A mechanism for the disappearance of propane during methane radiolysis
by Daniel Thomas Rogers

A thesis submitted, to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University

Abstract:
The kinetics of gaseous methane radiolysis at room temperature using X-rays as a high energy source was studied using as a reaction chamber a glass syringe with a stopcock attached to it. The rate of disappearance of 1,3-C 14-propane and the rate of formation of C 14methane was studied as a function of energy absorbed.

The G values in ultra-high purity methane as a function of propane concentration (molec/cc) were determined to be: (Formula not captured by OCR) The presence of air in all samples and the sensitivity of the reaction to the presence of water pointed to an ionic mechanism for methane formation. Since the water concentration needed to be much greater than the propane concentration in order to reduce G(CH4) by 50%, it was concluded that the heavy ions involved in methane polymerization were the only ions which could reasonably explain why propane reacts more efficiently with a positive ion than does water. Thus, to explain the above equation for G(CH4), the following reactions were proposed: where X+ is a heavy polymerizing ion. The ΔH values were estimated from theoretical ΔHf values and adjusted to give reasonable consistency with the observed G values.

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in

Chemistry

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March, 1973

ACKNOWLEDGMENT

The author would like to express his appreciation for the time and encouragement generously given by Dr. Reed A. Howald, who directed this research.

Sincere thanks are also extended to my wife, Dinaz, who did what she could to help in the completion of this thesis.

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ABSTRACT

The kinetics of gaseous methane radiolysis at room temperature using X-rays as a high energy source was studied using as a reaction chamber a glass syringe with a stopcock attached to it.

The rate of disappearance of 1,3-C^{14}-propane and the rate of formation of C^{14}-methane was studied as a function of energy absorbed.

The G values in ultra-high purity methane as a function of propane concentration (molec/cc) were determined to be:

$$G(-C_3H_8) = 1.18 \times 10^{-15}[C_3H_8]$$

$$G(CH_4) = \frac{1.6[C_3H_8]}{[C_3H_8] + 2.5 \times 10^{15}}$$

The presence of air in all samples and the sensitivity of the reaction to the presence of water pointed to an ionic mechanism for methane formation. Since the water concentration needed to be much greater than the propane concentration in order to reduce $G(CH_4)$ by 50%, it was concluded that the heavy ions involved in methane polymerization were the only ions which could reasonably explain why propane reacts more efficiently with a positive ion than does water. Thus, to explain the above equation for $G(CH_4)$, the following reactions were proposed:

$$X^+ + C_3H_8 \rightarrow XC_2H_4^+ + CH_4 \quad \Delta H = -13 \frac{kcal}{mole} \quad (1)$$

$$X^+ + C_3H_8 \rightarrow XC_3H_6^+ + H_2 \quad \Delta H = 0 \frac{kcal}{mole} \quad (2)$$

$$X^+ + CH_4 \rightarrow XCH_2^+ + H_2 \quad \Delta H = +3 \frac{kcal}{mole} \quad (3)$$

where X^+ is a heavy polymerizing ion. The ΔH values were estimated from theoretical ΔH_f values and adjusted to give reasonable consistency with the observed G values.

This kinetic scheme predicts that at 300 ppm C_3H_8 the only polymerization reaction of importance proceeds by reactions (1) and (2). This apparently conflicts with previous literature studies, which indicate no dependence of CH_4 polymerization on reaction products (such as propane). These conflicts are explained by a reinterpretation of the data of previous studies.

INTRODUCTION

Much research has been done on the reactions which occur in methane exposed to high energy sources (such as α-particles, electrons, X-rays and γ-rays). Yet due to the diversity of reactions occurring, much more research will be done in the future. Such diversity is only hinted at when we consider that mass spectrometric and other studies[1] show the primary species produced to be: CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, H_2^+, H^+, CH_3, CH_2, CH, C, H_2 & H (along with electrons and very minute traces of negative ions). Of course, consideration of relative abundances and reactivities of these species will focus our attention only on reactions of a limited number of these species and thus simplify the task.

It should be additionally noted that the type of radiation in these studies will make only small differences in the product yields[2,3]. Thus we can compare data from one type of radiation to that of another and be fairly certain they represent the same reaction system. It is, however, not completely legitimate to compare gaseous radiolysis to condensed phase radiolysis (liquids and solids). In condensed phases the L.E.T. (Linear Energy Transfer) effect concentrates primary species (CH_4^+, H_2, etc.) in a limited region of the medium and increases the chances of reaction

between such primary species. In the gas phase, however, the high mobility of atomic and molecular entities allows primary species to quickly leave the site of their production and become mixed more or less homogeneously with the medium, greatly increasing the probability that the primary species will react only with the surrounding unexcited gas molecules.

The most important initial products in methane radiolysis are C_2H_6, H_2 and a highly branched polymer of the approximate composition $(CH_2)_{20}$.

Studies done on condensed phase methane show the polymer size varying from about 10 to 25 carbon atoms with only limited amounts of hydrocarbons being produced in the region between propane and decane[4-6]. These studies consider the polymerization mechanism to be similar in both gaseous and condensed phase radiolysis. Certainly the studies done on liquid argon solutions might be compared to a gas since argon may act as an inactive "solvent", keeping the methane molecules apart and thus simulating gaseous conditions at a temperature of 87°K.

It is presently considered that methane polymerization must be initiated by such highly energetic species as

C^+, CH^+ and possibly CH_2^+[4,5,7,8]. Since methane polymer yields are independent of the buildup of reaction products over a wide dose range (1-150 Mrad), polymerization seems to involve an ionic reaction with methane rather than with ethane or other reaction products.

There are two important mechanisms which have previously been considered in methane polymerization. The first is the classical stepwise buildup of polymer where the active species combines with one monomer molecule (i.e., methane) to form another active species which can react again:

$$X^+ + CH_4 \rightarrow XCH_2^+ + H_2$$

$$XCH_2^+ + CH_4 \rightarrow X(CH_2)_2^+ + H_2$$

$$X(CH_2)_{n-1}^+ + CH_4 \rightarrow X(CH_2)_n^+ + H_2$$

The second mechanism is the virtually instantaneous formation of polymer from an active species and a large number of monomer molecules. This might be represented by

$$X^+ + nCH_4 \rightarrow X(CH_2)_n^+ + nH_2$$

The word "instantaneous", as used above, implies that the intermediate ions (XCH_2^+, $X(CH_2)_2^+$, etc.) are

not completely formed before another CH_4 molecule collides with the reaction center around X^+. "Instantaneous" also refers to the low probability of observing the intermediate ions during mass spectrometric studies of methane radiolysis.

The latter mechanism is an ideal explanation for the absence of low molecular weight polymer (which could be formed after neutralization of the intermediate ions just mentioned). However, polymer formation requires 5-6 eV of energy to be formed from methane during solid phase radiolysis[4]. Therefore, the initiating ion, X^+, must provide this energy. Dilute methane solutions in liquid argon also give polymer. The argon excess would likely energetically deactivate the polymerizing species (X^+, XCH_2^+, etc.) long before methane molecules could react to form polymer. Thus, the mechanism must be rejected in the absence of a method to prevent deenergization. Auger election emission is a possible explanation[5]. Auger emission (246 eV electrons from carbon[5]) would provide for a high concentration of excited particles in a small volume thus insuring that the necessary energy is not dissipated through collision with thermal methane molecules. However, the same authors proposing this mechanism consider it unlikely since a mixture

of ethane and ethylene gave polymer of molecular weight similar to that of methane. Their argument is that since ethane and ethylene samples contain twice as many carbon atoms per unit volume there would be twice as many carbon atoms in the Auger emission area as there would be for methane, one would expect a doubling of the molecular weight. All that was observed was an increase in polymer yield.

Following this revelation, the first mentioned mechanism involving a stepwise ionic polymerization had to be considered. This mechanism had previously been considered inadequate on energetic grounds--the polymerizing ion would run down energetically long before incorporating 20 methane molecules. However, if an efficient energy transfer mechanism exists to re-energize the ion before it runs down, the mechanism would still be acceptable. Any of a number of ionic species previously mentioned might perform this transfer.

Methane seems to be an ideal medium for polymerization. The unusually high ionization potential of methane (12·5 eV) makes methane an excellent source of high energy ions as compared to other hydrocarbons. Also since methane in comparison to the heavy n-alkanes does not have its carbon atoms previously committed to a particular set of

carbon-carbon bonds, it can form a more highly-branched polymer than the heavy n-alkanes. Thus, on these two counts methane seems to be the n-alkane most likely to polymerize. Observations bear this out. Ethane and propane have polymer formulas corresponding to the incorporation of 11 and 5 hydrocarbon molecules, respectively. One should note that both ethane ($\frac{-20.2}{2}\ \frac{kcal}{mole}$) and propane ($\frac{-24.82}{3}\ \frac{kcal}{mole}$) have greater thermodynamic instability (as measured by enthalpies of formation, ΔH_f) per carbon atom than does methane ($\frac{-17.9}{1}\ \frac{kcal}{mole}$). This information by itself indicates that larger polymers could be formed with the heavier hydrocarbon (this is true in the case of ethane polymerization giving $C_{23}H_{46}$).

A number of mechanisms for formation of lower molecular weight products have been established. Hydrogen is formed primarily by the following mechanisms.

$$CH_4 \text{ (excited)} \rightarrow CH_2 + H_2 \qquad (1)$$

$$H\cdot + RH \rightarrow H_2 + R\cdot \qquad (2)$$

Where the RH is a suitable hydrogen donor--such as an alkane. It should be noted here that at room temperatures methane is considered to be a poor hydrogen donor while propane is an excellent one[9]. Studies indicate that steel walls of the

sample cell can effectively eliminate reaction (2) where RH is methane. Propane can, however, compete effectively with this hydrogen scavenging reaction at the walls.

Ethane and other alkanes are formed predominantly by radical recombination

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (3)$$

$$R + R' \rightarrow RR' \qquad (3a)$$

where R and R' are alkyl radicals. The radical recombination mechanism is confirmed by addition of radical scavengers such as NO or O_2 to the methane and noting the large reduction (85% or more) in alkane yields[10].

Addition of radical scavengers also increases alkene yields to detectable levels. This is understandable since alkenes are radical scavengers themselves, scavenging predominantly hydrogen atoms. Addition of another radical scavenger protects ethylene against further radical reactions.

Ethylene is formed mainly by the insertion reaction[11].

$$CH + CH_4 \rightarrow [C_2H_5]^{excited} \rightarrow C_2H_4 + H \qquad (4)$$

and possibly to a lesser extent by removal of a proton from $C_2H_5^+$[11]. It is also well known that disproportionation

reactions such as

$$C_2H_5\cdot + C_2H_5\cdot \rightarrow C_2H_6 + C_2H_4 \qquad (5)$$

and $$CH_3\cdot + C_2H_5\cdot \rightarrow CH_4 + C_2H_4 \qquad (6)$$

can produce ethylene.

Then in the absence of scavengers we have the following mechanism for ethylene removal

$$C_2H_4 + H \rightarrow C_2H_5 \qquad (7)$$

$$C_2H_5 + R \rightarrow C_2H_5R \qquad (3b)$$

Ionic reactions are also of importance in producing small molecules. The following ionic reactions are generally considered to be the important ones occurring in methane[12]

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \qquad (8)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \qquad (9)$$

$$CH_2^+ + CH_4 \rightarrow C_2H_4^+ + H_2 \qquad (10)$$

$$CH_2^+ + CH_4 \rightarrow C_2H_3^+ + H_2 + H \qquad (11)$$

followed by

$$C_2H_3^+ + CH_4 \rightarrow C_3H_5^+ + H_2 \qquad (11a)$$

$$CH_3^+ + 2CH_4 \rightarrow C_2H_7^+ + CH_4 \quad (12)$$

$$CH_3^+ + 2CH_4 \rightarrow C_3H_7^+ + 2H_2 \quad (13)$$

$$CH^+ + CH_4 \rightarrow C_2H_2^+ + H_2 + H \quad (14)$$

followed by further reactions of $C_2H_2^+$ to give probably $C_3H_3^+$.

