must be increased by a factor of three to account for the number of collisions necessary to de-excite the radicals below the energy needed to react with tritium. An additional factor of two must be added since reactions (56) and (57) produce a reactive T atom.

The result is $(2.2 \times 10^{10})(3)(2) \cong 1.3 \times 10^{13}$ radicals/mC-min. This is definitely within the desired range. In addition, it must be noted that the methylene radical as formed is in a highly excited singlet requiring fifty or so collisions to bring it to the lowest excited triplet and a remaining four hundred or so to bring it to the singlet ground state.[53] These transitions are symmetry-forbidden. A consequence of this could be

$$(CH_2)^* + CH_4 = (C_2H_6)^{**} = 2CH_3 \qquad (59)$$

to increase the radical concentrations. However, collisional deactivation of the excited ethane would be thought to occur. The result above does not consider the number of collisions to deactivate the methylene radical. This could bring the quoted rate of radical production even nearer to the observed magnitude of the radiation-induced labeling.

The reaction schemes involving CH_2, CH_3, T_2, and T which give radiation-labeled methane and ethane are given below.

<u>The labeled methane from the radiation</u> is produced from

$$(CH_3)^* + T_2 = CH_3T + T \qquad (60)$$

or by combination of the methyl radicals and T atoms

$$CH_3 + T + M = CH_3T + M^* \qquad (61)$$

The tritiated ethane may be produced by reactions of the type:

1) Methylene insertion into previously labeled methane.

$$(CH_2)^* + CH_3T = C_2H_5T \tag{62}$$

2) Excited ethyl radical attack on tritium.

$$(CH_2)^* + (CH_2)^* = (CH_2\text{-}CH_2)^{**} \tag{63}$$

$$(CH_2\text{-}CH_2)^{**} + H = (C_2H_5)^{**} \tag{64}$$

$$(C_2H_5)^{**} + T_2 + M = C_2H_5T + T + M^* \tag{65}$$

or the excited ethyl radical may be formed from reaction between thermalized radicals,

$$CH_3 + CH_2 = (C_2H_5)^* \tag{66}$$

3) Combination of ethyl radicals and T atoms.

$$C_2H_5 + T + M = C_2H_5T + M^* \tag{67}$$

4) Combination of a labeled and an unlabeled methyl radical.

$$CH_2T + CH_3 + M = C_2H_5T + M^* \tag{68}$$

Doubly-labeled ethane may be formed by:

5) Attack of excited ethylene, which is produced in reaction (63), on tritium:

$$(CH_2\text{-}CH_2)^{**} + T_2 + M = C_2H_4T_2 + M^* \tag{69}$$

6) Methyl radical combination.

$$CH_2T + CH_2T + M = C_2H_4T_2 + M^* \qquad (70)$$

The chain terminating reactions are combination of the methyl radicals,

$$CH_3 + CH_3 + M = C_2H_6 + M^* \qquad (71)$$

and methylene insertion which can be considered to be the method for the buildup of higher hydrocarbons

$$(CH_2)^* + CH_4 = C_2H_6 \qquad (72)$$

$$(CH_2)^* + C_2H_6 = C_3H_8 \qquad (73)$$

and, as the concentration of hydrogen produced by radiolysis of the methane increases, reaction (60) through (70) involve it rather than tritium.

Reaction (71) is about twice as rapid as reaction (63), but both happen at the first collision.[18]

In view of the concentrations of the various species present, that is, the radicals, the molecular tritium, and the tritium atoms, the predominant reactions for formation of mono-labeled methane are reactions (60) and (61). Again considering the concentrations, ethane, labeled by the radiation series, is primarily formed by five of the six reactive series. Methylene insertion, reaction (62), results in the formation of singly-labeled ethane at the expense of the methane previously formed. That this reaction takes place is evident from inspection of the ratios of mono-tritiated products, CH_3T/C_2H_5T, is 1.12/1.40, or 0.79, whereas the CH_3/CH_2 ratio is 1.41.

From the work of Maurin,[16] the production of CH_3 radicals by excitation and ionization is 20% greater than that of CH_2. The ratio from the proposed scheme is 1.4:1. Thus, the steady state concentration of methyl relative to methylene should be greater. Reaction (60) would be expected to proceed more rapidly than the series, reactions (62) through (70). Since the ratio of singly labeled methane to singly-labeled ethane is less than one, methylene insertion takes place and reduces the concentration of tritiated methane.