Reaction (12) involves an extra CH_4 molecule to remove the excess energy which might decompose $C_2H_7^+$ to $C_2H_5^+$ and H_2. The intermediate ion involved in reaction (13) has not been identified. The relative intensities of the above mentioned end product ions at 1·9 mm pressure are, according to the mass spectrometric studies of Field and Munson[12]

CH_5^+	.452	$C_2H_6^+$	.024
$C_2H_5^+$	.349	$C_2H_7^+$	.0055
$C_3H_5^+$	.053	$C_3H_3^+$	.00036
$C_3H_7^+$	.028		

These ions can further react with other alkanes (such as ethane and propane) which may be present during radiolysis. It is found experimentally that of the five

most abundant ions just mentioned (which in comparison to their precursor ions are relatively inert toward methane). CH_5^+ reacts rapidly with ethane and propane[13].

$$CH_5^+ + C_2H_6 \rightarrow [C_2H_7^+] + CH_4 \rightarrow C_2H_5^+ + H_2 + CH_4 \quad (15)$$

$$CH_5^+ + C_3H_8 \rightarrow [C_3H_9^+] + CH_4 \rightarrow C_3H_7^+ + CH_4 + H_2 \quad (16)$$

$$\rightarrow C_2H_5^+ + 2CH_4 \quad (17)$$

$C_2H_4^+$ and $C_3H_5^+$ react rapidly with propane but not with ethane

$$C_2H_4^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_6^+ \quad (18)$$

$$C_3H_5^+ + C_3H_8 \rightarrow C_3H_6 + C_3H_7^+ \quad (19)$$

While $C_2H_5^+$ reacts rapidly with propane by hydride transfer

$$C_2H_5^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_7^+ \quad (20)$$

The following condensation reactions have been shown through mass spectroscopic studies to be important in radiolysis at high pressures (up to 200 mm)[6]

$$C_2H_5^+ + C_2H_6 \rightarrow C_4H_9^+ + H_2 \quad (21)$$

$$C_3H_7^+ + C_3H_8 \rightarrow C_6H_{13}^+ + H_2 \quad (22)$$

Additionally ion-cyclotron resonance studies confirmed the existence of reaction (21) and another reaction path[14]

$$C_2H_5^+ + C_2H_6 \rightarrow C_3H_7^+ + CH_4 \qquad (23)$$

The literature does not mention a similar reaction path for the propane reaction although it can be calculated to be more exothermic*[15] than the near thermoneutral reaction (22)

$$C_3H_7^+ + C_3H_8 \rightarrow C_5H_{11}^+ + CH_4 \quad (\Delta H = -9 \text{ to } -19) \qquad (24)$$

Exothermicity is considered to be a necessary though not sufficient condition for gas phase reactions to occur, although this may be circumvented by the presence of sufficient excitation energy in the ion reacting. Often exothermic reactions do not go. In addition to the possibility of a high activation energy requirement, a suitable reaction path may not be available. Molecular rearrangements may slow down or possibly eliminate a reaction. A recent example of this reaction slowdown is[16]

$$C_6H_{14} + C_2H_5^+ \rightarrow C_4H_9^+ + C_2H_4 + C_2H_6 \,.$$

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*Formation of the neo-pentyl cation is the only reaction not considered here ($\Delta H = +13 \frac{\text{kcal}}{\text{mole}}$).

This reaction goes smoothly except when the hexane involved is 2,3-dimethyl butane. Presumably a methyl migration is necessary for the reaction only in the case of this particular hexane isomer.

If one summarizes the typical ionic reactions found to occur in hydrocarbon radiolysis, we find (where RH_2 and $R'H_2$ represent alkanes)[7].

a. Hydride (H^-) transfer $RH^+ + R'H_2 \rightarrow RH_2 + R'H^+$

b. Proton (H^+) transfer $RH_3^+ + R'H_2 \rightarrow RH_2 + R'H_3^+$

c. H_2- transfer $R^+ + R'H_2 \rightarrow RH_2 + R'^+$

d. H_2 transfer $R + R'H_2^+ \rightarrow RH_2 + R'^+$

e. Condensation $RH^+ + R'H_2 \rightarrow RR'H_3^+$

f. Decomposition (fragmentation) of ions (typically occurring after reaction types b & c above)

Hydride transfer occurs when a more stable carbonium ion is formed (reaction 20). Proton transfer is favorable when $R'H_2$ is the heavier of the alkanes involved (reactions 15,16). Decomposition is an important reaction when no third body is available to stabilize the new highly excited ion.

Thus far we have traced various radical and ionic reactions to form other radicals and ions. What happens to these obviously unstable species once they reach a point of relative stability in the reaction scheme? The ion $C_2H_5^+$, for example, has a low degree of reactivity with methane. Generally its fate is discussed only in conjunction with higher alkanes (RC_2H_5) where hydride transfer occurs

$$C_2H_5^+ + RC_2H_5 \rightarrow C_2H_6 + RC_2H_4^+ \qquad (20a)$$

Some authors discuss the wall of the reaction cell as a sink for such unreactive species[3,6]. Electron neutralization of ions in the gas phase is reasonable only if another molecule X can remove the ionization energy excess that exists:

$$R^+ + e^- + X \rightarrow R\cdot + X^{(excited)}$$

Presently no general methods have been developed for direction detection of these neutralization reactions. The best methods for studying ion reactions, which involve the use of mass spectrometer, generally elucidate only ion-molecule reactions. Thus the fate of these ions of low reactivity is seldom discussed in methane radiolysis studies. The lower energy radicals of course are typically removed either

by recombination with another radical (reaction (3a)), or by disportionation reactions such as (5) and (6). Disportionation reactions can even be the most important mode of radical disappearance (as in the case of two t-butyl radicals reacting)[20].

Methane radiolyses are sometimes complicated by trace impurities. Oxygen, as an impurity, has the desirable property of suppressing radical reactions so that one can study the predominantly ionic reactions which remain. However, at high radiation doses, oxidation products such as CH_3OOH, CH_3OH, C_2H_5OH and HCHO can be formed[18]. These in turn may scavenge the ionic reactions one is trying to study. Traces of ethane (20 ppm) and higher hydrocarbons typically present in highly pure methane may introduce confusion as to whether methane or some other hydrocarbon is the direct source of certain ions[19]. Because of such impurities, the observations of heavy ions cannot be readily attributed to ion-molecule reaction sequences involving methane incorporation only. For example, the production of $C_6H_{13}^+$ could possibly be entirely attributed to reaction (22) in the presence of less than 1-7 ppm C_3H_8 impurity[19].

THE PROBLEM

The reactivity of low molecular weight alkanes during methane radiolysis has not been extensively studied. Thus, the observation that $C_3H_7^+$ is present in large amounts at pressures up to 200 mm focuses one's interest on propane, the only source from which this ion can be produced--through hydride transfer

$$C_2H_5^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_7^+ \qquad (20)$$

and protonation

$$CH_5^+ + C_3H_8 \rightarrow C_3H_7^+ + CH_4 + H_2 \qquad (16)$$

It is thus intended in this study to follow reactions of propane by the addition of C^{14}-labeled propane. The inspection of experimental rate equations for the disappearance of C_3H_8 and the formation of reaction products then should give information on possible mechanisms.

In order to test the importance of $C_3H_7^+$ as an intermediate in propane reactions forming other neutral products, one can add the ion scavenger H_2O. Water might be expected to slow $C_3H_7^+$ reactions by a complexation reaction such as

$$C_3H_7^+ + H_2O \rightarrow C_3H_7(H_2O)^+$$

or even slow the aforementioned reactions (16) and (20) which produce $C_3H_7^+$.

The importance of radical reactions involving C_3H_8 can be tested by the addition of radical scavengers such as NO or O_2 (which would slow radical reactions).

Kinetic measurements involving decreases in the C^{14}-propane peak and increases in C^{14}-product peaks can be readily achieved using gas chromatography for chemical separation and a proportional counter through which the samples flow and are counted. Using an irradiation chamber (containing methane doped with C^{14}-propane) from which precisely measured samples can be removed from time to time, one can determine reaction rates as a function of energy absorbed.

Past methods involved the use of a number of samples, each containing enough gas for only one analysis. To follow the course of reaction, samples which may have had significant differences in gaseous content, were irradiated to different degrees and the kinetics followed as a function of energy from one sample to the next. Thus, data scattering could produce large uncertainties in the kinetic data. In this experiment, scatter will hopefully be minimized since concentration data points are all obtained on the same sample, giving more reliable kinetic data.

EXPERIMENTAL PROCEDURES

The sample tubes were constructed by fastening a stopcock and ground ball joint onto a BD Yale 30 ml syringe (Fig. 1). Either a stopcock tension clip or two retainer clips were used to insure that high pressures would not force channels to form in the vacuum grease (Dow Corning vacuum grease silicone lubricant) used in the stopcock. This vacuum grease was also used to make an airtight seal between the syringe and its plunger.

The vacuum system (with vacuum pump and mercury diffusion pump) used to prepare methane samples is pictured in Fig. 2, all stopcocks were greased with the Dow Corning grease previously mentioned. To test for leaks in the systems, a Tesla coil was used. Methane stored in the vacuum system was periodically flushed out to insure purity. The $LiAlH_4$ chamber was prepared by pouring a diethylether suspension of $LiAlH_4$ onto a glass wool plug and then removing the ether under vacuum.

To prepare radioactive propane samples, the $LiAlH_4$ chamber was cooled in liquid N_2 and then opened briefly to a chamber containing $\underline{1,3\text{-}C^{14}}$ isopropyl iodide (obtained from Amersham Searle Corp. in activities of 4.9 or 10.3 $\frac{mc}{mmol}$).