The large concentration of H atoms in the system and the diradical nature of the $(CH_2\text{-}CH_2)^{**}$ makes reactions (64) and (65) possible.

The $C_2H_4T_2$ is mainly formed by reaction (69). In support of this reaction, Hauser[14] stated that the $G(C_2H_4)$ may be as high as 1.1 at low conversions of methane. In the radiolysis of mixtures of methane and the noble gases in the presence of iodine, Meisels, Hamill and Williams[13] obtained a $G(C_2H_4)$ from 26% to 77% that observed for the formation of hydrogen. They were also able to demonstrate the presence of ethylene and acetylene by the use of a cold finger at liquid nitrogen temperature during the radiolysis of methane. A value about three to four percent of the hydrogen value was found in this manner. However, the efficiency of the trapping could not be evaluated. Gevantman and Williams[59] demonstrated with the presence of iodine scavenger that methylene radicals are definitely present. Lind[12] states that the ethylene as originally formed has two free valences which explains the rapid polymerization to higher hydrocarbons.

Goldfarb and Pimentel[56] observed a luminescence in the study of the photolysis of diazomethane at 16,700 cm^{-1}. They assigned this to an excited state of ethylene, which then decays to a lower excited state on emission of radiation. Since $\Delta H = -122$ kcal/mole for the reaction

$$2CH_2 = (C_2H_4)^* \qquad (74)$$

the investigation was restricted to excited states in this region. There are three; T, the first excited triplet state of ethylene, V, the first excited singlet, and Z, the second excited singlet. The ground state is denoted by N. Transitions between the non-planar configuration of the three excited states and the planar configuration of the ground state are symmetry forbidden. The observed emission was assigned to the Z → V transition of excited ethylene from the recombination of methylene radicals or by:

$$CH_2 + CH_2N_2 = C_2H_4^* + N_2 \qquad (75)$$

Setser et al.[57] investigating the mercury sensitized photolysis of ethylene estimated that, based on the ΔH_f of CH_3CH, a singlet ethylene formed from ethylidene should have an energy greater than 100 kcal/mole. Reactions of this excited state were seen. Parr[58] calculates a π-π^* transition energy of 6.0 eV using the experimental values that the π-π^* singlet is 7.6 eV and the π-π^* triplet is 4.6 eV. In view of these results, the second excited ethylene singlet has sufficient energy to react as in reaction (69) to produce doubly-labeled ethane.

It is obvious that normal ethylene cannot be excited to the non-planar configuration, since the transition is forbidden. Also, it cannot react with tritium to produce tritiated ethane unless this excitation energy is present. Experimental results confirm this.

Reaction (70) is not the source of di-tritiated ethane since the relative concentration of CH_2T is so small. The double labeling must occur in a one-step process with molecular tritium as the reactant, such as reaction (69).

C. Xenon Effect

Xenon, added to the system, increases the rate of labeling of methane and ethane by 15% in the second term of the rate expression as shown in Fig. 42. It also increases the amount of other labeled hydrocarbons, as shown in Table I. Further, on HT analysis, it was shown that the amount of HT present increased by 13% with 15 mol% of xenon present.

Consistent with these observations, the increase must be due to the sensitization of a common precursor for all products. The initial reactions in the radiation induced series, reactions (36) to (48), yield the most radicals. The xenon effect is a result of the enhancement in the primary yield of CH_4^+, CH_3^+, and CH_2^+. This is in agreement with the results of Field and Franklin.[25] Xenon is both ionized and excited to the $(^2P_{1/2})$ of the doublet lowest level in the ion. This state has an ionization potential of 13.44 volts, while that of methane is 13.02 volts. Charge exchange occurs:

$$Xe \rightsquigarrow Xe^{\dagger} \tag{76}$$

$$Xe^{\dagger} + CH_4 = (XeCH_4)^+ + e^- \tag{77}$$

The $(XeCH_4)^+$ is a transient species which cannot be observed. The following reactions then take place:

$$(XeCH_4)^+ = \begin{cases} XeH^+ + CH_3 \\ XeCH_3^+ + H \\ XeCH_2^+ + H_2 \end{cases} \tag{78}$$

This enhances the concentration of the primary ions and radicals in the radiation series. These ions and radicals then react as in the preceding section.

The general shape of the curve in Fig. 42 is dependent upon the amount of xenon present and the amount of energy that it absorbs.

The linear absorption coefficient of xenon is 33.4 cm^{-1}, while that of methane is 8.4 cm^{-1}. The reaction:

$$Xe^{\dagger} + Xe = Xe_2^{+} + e^{-} \qquad (79)$$

is nine times more probable than reaction (77).[28] At lower xenon concentrations, reaction (76) takes place along with the normal radiolytic reactions of methane. As the concentration of xenon is increased absorption of energy by the xenon decreases the primary yield from the radiolysis of methane, but formation of the $(XeCH_4)^+$ intermediate increases to a greater degree. Finally, above 30 mol% xenon, energy absorption by the xenon decreases the primary radiolytic products, reaction (79) takes place and overall production of CH_4^+, CH_3^+, and CH_2^+ ions is decreased. This results in the decrease in the observed yield.

In the surface-to-volume experiments, xenon becomes an inhibitor of the reaction at 5 mol% concentration. Wall collisions deactivate the $Xe^{\dagger}$, and reduce the formation of $(XeCH_4)^+$. The ground state xenon, with ionization potential of 12.2 volts, can then charge exchange with the CH_4^+ produced by the radiation to further inhibit the reaction.

D. Ethylene Effects

Ethylene, as a radical and ion scavenger in addition to being an excellent medium for charge exchange reduces the concentration of primary radicals and ions resulting in formation of polymer-like compounds. These could not be detected by the analytical system (refer to Table I). It has been reported that ethylene decreases the G values in the methane system under radiolysis and increases the formation of polymer by a factor of 10 at 3 mol% concentration.[32]

The reduction in labeled ethane indicates that the ethylene excited singlet state transition from the ground state cannot be

promoted by radiation. This would also be determined from symmetry considerations. Its suppressive action is to scavenge the radicals formed as well as reduce the concentration of ionic species.

Ethylene can react with the ion precursors of labeled product to form higher molecular weight hydrocarbons.

$$C_2H_4 + \begin{cases} C_2H_5^+ = C_4H_9^+ \\ C_2H_4T^+ = C_4H_8T^+ \end{cases} \qquad (80)$$

By consecutive ion-molecule reactions with methane, even higher weight products can be formed.

$$C_4H_9^+ + CH_4 = C_5H_{11}^+ + H_2, \text{ etc.} \qquad (81)$$

Sieck and Johnsen[32] noted that the addition of nitric oxide to the methane system under radiolysis had no effect on the G(polymer) and added ethylene enhanced G(polymer). This is consistent with an ion-molecule reaction series for polymer formation, substantiating reactions (80) and (81) and continuing the series.

Ethylene is a radical scavenger for H atoms and CH_2 radicals.

$$C_2H_4 + H = (C_2H_5)^* \qquad (82)$$

and

$$C_2H_4 + CH_2 = \begin{array}{c} CH_2 \\ / \quad \backslash \\ CH_2 — CH_2 \end{array}^* \qquad (83)$$

The excited cyclopropane may be stabilized by collisional deactivation, or may isomerize to propylene:[53]

$$\begin{array}{c} CH_2 \\ / \quad \backslash \\ CH_2 — CH_2 \end{array}^* = (CH_2 = CH - CH_3) \qquad (84)$$

If this occurs, it can then scavenge another methylene radical by forming methyl cyclopropane, and so on. The methylene radical will add to a double bond at almost every collision.[53] Ethylene is virtually unreactive with methyl radicals.

The scavenging effect of ethylene can be further explained by charge exchange from the ethylene to the HeT^+ ion, blocking formation of the CH_4T^+ ion and the remainder of the decay-labeling series.

The ions and radicals which must be considered are HeT^+, $C_2H_5^+$, CH_2, and H. From the radiation-induced series,

$$\frac{d(C_2H_5^+)}{dt} = (0.57)(9.6/100eV)(2.22\times10^9 d/mC)(5.69\times10^3 eV/d)$$

$$= 6.98\times10^{11}\ C_2H_5^+/mC\text{-}min \qquad (85)$$

This assumes that all reactions in the ionization portion of the radiation series form this intermediate. The concentration of the ethyl ion is the same as that for the methylene from this series, since neutralization gives a methyl plus a methylene. From the excitation portion of the radiation series, methylene radicals are formed in 50% of the events:

$$\frac{d(CH_2)}{dt} = (0.43)(0.50)(9.6/100eV)(2.22\times10^9 d/min)(5.69\times10^3 eV/d$$

$$= 2.6\times10^{11}\ (CH_2)/mC\text{-}min \qquad (86)$$

The rate of formation of HeT^+ is the decay rate of tritium, 2.22×10^9 HeT^+/mC-min. The rate of formation of H atoms relative to molecular hydrogen takes place in the ionization series when CH_3^+ is formed, and in the excitation part by formation of CH_3 to give a total value of $2.8 \times 10^{11} + 2.6 \times 10^{11} = 5.4 \times 10^{11}$ H atoms/mC-min. Each ethylene molecule is conceivably able to scavenge two H atoms, first by the formation of C_2H_5 and then to form C_2H_6. An upper limit for the ethylene "burn-up" can be obtained.

At 0.1 mol% concentration, the ethylene amount is 2.3×10^{16} molecules/cc. $d(C_2H_5^+ + HC_2 + HeT^+ + H)/dt = 6.98 \times 10^{11} + 2.60 \times 10^{11} + 2.22 \times 10^9 + 5.4 \times 10^{11}/2 = 1.23 \times 10^{12}$/mC-min. At the experimental concentration of 1 mC/cc, the ethylene will be completely reacted by

$$\frac{2.3 \times 10^{16} \text{ molecules/cc}}{(1.23 \times 10^{12} \text{ radicals + ions/mC-min.})(1 \text{ mC/cc.})}$$

or 1.87×10^4 minutes. The time at which an increase in the rate of production of labeled products as seen in Fig. 36 is between 2.0 and 2.5×10^4 minutes. This value does not consider consecutive unsaturate formation, reaction (84), but is the maximum value. Portions of the other radicals can be scavenged by reaction with themselves. Addition of ethylene in amounts 0.2 mol% and greater suppressed labeled product formation even more than the mixture containing 0.1 mol%.

Reactions (80) to (84), as well as the inability of ethylene to scavenge methyl radicals, explain the general shape of the curves in Figs. 36 to 39. The formation of tritiated ethane is largely dependent on CH_2 radicals in the radiation-induced portion of the labeling. These are effectively scavenged by ethylene. When the ethylene has finally reacted, the methylene concentration increases and tritiated ethane is produced. If the $C_2H_5^+$ radical precursor does not react with the ethylene before neutralization and breakup, then the resulting methyl radicals can react with tritium. There is a slow rate of production of methane as a result. As the ethylene concentration decreases, more reactive methyls are formed from the decomposition of $(C_2H_5)^*$ while the methylene radicals are being scavenged. There is an increased rate of formation of tagged methane relative to labeled ethane. This also explains the observation that the labeled ethane yield follows that expected from the decay-induced series only near the end of the burnup of the ethylene. At this time,

tritiated methane is formed at a rate below that of the unscavenged system, but greater than the first-order term would predict.

E. Surface to Volume Effects

At the ratio of 2:1, the rates of production of labeled product can be interpreted by an increase in tritiated ethane from the radiation induced series, and a decrease in tagged methane from the same source. This is shown in Table I. The increased surface is deactivating the methyl radicals and the methylene insertion reaction, reaction (62), for which the ΔH_r is -61 kcal/mole, occurs at the expense of labeled methane. At this ratio, 92% of the tritium beta energy is absorbed in the gas.

At a ratio of 17:1, labeled methane production is greater than that of labeled ethane. The rate of incorporation of tritium into methane is linear, being equal to $4.69 \times 10^9 \ (T_2)_a$, while the decrease in ethane labeling is explained by a decrease of 84% in the second term coefficient. The amount of radiation absorbed in the gas is only 35% that in the normal reaction bulbs. The production of methylene radicals by the radiation field may be decreased markedly, while that of the methyl radicals might increase. If this were the case, then the cause for this would be the neutralization of the CH_5^+ ion precursor of the CH_2 at the surface. Then, decomposition and formation of methyl radicals only would take place:

$$CH_5^+ + e^- = (CH_5)^* = CH_3 + H_2 \qquad (87)$$

resulting in the production of more CH_3T by reaction (31). Another explanation more consistent with the observations in the system with the S/V ratio of 2:1, is deexcitation of the methylene radicals formed in the radiation series. Below 100° C, the predominant reaction of the methylene radical with hydrogen, or, in this case, tritium, is:[53]

$$CH_2 + T_2 + M = CH_2T_2 + M^* \qquad (88)$$

Since the surface is a highly efficient means of thermalizing excited species, reaction (88) is the more probable of the two. This reaction decreases the reactive methylene concentration that would normally lead to radiation labeled ethane. Further, since doubly labeled methane is formed, a much greater overall rate for tritium incorporation into methane would be anticipated.