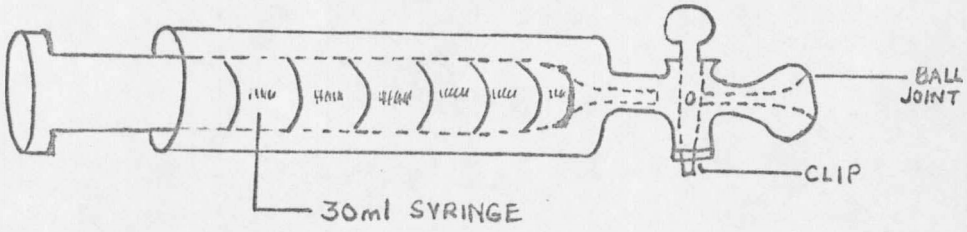

Fig. 1. The Sample Tube

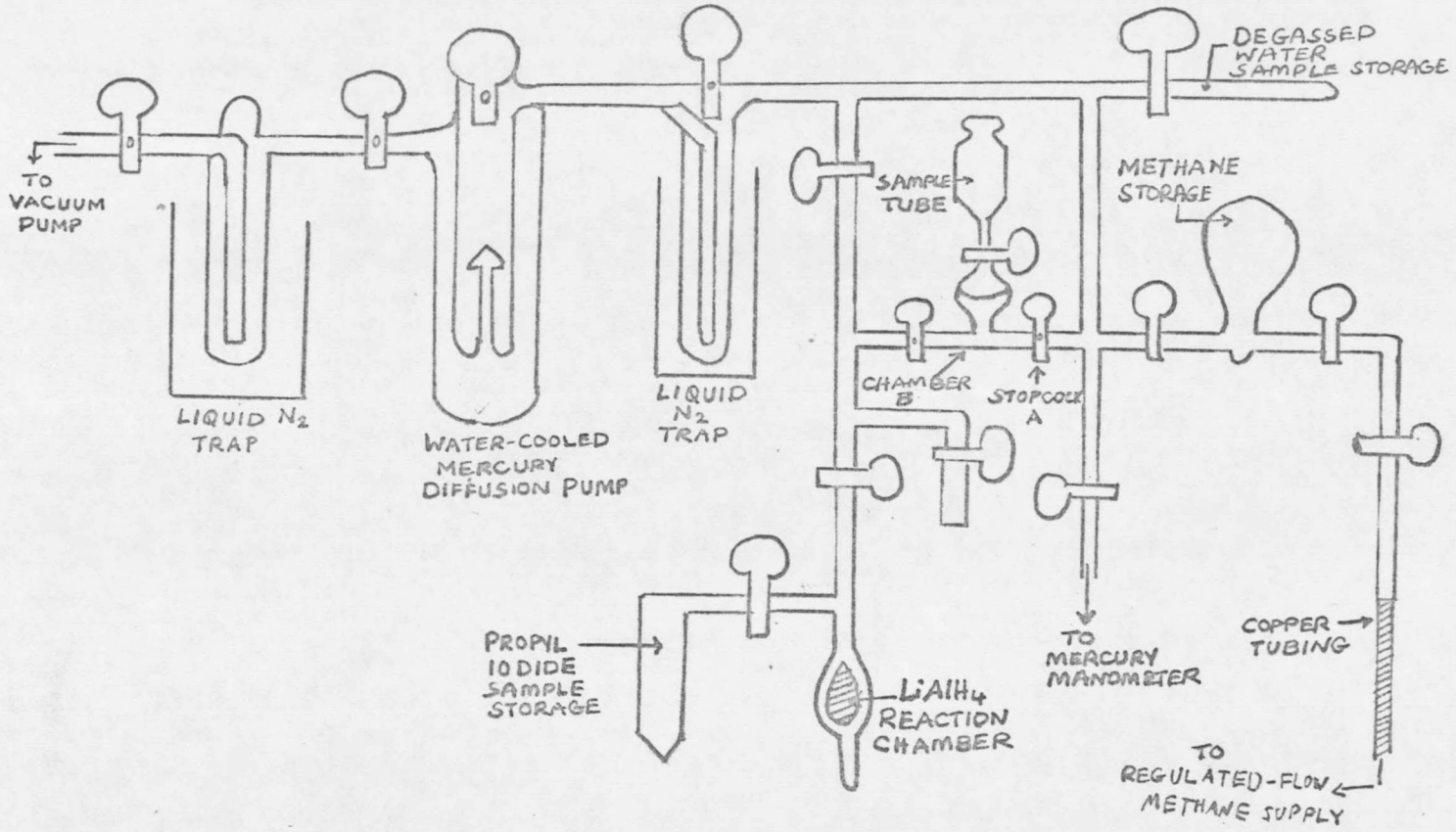

Fig. 2. The Vacuum System

A portion of the $LiAlH_4$ chamber was intermittently warmed and cooled to permit mixing which would allow the iodide time to find a reactive site in the chamber. Occasionally, the presence of methane during sample preparation allowed formation of considerable amounts of propene which disappeared only after a long reaction time.

Time dependence for the disappearance of propene is demonstrated in Table I as a function of the $[C_3H_6]/[C_3H_8]$ radioactive count ratios in consecutively filled samples.

TABLE I

PROPENE DISAPPEARANCE IN $LiAlH_4$ CHAMBER

Time (Hrs.)*	$[C_3H_6]/[C_3H_8]$
0	.367
1	.082
528	.000

* Since this reaction was not being studied, the exact time was not recorded.

The propane sample prepared was transferred to the sample tube by cooling chamber B below the tube and allowing propane to condense into it. On warming, the propane was swept into the sample tube by a stream of methane creating a final pressure of between 600 and 700 mm Hg. The sample

tube was evacuated before filling, while the plunger was held in place by a hose clamp holding a band of rubber around the plunger. Except for the earliest experiments, prior to using each sample tube it was wiped clean of vacuum grease in order to remove possible residues from a previous sample.

Methane samples used were CP grade and Ultra High Purity from Matheson. Typical impurity analyses of these samples are listed in Table II and are taken from the Matheson Gas Data Book[21].

TABLE II

METHANE IMPURITY ANALYSES

Compound	CP Grade	Ultra High Purity
Methane	99.1 %	99.98 %
O_2	50 ppm	8-10 ppm
N_2	6000 ppm	40-50 ppm
C_2H_6	1200 ppm	20-30 ppm
CO_2	2000 ppm	40-50 ppm
C_3H_8	300 ppm	5 ppm
H_2O	not listed	4-6 ppm

In order to add known amounts of air to the samples, air was admitted (passing through a $CaCl_2$ tube for drying) to a manometrically measured pressure. Stopcock A was

closed with air inside the bore and the remaining air pumped out of the system. This air was flushed into the sample tube by a stream of methane during methane addition. The final air pressure in the sample was approximately 1·0% of the manometer reading.

Degassed H_2O was admitted to the sample tube and chamber B while noting the manometer pressure reading. Then methane flushed through chamber B effectively gave a true H_2O pressure in the sample of about 20% higher than the originally observed manometric H_2O pressure.

Methane samples prepared by the above techniques were irradiated with X-ray energies up to 225 KeV from a G.E. Maximar 250-III. The voltmeter reading under load was 195 volts at a current of 15 ma. The samples were placed on a table located 17 cm from the face of the X-ray machine. To prevent vacuum grease deterioration, lead sheets were placed over parts of the sample which did not contain gas to be irradiated. The X-ray machine was monitored to insure a relatively constant dose rate. After each irradiation, samples were analyzed by a method to be mentioned later.

Dosimetry was done with 1M $FeSO_4$ solutions placed in 10 ml Erlenmeyer flasks. The absorption at 305 mμ was used to calculate the change in Fe^{+2} concentration using the equation in Radiation Chemistry of Gases[3] and multiplying

this by the ratio of X-ray attenuation coefficients for methane and H_2O[22] ($\mu CH_4/\mu H_2O = 1.11$). The dose rate was determined to be 5.3×10^{17} eV per 55 min interval (55 minutes is redefined as an hour in this study).

The analytical system for measuring radioactivity in the methane samples was an Aerograph A-90-C gas chromatograph equipped with a gas sampling valve and a radioactivity monitoring (RAM) system attached to the exhaust. This RAM system consisted of a Barber-Colman furnace module to convert all carbon to CO_2, followed by a proportional counting tube module through which flowed the carrier gas (helium) and a quench gas (commercial grade propane). Helium flows through the entire analytical system while propane enters the system just before the proportional counter. Three recorders were available to measure (1) GC (Aerograph) heat conductivity sensitive trace, (2) proportional counter radioactive peak trace (from Nuclear Chicago Single Channel Model 8731 and Amplifier Discriminator, and (3) a pulse for every 100 counts (from a modified Nuclear Chicago Educational Scaler Model 8770).

The gas sampling valve is attached to the sample tube through a 1/8" copper tubing to the injection chamber pictured in Fig. 3. The vacuum pump used to evacuate the

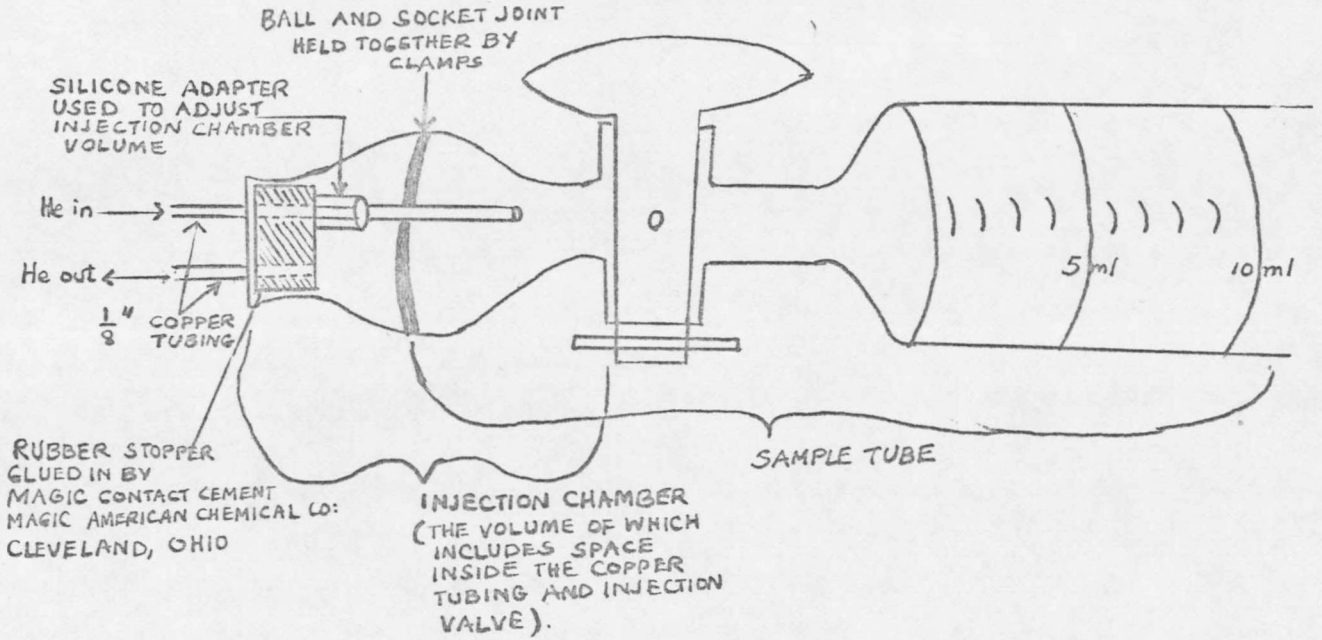

Fig. 3. The Injection Chamber

injection chamber takes residual gas pressures down below the air detection limits of the GC detector.

The injection chamber volume was adjusted to 2·0 ml by adding silicone rubber adaptors to the copper tubing in the chamber. Accurate adjustment to 2·0 ml was obtained by successively analyzing 2·0 ml air samples obtained from the syringe and noting the change in the GC air peak height. If the change in peak height all the way down to 0·0 ml volume in the syringe appeared to be negligible except for random fluctuations, the chamber volume was considered to be 2·0 ml. It is believed, however, since successive air injection series did not always give the same results, that redistribution of vacuum grease within the system gives some degree of uncertainty (this uncertainty is usually estimated at less than 0·05 ml).

Samples (both in volume calibration and regular analysis) are transferred from the sample tube (i.e., the BD syringe) into the injection chamber by the following procedure: (1) evacuation of injection chamber by a vacuum pump, (2) opening of stopcock between syringe and injection chamber, (3) pushing syringe plunger in by 2·0 ml, and (4) reclosing stopcock.

In a typical analysis it is found that residual radioactivity remains in the injection chamber after a previous run (even after evacuating all gas from the chamber). Thus, except for earlier samples, the chamber was always swept out with helium (pressure 40 lbs. above atmospheric pressure) in between runs to reduce this residual.

The column in the GC was Poropak Q from Waters Associates, Inc.

Absolute radioactivity of methane samples was determined by calibration with radioactive toluene ($3{\cdot}7 \times 10^5$ dpm/ml) injected with 10 µl syringes through the teflon injection port. On typical runs at 40 ml/min helium flow and 10 ml/min propane flow with a proportional counter voltage of either 1850 or 1900 volts, the following data was obtained (after subtracting background of typically 35 counts/minute):

ml toluene	counts
$7{\cdot}85 \times 10^{-3}$	501
$8{\cdot}7 \times 10^{-3}$	653

From this a typical $10{\cdot}3 \frac{\text{curie}}{\text{mole}}$ propane sample of C counts was determined to have a concentration of

$$[C_3H_8] = 9.8 \times 10^{10} \text{ C } \frac{\text{molec}}{\text{cc}} \pm 10\%$$

Retention times of radioactivity peaks detected by the counter occurred typically 30 seconds or more later than GC detector peaks. With longer retention times on the same compound, the difference in retention times increased. Checks on the retention times were made by comparison to literature on Poropak columns[23]. Propene and propane peak separations with small overlap were obtained only at 75°C.

Carrier gas (helium) flow was 40 ml/min and quench gas 10 ml/min in all except some of the earlier experiments. The total gas flow through the proportional counter (50 ml/min) was never recorded to vary by more than 3 ml/min during a one hour analysis. Occasionally quench gas flow varied by up to 1 ml/min. Counting efficiencies were observed to be affected predominantly by changes in the total gas flow through the counting tube.

EXPERIMENTAL RESULTS AND INTERPRETATIONS

The original intent of this work was to study the reactions of C^{14}-labeled compounds in pure methane. However, gas chromatographic analyses of the samples indicated that they contained approximately 0.1 to 0.5% air (even in ultra-high purity (UHP) methane). The reproducibility of these percentages from one measurement to the next was such that they could not be considered quantitative. Thus, since oxygen (a radical scavenger) in the samples will have a considerable effect on the course of reactions in methane, air was at times added as a check on the presence of oxygen. Such additives had no effect (air additives did not exceed 0.2%) indicating either that sufficient oxygen was already present to scavenge all radical reactions, or that the reactions studied did not involve radicals. In either case, we are not concerning ourselves with the study of radical reactions.*

Kinetic data was obtained in this experiment exclusively from C^{14}-labeled compounds. On obtaining this data for each run, it was fed into the computer to determine

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*Meyers and Schmidt-Bleek[24] find that even at 11 ppm O_2, the rate of ethane production via the radical route is essentially reduced to zero.

the best least squares fit to a straight line. Straight lines are expected to be a good instantaneous measure of a reaction rate at any given time during a kinetic run when only a relatively small amount of reactant disappears. This best linear fit was then used as a measure of the rate of decrease or increase of a particular C^{14}-labeled compound for a particular sample (e.g., see Fig. 4). Reliability of a particular rate value was tested by determining standard deviations on the computer. Any data which had atypically large standard deviations was not used for calculations in this study, but is nevertheless summarized in the Appendix. Only about 5% of the data was thus ignored. The source of these deviations giving poor data was not ascertained, although leakage in the analytical system could be a partial explanation.

Kinetic data was obtained for a number of separate peaks in each sample and listed in the Appendix. Radioactive peaks present in samples analyzed were in order of increasing retention time: CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, i-C_4H_{10}, C_2H_5OH, i-C_3H_7OH, C_5H_{12}, C_6H_{14}*.

*Using GC retention times this hexane is thought to be either 2,2-dimethyl hexane or 2,3-dimethyl hexane. The possibility that this is a hexene is ruled out on the grounds that it reacts at a rate more closely resembling that for propane than that for propene.

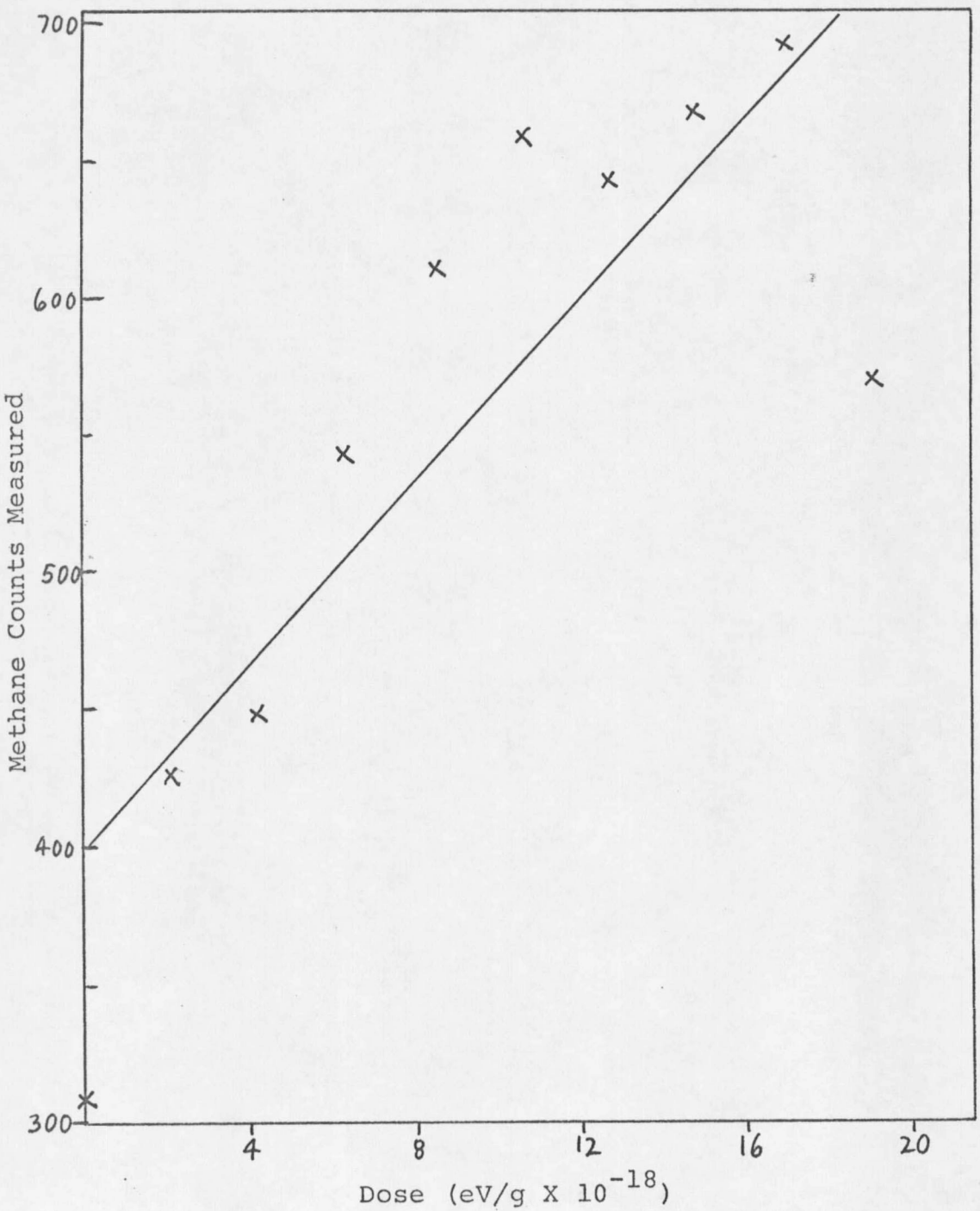

Fig. 4. Typical Methane Production Data (Tube 32)

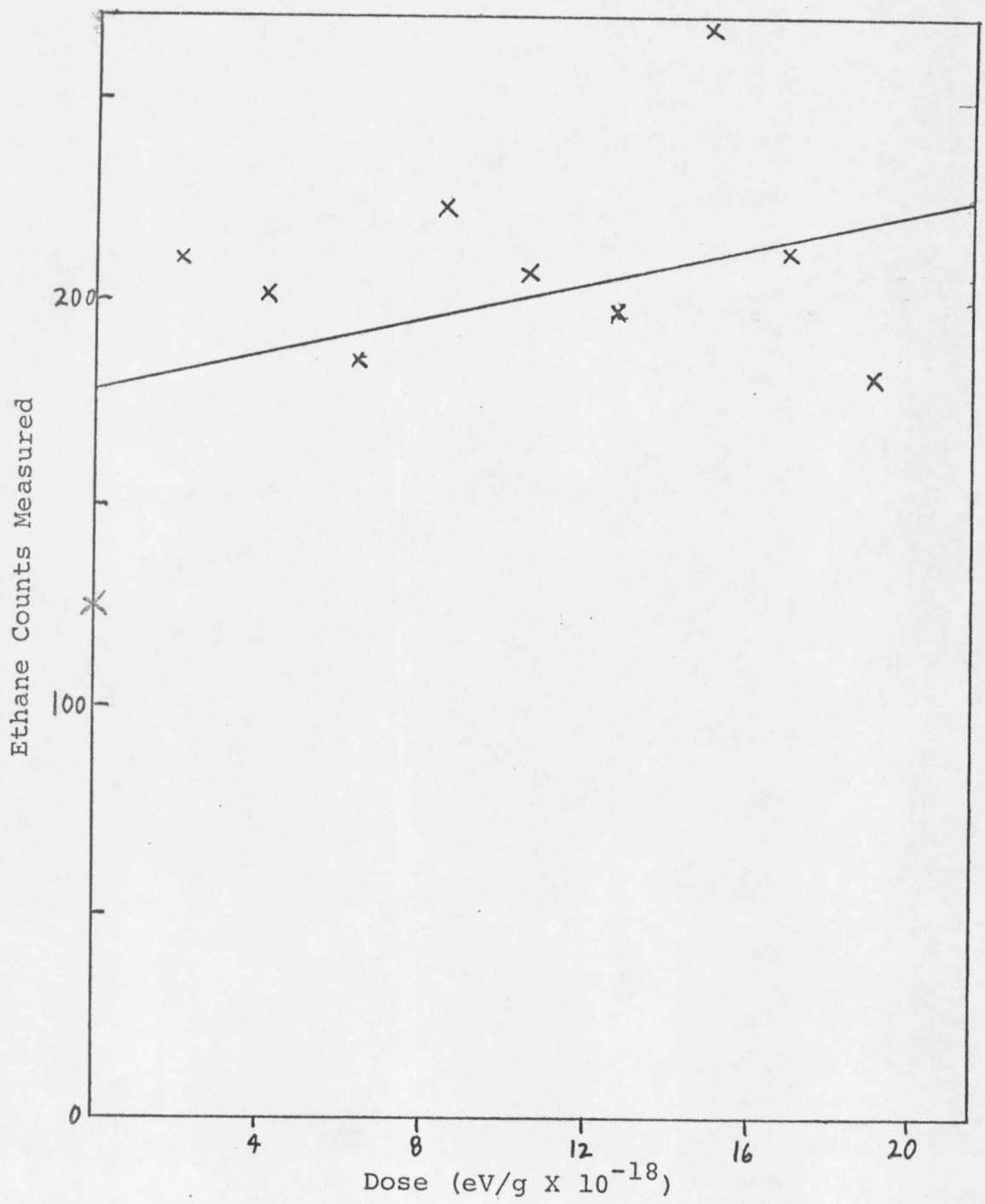

Fig. 5. Typical Ethane "Production" Data (Tube 32)