Xenon, at 5 mol% concentration, exhibited a suppressing effect, inhibiting the formation of labeled ethane more than that of tritiated methane. Xenon no longer sensitizes the reactions in the radiation series because the excited xenon in reaction (77) is deactivated at the wall. In addition, charge exchange to the CH_4^+, as well as to the CH_5^+, decreases the formation of radicals which can react to form labeled methane and ethane as a result of the radiation.

V. CONCLUSIONS

The reaction between tritium and methane in the gas phase to produce labeled methane and ethane may be divided into a decay-induced series and into a radiation-induced portion.

A. The Decay-Induced Mechanism

$$T_2 = HeT^+ + \beta^-$$

$$HeT^+ + CH_4 = CH_4T^+ + He$$

$$CH_4T^+ + CH_4 = \begin{cases} C_2H_4T^+ + 2H_2 \\ C_2H_5^+ + HT + H_2 \end{cases}$$

$$C_2H_4T^+ + e^- = \begin{cases} (CH_3)^* + (CHT) \\ (CH_2T)^* + (CH_2) \end{cases}$$

$$(CH_2T)^* + CH_4 = CH_3T + CH_3$$

$$\text{or} \quad (CH_2T)^* + H + M = CH_3T + M^*$$

$$(CHT)^* + CH_4 + M = C_2H_5T + M^*$$

B. The Radiation-Induced Mechanism

$$CH_4 \rightsquigarrow \begin{cases} CH_4^+ + e^- \\ CH_3^+ + H + e^- \\ CH_2^+ + H_2 + e^- \\ CH_3 + H \\ CH_2 + H_2 \end{cases}$$

These radicals and ions react with methane to form $(CH_3)^*$ and $(CH_2)^*$, which then react with tritium to ultimately yield CH_3T, C_2H_5T, $C_2H_4T_2$

as well as labeled saturated hydrocarbons of higher molecular weight. These label-compounds, propane and above, are predominantly formed by methylene insertion into previously labeled compounds.

To contrast to an earlier investigation into the CH_4-T_2 system,[20] the labeling rate with no added hydrogen may be expressed by a two-term expression. In this expression for the rate of incorporation of tritium into labeled methane and ethane, the first term is independent of time, the decay induced portion, and the second is inversely proportional to time, the radiation induced portion:

$$\frac{d(\text{T stabilized in product})}{dt} = a(T_2)_a + b\,\frac{c(T_2)_a}{k_1 t + c}$$

in which

$$c = 1.03 \times 10^{16} \text{ molecules/mC}$$
$$k_1 = 7.00 \times 10^{11} \text{ molecules/mC-min}$$
$$a(\text{Methane}) = 1.17 \times 10^{9} \text{ T atoms/mC-min}$$
$$b(\text{Methane}) = 9.36 \times 10^{9} \text{ T atoms/mC-min}$$
$$a(\text{Ethane}) = 0.85 \times 10^{9} \text{ T atoms/mC-min}$$
$$b(\text{Ethane}) = 2.18 \times 10^{10} \text{ T atoms/mC-min}$$

The experimental results negate the existence of a 3/2 power term, as well as one which is squared. In addition, compared with the previous results, the rate of incorporation of tritium into labeled ethane is larger than that for methane. No definite explanation for this discrepancy can be offered.

C. The Effect of Xenon

In concentrations up to 30 mole percent, xenon enhances the products in the radiation induced series by sensitizing the ionization of methane:

$$Xe \rightsquigarrow Xe^{\dagger}$$

$$Xe^{\dagger} + CH_4 = (XeCH_4)^{+} + e^{-}$$

This is the value assumed in the discussion of the decay-labeling for the bond strength of C-T relative to C-H. The rate of reaction of normal and of isotopically substituted reactants, in the high temperature limit, reduces to the ratio of their reduced masses. This can then be restated to say that ultimately it is dependent on the relative bond strengths.

For the initial analysis involving hydrogen and deuterium transfer reaction, the basis of the above discussion, the reader is referred to the previously cited publications.

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