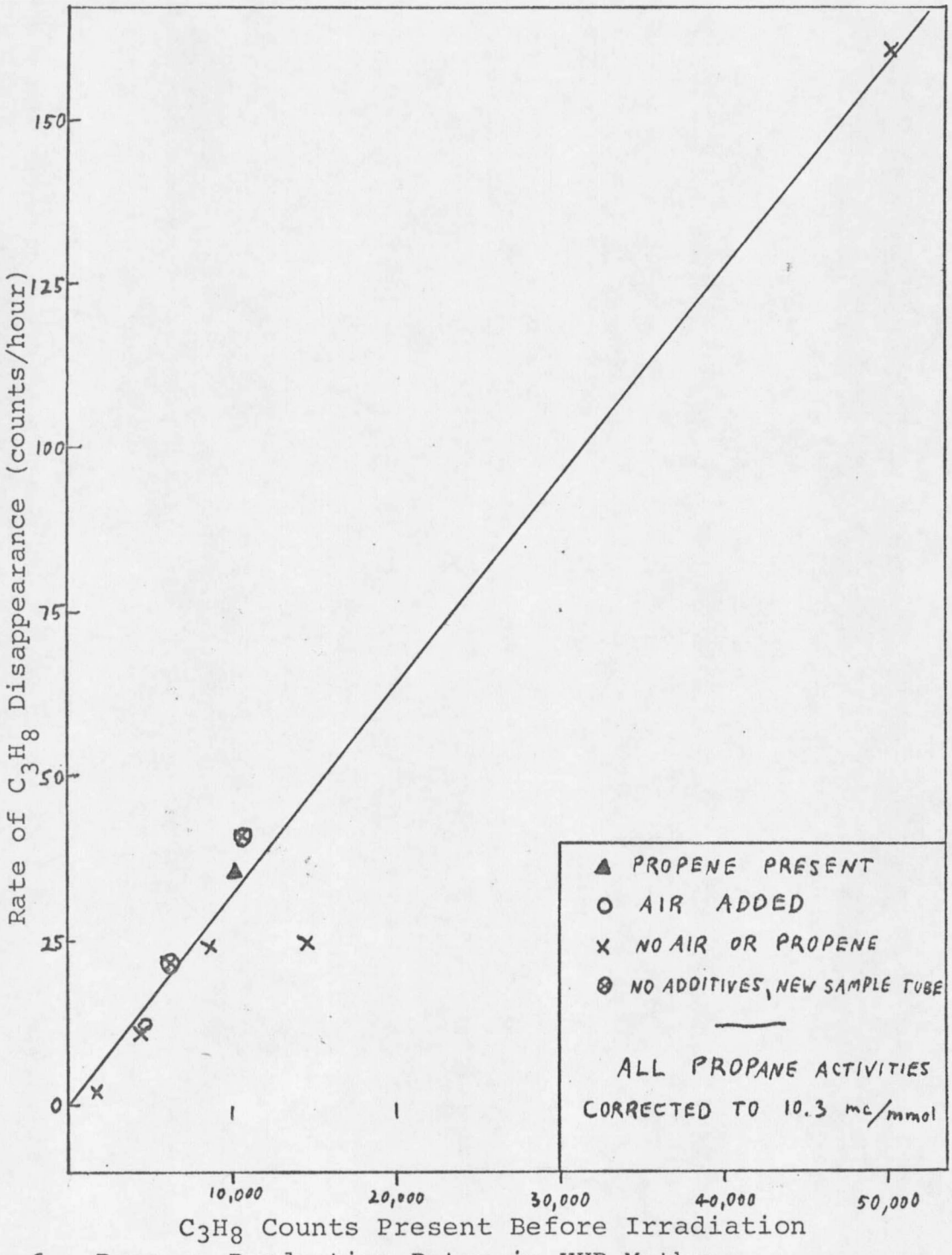

Fig. 6. Propane Production Rates in UHP Methane

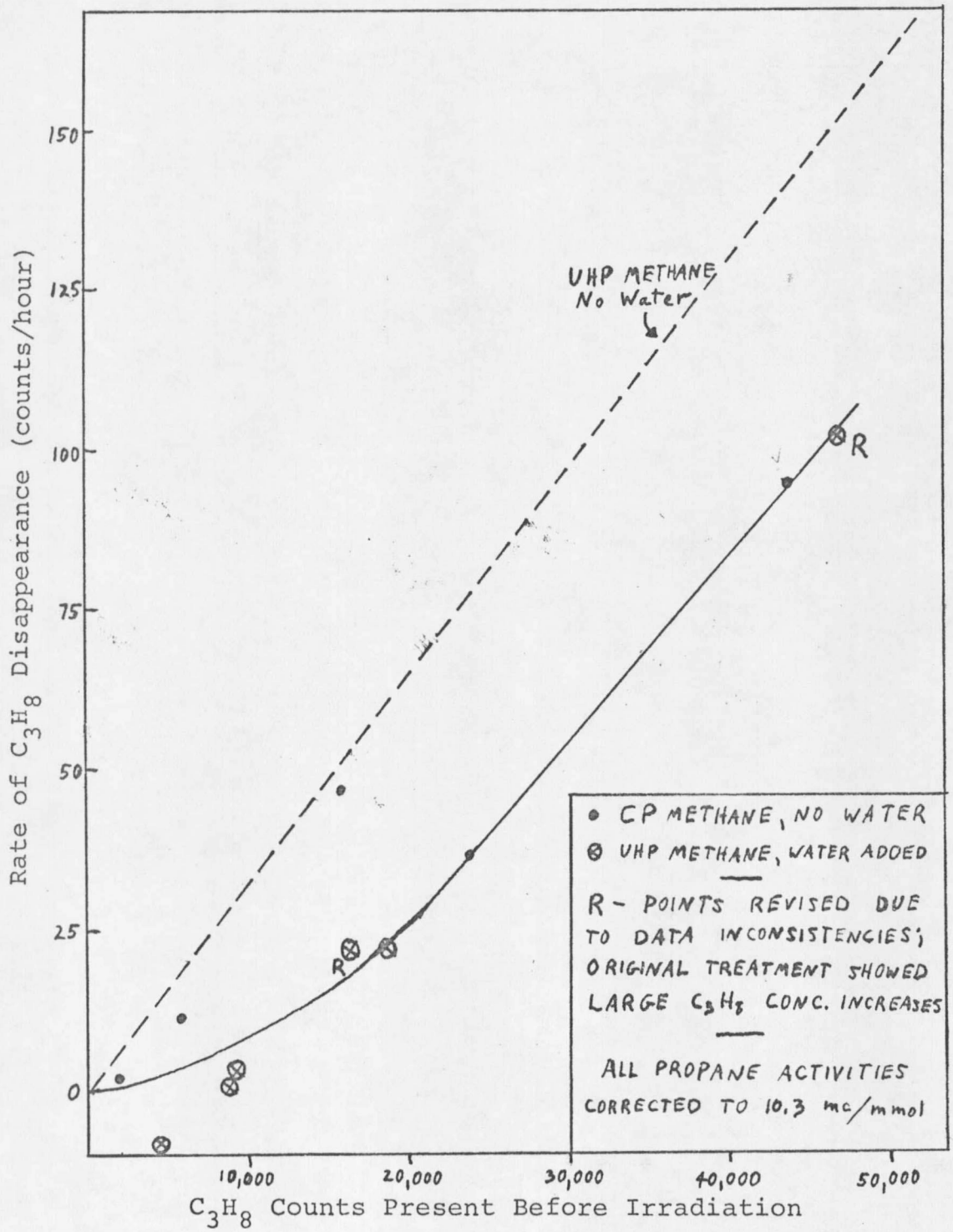

Fig. 7. Propane Production Rates in CP Methane and UHP Methane plus Water.

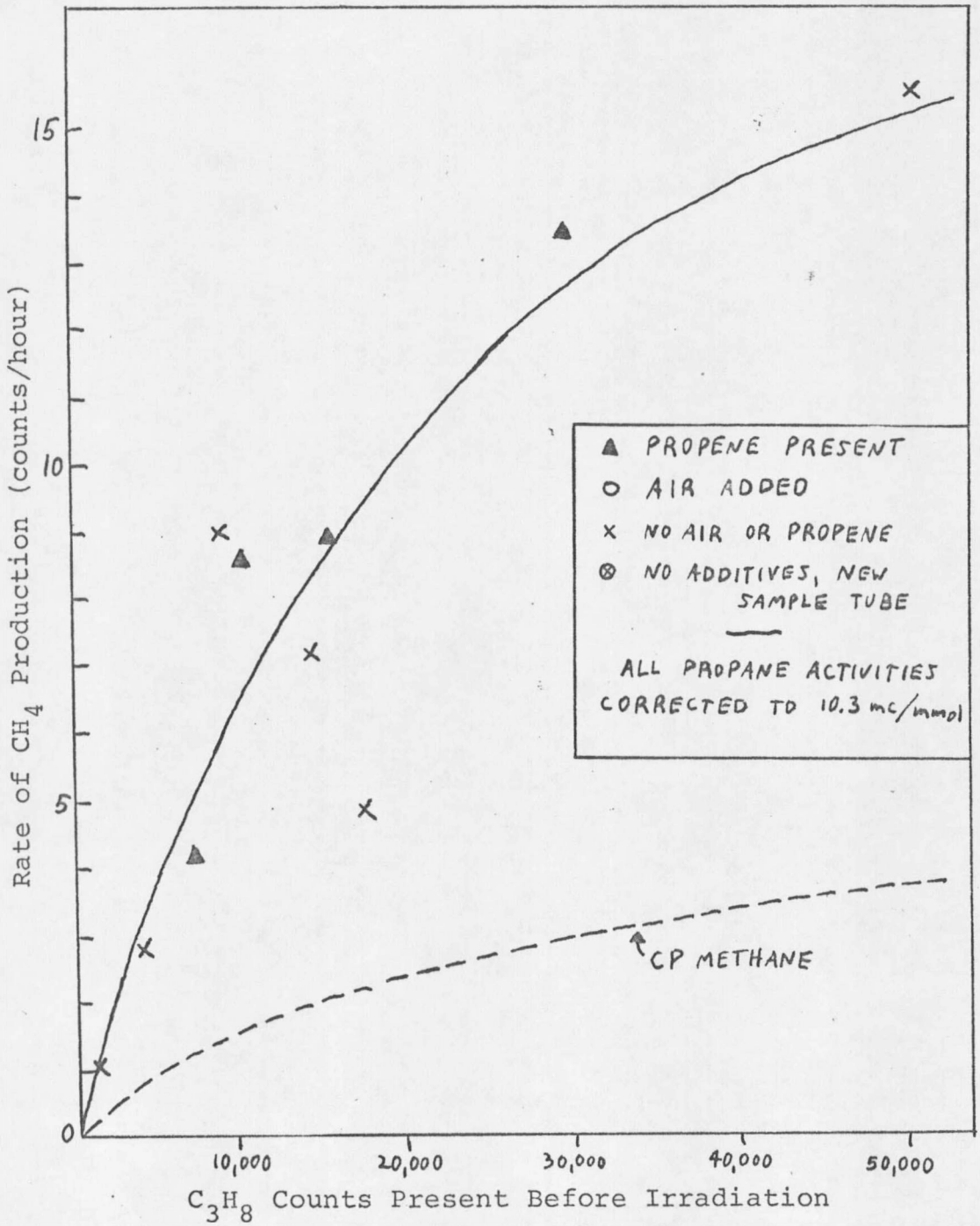

Fig. 8. Methane Production Rates in UHP Methane.

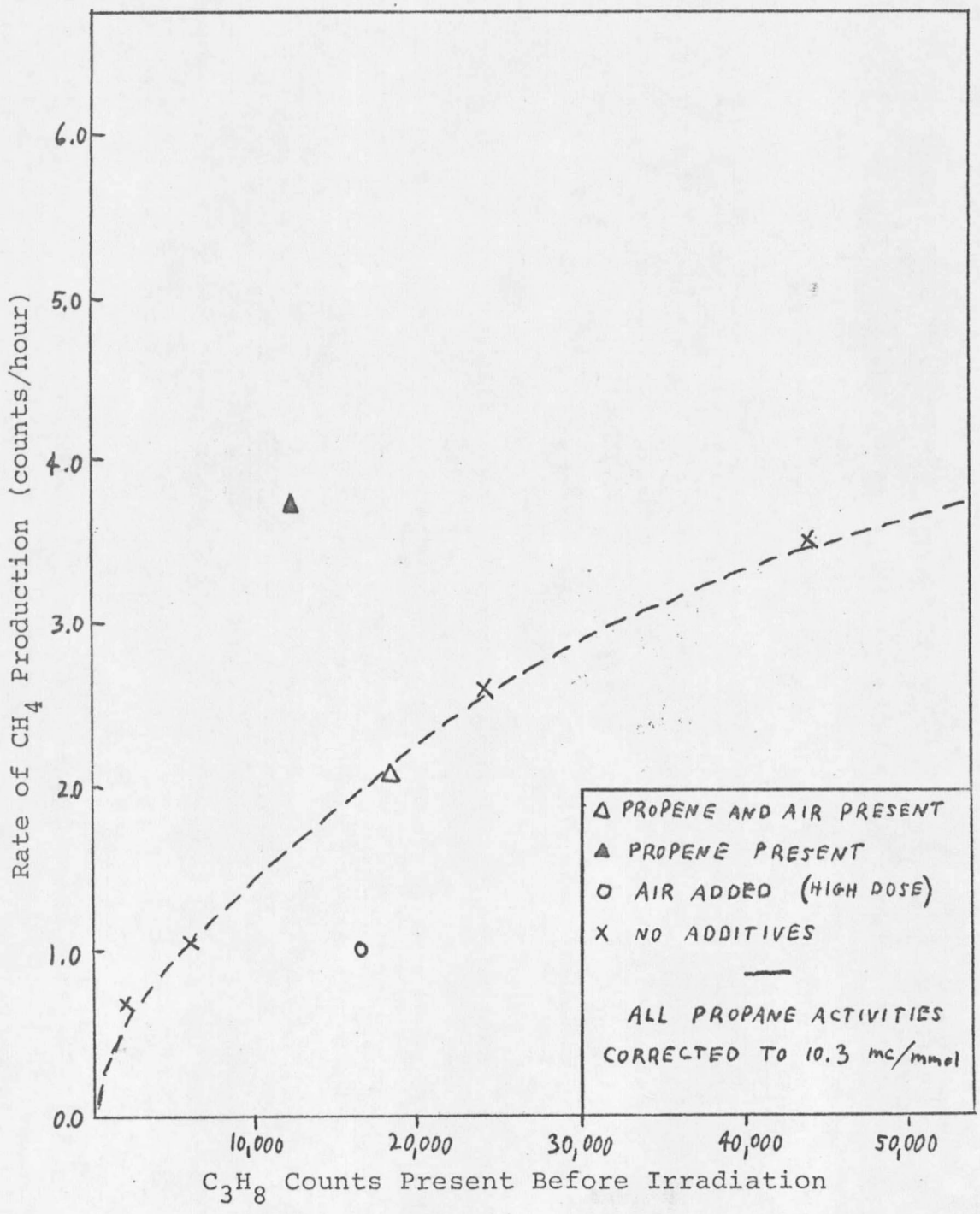

Fig. 9. Methane Production Rates in CP Methane

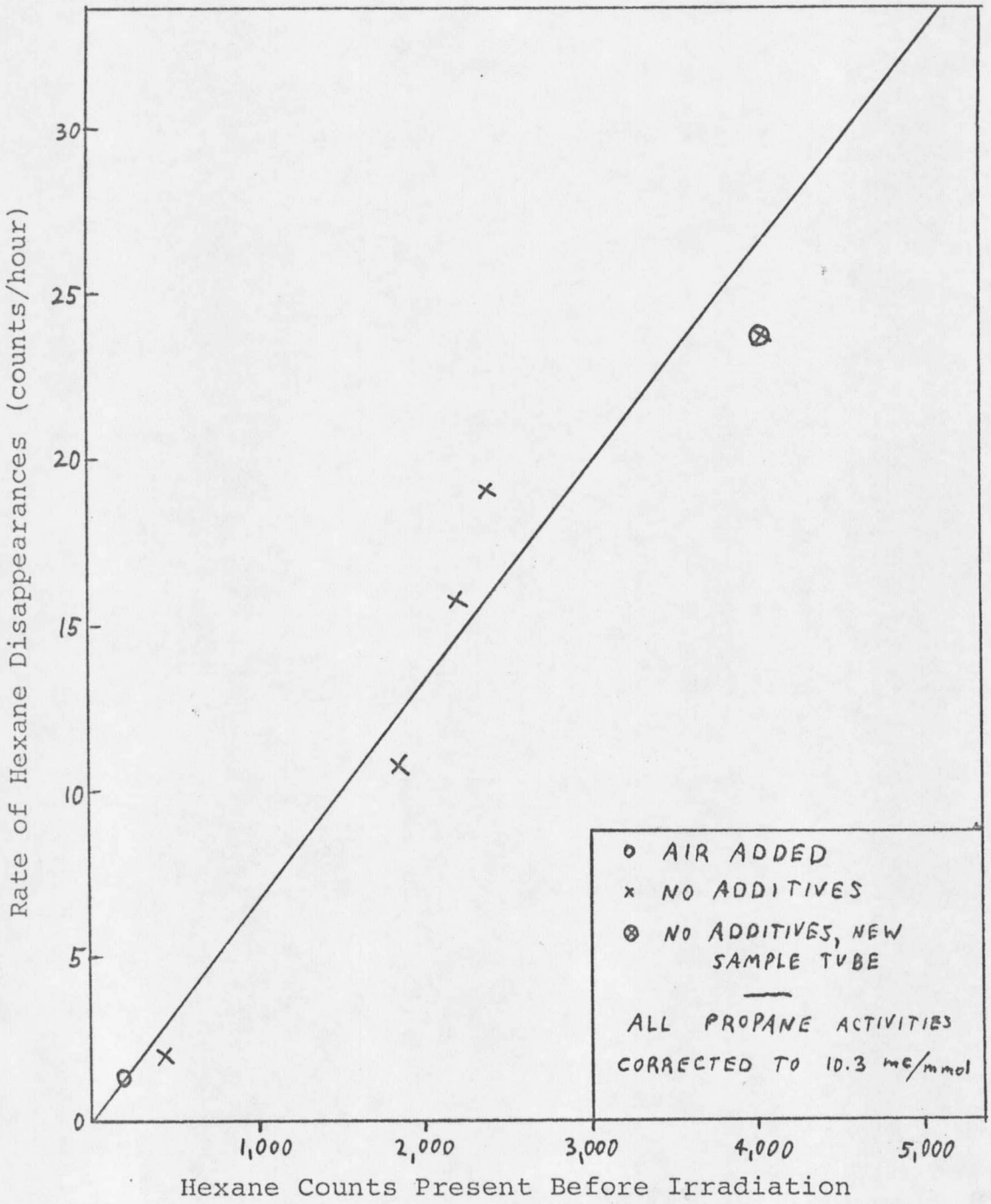

Fig. 10. Hexane Production Rates in UHP Methane

Of these, only CH_4, C_3H_6, C_3H_8, $i\text{-}C_3H_7OH$, and C_6H_{14} showed any consistent concentration increases or decreases which could be correlated with kinetic variables. All other peaks were apparently constant with a certain amount of experimental variation. For example, ethane rates varied from -3.8 counts/hour to +2.5 counts/hour. Fig. 5 shows how ethane concentrations varied in a typical run. The rate variations could not be correlated with concentrations of other species know to be present in the mixture.

A reaction observed in samples containing propene was apparently the conversion of C_3H_6 to isopropanol ($i\text{-}C_3H_7OH$). However, this reaction was not studied systematically. This data is summarized in the Appendix.

For the other compounds rate data is shown graphically (see Figs. 6-10) and expressed in G values (i.e., the number of molecules gained or lost per 100 electronvolts absorbed by the total sample) where concentrations are expressed in molecules/cc:

In UHP methane (99.98% pure)

$G(-C_3H_8) = 1.18 \times 10^{-15} [C_3H_8]$

$G(-C_6H_{14}) = 1.16 \times 10^{-15} [C_6H_{14}]$

$G(CH_4) = 0.64 \times 10^{-15} [C_3H_8]$ at low $[C_3H_8]$

$G(CH_4) \simeq 1.6$ at high $[C_3H_8]$

In CP methane (99.1% pure)

$G\ (-C_3H_8) = -1.07 + 1.06 \times 10^{-15}\ [C_3H_8]$ at high $[C_3H_8]$

$G\ (-C_6H_{14})$ was not determined due to large amount of scatter in experimental points.

$G\ (CH_4) \simeq 0.4$ at high $[C_3H_8]$

The counts/hour rates for methane were multiplied by two because only half the propane 1-C^{14} molecules reacting will give C^{14}-methane by the removal of the two chemically equivalent methyl carbon atoms:

$$CH_3CH_2C^{14}H_3 \rightarrow C^{14}H_4 + C_2H_4 \text{ residue}$$
$$CH_3CH_2C^{14}H_3 \rightarrow CH_4 + C^{14}H_2CH_2 \text{ residue}$$

The term "C_2H_4 residue" implies that C_2H_4 is not necessarily the molecular form of the product. In fact, it is most likely that the other carbon atoms are incorporated into polymer (as will be seen later).

The counts/hour rates for hexane were divided by two since each hexane molecule is presumed to have been prepared through a condensation of two propane molecules (giving twice as much activity per molecule) while preparing propane samples in the $LiAlH_4$ chamber.

In CP (low purity) methane much lower rates of methane production (Figs. 8 and 9) and propane disappearance (Figs. 6 and 7) were observed (although on a percentage basis the propane reaction rate was only slightly decreased). This suggests that an impurity in the CP methane decreased a particular reaction or group of reactions which involved the conversion of propane into methane. One sees that the difference between the rates for the two different methane samples is approximately $\Delta G(-C_3H_8) = 1.3$ and $\Delta G(CH_4) = 0.7$ at propene concentrations of between 30,000 and 50,000 counts per sample (where ΔG is relatively constant). The uncertainty in $\Delta G(-C_3H_8)$ is large due to relatively large scatter in the experimental points in Fig. 7. However, one sees that approximately two propanes react for each methane molecule produced.

A study by Kebarle and Haynes[19] revealing some interesting condensation reactions involving $C_3H_7^+$ and C_3H_8 may be pertinent. The $C_3H_7^+$ ion is produced by reactions (18) and (20). This may react with propane

$$C_3H_7^+ + C_3H_8 \rightarrow C_6H_{13}^+ + H_2 \qquad (22)$$

However, one needs methane as a product. A plausible reaction such as

$$C_3H_7^+ + C_3H_8 \rightarrow C_5H_{11}^+ + CH_4 \qquad (24)$$

which was discussed in the introduction, is a possibility.

The impurity involved in slowing down this reaction which uses approximately 2 molecules of propane to produce 1 molecule of methane is undoubtedly an ion scavenger--because CP methane and water both slow down methane production (see Table III) and propane disappearance rates (Fig. 7) to the same degree.

TABLE III

EFFECT OF WATER ON METHANE PRODUCTION RATE

Water Pressure (mm)	Propane Conc. (counts)	Unscavenged Rate* (counts/hr.)	Scavenged Rate (counts/hr.)	Scavenged Rate / Unscavenged Rate
∿20	18,100	10.3	- .32	-.02
8	4,800	3.05	.31	.10
7	41,200	14.4	2.60	.18
3	15.100	9.6	4.59	.48
1	9,200	5.9	3.47	.59
.055	9,000	5.7	3.76	.66

* The unscavenged rate is read off the calculated line in Fig. 8.

Propane consumption data are presented in Fig. 6. The data plotted show $G(-C_3H_8)$ to be a linear function of propane concentration in UHP methane. Reference to Fig. 7 shows that only a small portion of the propane consumption is affected by the presence of water or CP methane. This portion, mentioned earlier as having a $\Delta G(-C_3H_8) = 1.3$ at high propane concentrations, seems to be about the same for calculations using either CP methane or water. This justifies treating CP methane impurities as ion scavengers.

There is, however, enough scattering of experimental points in Fig. 7 to cause some uncertainty as to the precise quantitative effects of these two ion scavengers. As a matter of fact, two of the water points (marked R) were recalculated because several apparently bad data points caused the propane concentration to increase rather than decrease. In general, $G(-C_3H_8)_{ionic}$ (i.e., $\Delta G(-C_3H_8)$) is less accurate than $G(CH_4)$ due to the fact that small errors in measuring propane concentrations caused large errors in measuring $G(-C_3H_8)$. This is demonstrated by the fact that standard deviations on propane consumption rates averaged much higher, percentagewise, than those on methane production rates.

Methane production rates as affected by various partial pressures of water are shown in Fig. 11. Fifty percent rate reduction corresponds to 1.5 mm or 4.8×10^{16} molec H_2O/cc. If propane reacted with the ion of interest (i.e., the one responsible for CH_4 production) at a rate equal to that for water, one would require an equal concentration of propane (corresponding to 490,000 counts of radioactive propane of specific activity 10.3 millicuries/millimole). No more than 60,000 counts was ever used in any of the experiments. We can thus conclude that <u>if</u> water competes with propane, it does so inefficiently in our experiments.

Literature values[13,25], on the other hand, indicate that water reacts with CH_5^+ or $C_2H_5^+$ (the two major ions present during methane radiolysis) roughly 10 times faster than with C_3H_8. Then since $C_3H_7^+$ ions are produced almost exclusively by reactions of CH_5^+ and $C_2H_5^+$, one apparently must reject the idea that methane production is mediated by these two ions. Then reaction (24) cannot be the source of methane production. This brings us to the possibility that water is competing with CH_4 for methane reactive ions such as C^+, CH^+, CH_2^+, CH_3^+, CH_4^+, and $C_2H_3^+$.

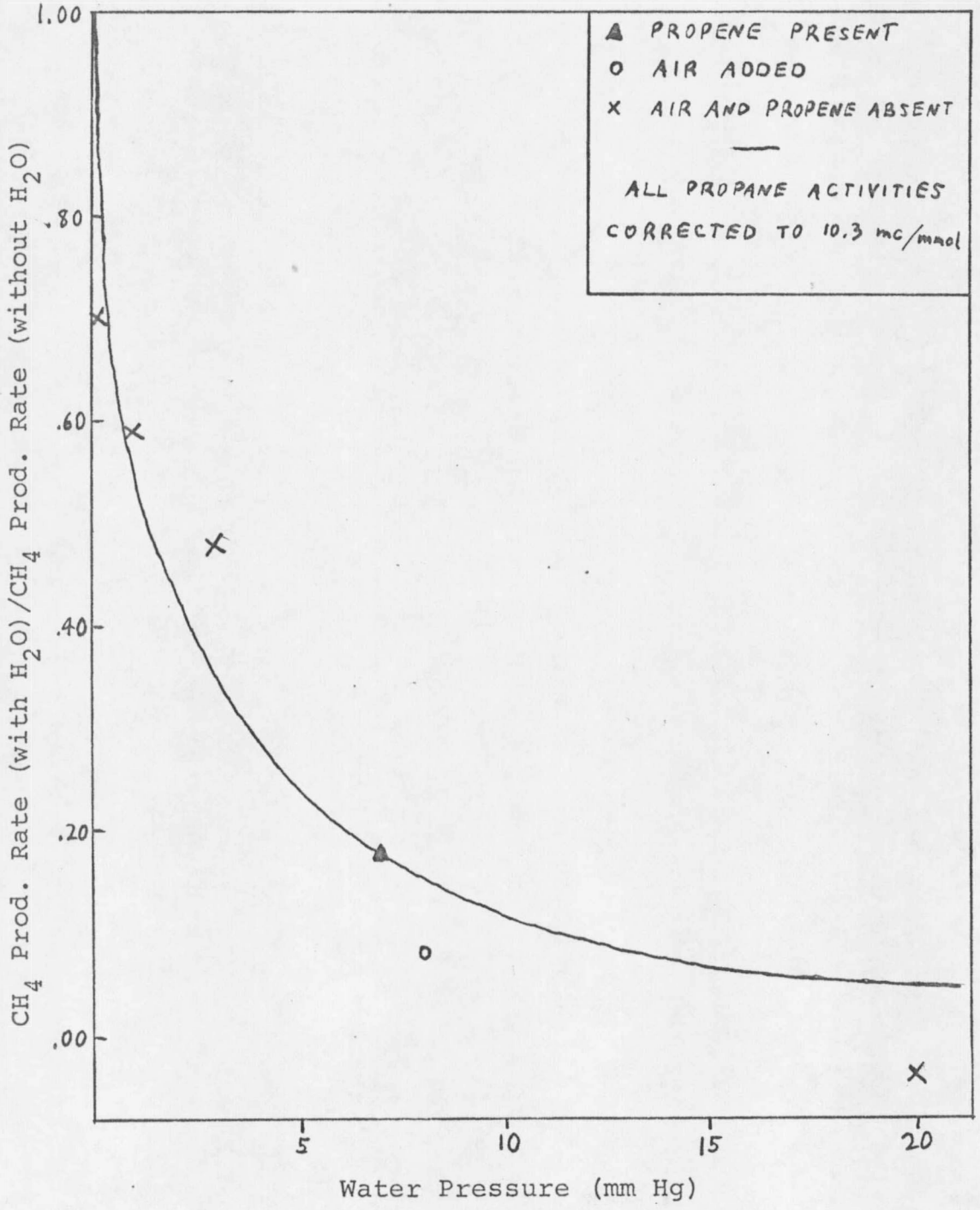

Fig. 11. Methane Production Rate Dependence on Water Pressure

A mass spectrometric study[25] of methane radiolysis in the presence of 1% ammonia or 1% water indicates that water is not likely to compete effectively with methane for reaction with the ions CH_4^+, CH_3^+ and CH_2^+. Ammonia, which seems to react more effectively with these and other carbonium ions than does water, still cannot compete with methane when methane is in great excess. Wexler and Jesse[26] list reaction cross sections for methane reactions with CH_4^+, CH_3^+, CH_2^+ and CH^+ which do not differ from each other by more than a factor of two. It would seem then that the primary ions all react sufficiently fast to preclude any competition from H_2O at low concentrations (C^+, which was not mentioned, seems likely to fit into this category too). The logical conclusion is then that H_2O reacts with some of the heavier polymerizing ions. At 1·5 mm pressure of H_2O and approximately 620 mm pressure of CH_4, methane production is reduced 50%. Therefore, water must have a rate constant for the unknown ionic reaction which is roughly 400 times as large as that for methane. There is presently no literature information on the possible ionic reactions which would meet these specifications. It seems reasonable to assume, however, that the water reaction is highly exothermic and the methane reaction is only slightly exothermic. If the

methane reaction were also highly exothermic (as it is for the C^+, CH^+, and CH_2^+ ions), reaction would occur at nearly every collision and the rate constants would be nearly equal. Of course, exothermicity is not the only consideration involved in predicting reactions (as mentioned in the Introduction). Large differences in activation energies could also be important--although ion-molecule reactions are not normally considered to have activation energies. Nevertheless, a polymerizing ion now seems to be a logical candidate for the unknown ion.

It is now apparent that methane may be produced during the polymerization process which is initiated by C^+, CH^+ or CH_2^+. In order to get methane from propane, propane might be incorporated into polymer by the plausible mechanism (G = 1.6)*,

$$X^+ + C_3H_8 \rightarrow XC_2H_4^+ + CH_4 \qquad (26)$$

After having previously noted that C_3H_8 competes more effectively for the X^+ ion than does water, it is well

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*Obtained from the least squares curve fit in Fig. 8

$$G(CH_4) = \frac{1.6[C_3H_8]}{[C_3H_8] + 2.5 \times 10^{15}}$$

where $G(CH_4) = 1.6$ is the methane production rate when $[C_3H_8]$ is large enough to exclude competing mechanisms.

to note that $C_3H_7^+$ or larger alkyl ions are not significantly scavenged by such reactions as

$$C_3H_7^+ + H_2O \rightarrow C_3H_6 + H_3O^+$$

Later calculations will show the endothermicity of this reaction for heavy alkyl ions. The complexing reaction

$$(X^+ + H_2O \rightarrow X(H_2O)^+) \qquad (25a)$$

(which will hopefully not belie the low reactivity of X^+ toward water) is discussed later in this thesis.

Reaction (26), which with X^+ as $C_3H_7^+$ has been shown to occur, can be considered slightly exothermic ($\Delta H = -3$) if one considers the addition of two CH_2 groups to an alkane decreasing ΔH_f by 10 kcal/mole[28] to apply equally to the R^+ ion considered here.

The other mechanism should incorporate propane ($G = 1.4$) by a reaction such as

$$X^+ + C_3H_8 \rightarrow XC_3H_6^+ + H_2 \qquad (27)$$

which is exothermic only if the difference ($\Delta H_f(X^+) - \Delta H_f(XC_3H_6^+)$) is greater than +25 kcal/mole.

Several literature studies have been completed elucidating the nature of methane polymerization[4,5,29] in

liquids and solids. These studies concluded that the build-up of such products as ethane and propane had no noticeable effect on polymer formation. This assumes reactions of the following type to predominate

$$X^+ + CH_4 \rightarrow X_i^+ + H_2^* \qquad (28)$$

Thus, if one postulates the same polymer yields in the presence as well as in the absence of C_3H_8 (G(polymer) = .08 in methane-argon solutions), a mechanism involving polymer buildup attributed exclusively to propane reactions (26) and (27) in the ratio of the experimental G values determined in this study, a value of G($-C_3H_8$ to polymer) can be calculated as follows:

$G(-C_3H_8$ to polymer) = G(Reaction 26) + G(Reaction 27)

G(Reaction 26)/G(Reaction 27) = 1.6/1.4 = 1.143

G(Carbon to polymer) = 2G(Reaction 26) + 3G(Reaction 27)

Solving gives

$G(-C_3H_8$ to polymer) = .405 (G(carbon to polymer)

Thus for methane G(carbon to polymer) = 1.6 gives

$G(-C_3H_8$ to polymer) = .65

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*Later calculations will treat X^+ and X_i^+ as the same species since their reactivities are considered to be similar.

The same mechanism for polymerization in ethane-argon solutions (G(polymer) = .20) would give G(-C_3H_8 to polymer) = 1.86. There is no liquid phase argon-propane data. However indications from solid phase data tell us that yields may be higher. The solid phase values[4] are G(-C_2H_6 to $C_{23}H_{46}$) = 0.2 and G(-C_3H_8 to $C_{16}H_{32}$) = 0.15 based on the assumption that a mechanism such as (26) which gives carbon containing by-products, is of no importance. With this knowledge one can calculate their values to be

$$G(\text{polymer from } C_2H_6) = \left(\frac{2 \text{ carbon atoms}}{\text{ethane molecule}} \Big/ \frac{23 \text{ carbon atoms}}{\text{polymer molecule}}\right) \times \frac{0.2 \text{ ethane molecules}}{100 \text{ eV}}$$

$$= .017$$

$$G(\text{polymer from } C_3H_8) = (3/16) \times 0.15 = .028$$

Thus a value for G(-C_3H_8 to polymer) might be (.028/.017) X 0.2 X 16 X .405 = 2.14 for propane-argon solutions--under the assumption that the change from solid propane to liquid argon solutions will not change the relative polymer yields or formulas for each hydrocarbon. This assumption is probably poor. Propane has a somewhat lower ionization potential than ethane (IP(C_2H_6) = 11.65 eV, IP(C_3H_8) = (11.21eV[15])

This allows larger energy packets to be transferred per polymerizing ion in ethane than in propane. If then the size of these energy packets is important, the presence of argon with IP = 15.8 eV should cause greater increases in polymerization rates for propane than for ethane when going from solid phase hydrocarbon to argon solutions. Thus, the > sign is used to indicate propane G values in Table IV.

TABLE IV

PREDICTED G VALUES IN ARGON SOLUTIONS ASSUMING ONLY MECHANISMS (26) AND (27)

Solution	G(Polymer)	G(carbon to polymer)	G($-C_3H_8$ to polymer)
CH_4 - Ar	.08	1.6	0.65
C_2H_6 - Ar	.20	4.6	1.86
C_3H_8 - Ar	>.33	>5.3	>2.14

Since the G($-C_3H_8$ to polymer) values represent maximum rates in the various solutions, one asks the question as to why the particular hydrocarbon (CH_4, C_2H_6 or C_3H_6) present at less than 1 mole percent should have such a profound effect on the G values. Since this model assumes methane is not going into polymer, the only effect methane could have is through energy transfer. Energy transfer predicts

methane to be the most effective promoter of polymerization by virtue of the high energy content of a methane ion. That this is not the case (Table IV) tells one that the energy carrier is argon.

Further evidence in favor of the concept of the species with the higher ionization potential more effectively promoting polymerization is found in a paper by Hamlet et al.[5] Their data show polymerization to be more effective in methane-argon solutions with low methane content. Also, the presence of a greater percent methyl groups in their polymer at high mole percent of methane indicates a more highly branched polymer--an excellent indication that the less stable low-branched polymer is not as likely to form when the concentration of the highly energetic Ar^+ ion is decreased.

A reassessment of the G-values in Table IV then tells one that the presence of a non-polymerizing hydrocarbon at low concentrations has no measurable effect on the polymerization of propane and all G(-C_3H_8 to polymer) values in the presence of sufficient propane must be equal. This further means that the presumption of ethane and propane build-up products not affecting polymerization during methane radiolysis is misleading. These products can indeed have a

profound effect. Earlier studies[4] on solid methane indicating the contrary may well not apply to room temperature gases or liquid argon solutions. The present liquid argon studies[5] have revealed little about dose dependence of the polymerization process. Their minimum dose was 8.5 Mrad--enough to produce the sizable amount of 300 ppm ethane.*

Having reasonably established the probability of forming a pure propane polymer in the presence of excess methane, one can compare the experimental $G(-C_3H_8)_{ionic}$ = 3.0 to the calculated value for argon solutions (which is >2.14). There seems to be agreement due to the inequality sign. However, our experiment deals with a methane "solution" at room temperature. A correction of the argon solution value to a methane solution would of necessity reduce the "more than 2.14" value making agreement of the two values less easy to accept. Perhaps then one must assume that polymerization does proceed more readily at room temperature.

$$*8.5 \text{ Mrad} \times \frac{6.24 \times 10^{19} \text{ eV/g}}{\text{Mrad}} \times \frac{16 \text{g} CH_4}{6.02 \times 10^{23} \text{molec } CH_4} \times \frac{2.1 \text{ molec } C_2H_6}{100 \text{ eV}} \times 10^6 = 300 \text{ ppm ethane}$$

There may be a literature clue as to the reason for an increase in polymerization rates at higher temperatures. Davis et al.[4] give gas chromatograms of propane polymer produced at -196°C in the solid phase. They suggest that coarse structure in the chromatogram may indicate three-carbon-atom periodicity in the molecular weight of compounds comprising the propane polymer. However, comparison of the peaks in the chromatogram to those of standard n-alkanes indicates this may, in fact, be two-carbon-atom periodicity. If this is so, reaction (26) may be the predominant mechanism in their low temperature experiments. An increase in temperature then might supply sufficient energy for the less exothermic reaction (27) to become important at room temperature--thus increasing $G(-C_3H_8$ to polymer). Further speculation is unnecessary in the absence of direct measurement of propane incorporation into the polymer (at the dose rates in our experiments sufficient polymer to work with was never produced). However, the propane incorporation mechanism evidenced by reactions (26) and (27) seems entirely reasonable.

One other reaction observed in our experiment was the consumption of propane which could not be scavenged by water at partial pressures up to 20 mm. The $G(-C_3H_8)$ values

from Fig. 7 increase nearly linearly up to the highest measured value of 3.4 (after the ionic mechanism contribution has been subtracted) at a propane concentration of 5 X 10^{15} molec/cc. The fact that the presence of oxygen rules out a radical reaction calls our attention to a molecular decomposition such as reaction (1). However, no low molecular weight products were produced in sufficient quantities to allow consideration of a simple decomposition reaction. Possibly propane is incorporated into polymer by some ionic mechanism which cannot be scavenged by water. There is nothing in the literature to indicate what could be happening to this propane.

KINETICS OF METHANE RADIOLYSIS

It now remains to present a suitable reaction scheme for the ionic production of $C^{14}H_4$ and the ionic disappearance of 1-C^{14}-propane. In this scheme X^+ represents one or more of the polymerizing ions (C^+, CH^+, CH_2^+, polymer$^+$) for which CH_4 and H_2O may compete. Each * represents one C^{14}-atom per molecule, E is an unreactive end product which may be reactivated only at the expense of another X^+ ion, and $\bar{X}$, $\bar{Y}$, $\bar{Z}$ represent positive fractions equal to or less than 1.

$$\text{Methane sample} \xrightarrow{k_i} X^+$$

$$X^+ + CH_4 \xrightarrow{k_{28}} (1-\bar{X})X^+ + \bar{X}E \tag{28}$$

$$X^+ + C_3H_8^* \xrightarrow{k_{27}} (1-\bar{Y})X^+ + \bar{Y}E + H_2 \tag{27}$$

$$X^+ + C_3H_8^* \xrightarrow{k_{26}} (1-\bar{Z})X^+ + \bar{Z}E + \tfrac{1}{2}CH_4 + \tfrac{1}{2}CH_4^* \tag{26}$$

$$X^+ + H_2O \xrightarrow{k_H} \text{inactive products}$$

$$X^+ \xrightarrow{k_t} \text{inactive products}$$

In this scheme the larger the values $\bar{X}$, $\bar{Y}$ and $\bar{Z}$, the sooner polymerization through the X^+ ion will stop.

Using the usual steady state approximation that the change in the concentration of any intermediate species is zero, one obtains the following relationship:

$$\frac{d[X^+]}{dt} = k_i - \bar{X}k_{28}[X^+][CH_4] - (\bar{Y}k_{27} + \bar{Z}k_{26})[X^+][C_3H_8]$$
$$- k_H[X^+][H_2O] - k_t[X^+] = 0$$

The rates of formation and decrease for CH_4 and C_3H_8 are:

$$\frac{d[CH_4^*]}{dt} = 1/2\ k_{26}[X^+][C_3H_8^*]$$

$$-\frac{d[C_3H_8^*]}{dt} = (k_{27} + k_{26})[X^+][C_3H_8^*]$$

To convert to G values the rate constant, k_i, must be divided by the dose rate D (in $\frac{eV}{cc.sec}$) and multiplied by 100. The results obtained from the foregoing equations then are

$$G(CH_4) = \frac{(\frac{100}{D})k_i k_{26}[C_3H_8]}{(\bar{X}k_{28}[CH_4] + (\bar{Y}k_{27} + \bar{Z}k_{26})[C_3H_8] + k_H[H_2O] + k_t)}$$

$$G(-C_3H_8) = \frac{(k_{27} + k_{26})}{k_{26}}\ G(CH_4)$$

where $G(CH_4)$ was derived by multiplying $G(CH_4^*)$ by two to correct for the fact that only half the CH_4 molecules produced by reaction (26) are radioactive

The ratio $\frac{k_{27} + k_{26}}{k_{26}}$ is equal to the ratio $\frac{\Delta G(-C_3H_8)}{\Delta G(CH_4)}$ earlier determined to be $\frac{1.3}{0.7} = 1.9$. Thus $\frac{k_{27}}{k_{26}}$ equals 0.9.

Constants in the $G(CH_4)$ equation can be evaluated in the absence of water from the equation

$$G(CH_4) = \left(\frac{100}{D}\right) \frac{k_i k_{26}[C_3H_8]}{(\bar{Y}k_{27} + \bar{Z}k_{26})[C_3H_8] + \bar{X}k_{28}[CH_4] + k_t}$$

$$= \left(\frac{100\ k_i k_{26}[C_3H_8]}{D(\bar{Y}k_{27} + \bar{Z}k_{26})}\right) \Bigg/ \left([C_3H_8] + \frac{\bar{X}k_{28}[CH_4] + k_t}{(\bar{Y}k_{27} + \bar{Z}k_{26})}\right)$$

A least squares fit of this equation to the experimental data plotted in Fig. 8 gives the values for the two constants as:

$$\frac{100}{D} \frac{k_i k_{26}}{(\bar{Y}k_{27} + \bar{Z}k_{26})} = \frac{1.6 \text{ molecules}}{100 \text{ eV}}$$

$$\frac{\bar{Y}k_{28}[CH_4] + k_t}{\bar{Y}k_{27} + \bar{Z}k_{26}} = 2.5 \times 10^{15} \frac{\text{molec}}{\text{cc}}$$

From this the best value for $G(CH_4)$ at low concentrations is $G(CH_4) = 0.64 \times 10^{-15}[C_3H_8]$. At very high concentrations of propane one obtains $G(CH_4) = 1.6$.

The value $\frac{100\ k_i}{D}$ is actually $G(X^+)$ or the rate of formation of polymerizing ions. In estimating the rate of formation of C^+, CH^+ and CH_2^+ ions from Melton and Rudolph[1] one finds that 12% of the ions are of this type. With

G(positive ions) = $\frac{100}{W}$ (W = 29.4 eV, being the energy absorbed per ion pair produced[3] in methane) one obtains

$$G(C^+, CH^+, CH_2^+) = \frac{100}{29.4} \times .12 = .41 \frac{\text{molecules}}{100 \text{ eV}}$$

Thus one finds that

$$\frac{k_{26}}{\bar{Y}k_{27} + \bar{Z}k_{26}} = 3.9$$

Using $\frac{k_{27}}{k_{26}} = 0.9$, one can further find that

$\frac{k_{26}}{(0.9\bar{Y} + \bar{Z})k_{26}} = 3.9$ or $(0.9\bar{Y} + \bar{Z}) = .26$, indicating that the ratio of chain propagating to chain termination reactions during propane reactions (26) and (27) is

$$\frac{R_p}{R_t} = \frac{(1-\bar{Y})k_{27} + (1-\bar{Z})k_{26}}{\bar{Y}k_{27} + \bar{Z}k_{26}} = \frac{1.9-(0.9\bar{Y} + \bar{Z})}{0.9\bar{Y} + \bar{Z}} = 6.3$$

Substitution of the previously determined value

$$\bar{Y}k_{27} + \bar{Z}k_{26} = (0.9\bar{Y} + \bar{Z})k_{26} = .26k_{26}$$

into an earlier expression from page 56 also gives

$$\frac{\bar{X}k_{28}[CH_4] + k_t}{.26k_{26}} = 2.5 \times 10^{15} \frac{\text{molec}}{\text{cc.}}$$

$$\text{or} \quad \frac{\bar{X}k_{28}[CH_4] + k_t}{k_{26}} = 6.5 \times 10^{14} \frac{\text{molec}}{\text{cc.}}$$

The rate of polymerization as expressed by the number of carbon atoms added is

$$G(\text{C to polymer}) = 100k_i/D + k_{28}[X^+][CH_4] + 3k_{27}[X^+][C_3H_8] + 2k_{26}[X^+][C_3H_8]$$

Substituting $[X^+] = \frac{G(CH_4)}{k_{26}[C_3H_8]}$ gives

$$G(\text{C to polymer}) = 100k_i/D + \frac{k_{28}G(CH_4)[CH_4]}{k_{26}[C_3H_8]} + \frac{3k_{27}G(CH_4)}{k_{26}} + 2G(CH_4)$$

Dividing this by the rate of initiation $\frac{100k_i}{D}$ one gets the chain length

$$\nu = 1 + \left(\frac{k_{28}[CH_4]}{k_{26}[C_3H_8]} + \frac{3k_{27}}{k_{26}} + 2\right) \frac{G(CH_4)}{100k_i/D}$$

If one calculates ν for polymerization at its maximum, $G(CH_4) = 1.6$ (by realizing that methane cannot effectively compete with propane at these high propane concentrations

giving $\frac{k_{28}[CH_4]}{k_{26}[C_3H_8]} = 0$), we find that the polymer chain length is $\nu = 19$, this is a reasonable value compared to $\nu = 20$ in methane and $\nu = 16$ in propane. The agreement may, however, be fortuitous on the grounds that no direct evidence has yet been advanced for the general mechanism proposed in this thesis. Other mechanisms as yet undiscovered may predict the same result as our data do.

As $G(CH_4)$ approaches zero, we get the equation G(C to polymer) $= \frac{100k_i}{D} + \frac{k_{28}G(CH_4)[CH_4]}{k_{26}[C_3H_8]}$. In this limit calculus then gives

$$\frac{dG(CH_4)}{d[C_3H_8]} = \frac{k_{26}\left(G(\text{C to polymer}) - \frac{100k_i}{D}\right)}{k_{28}[CH_4]}$$

With the knowledge that $\frac{dG(CH_4)}{d[C_3H_8]} = .64 \times 10^{-15} \frac{cc}{100eV}$ and $[CH_4] = 2 \times 10^{19} \frac{molec}{cc}$, one uses the presumed value $\frac{100k_i}{D} = .41$ calculated earlier and the literature value G(-CH_4 to polymer) = 2.1 to obtain $\frac{k_{28}}{k_{26}} = .00013$.

This tells us the ratio of X^+ ions sufficiently reactive to give polymer by mechanisms (28) and (26). The

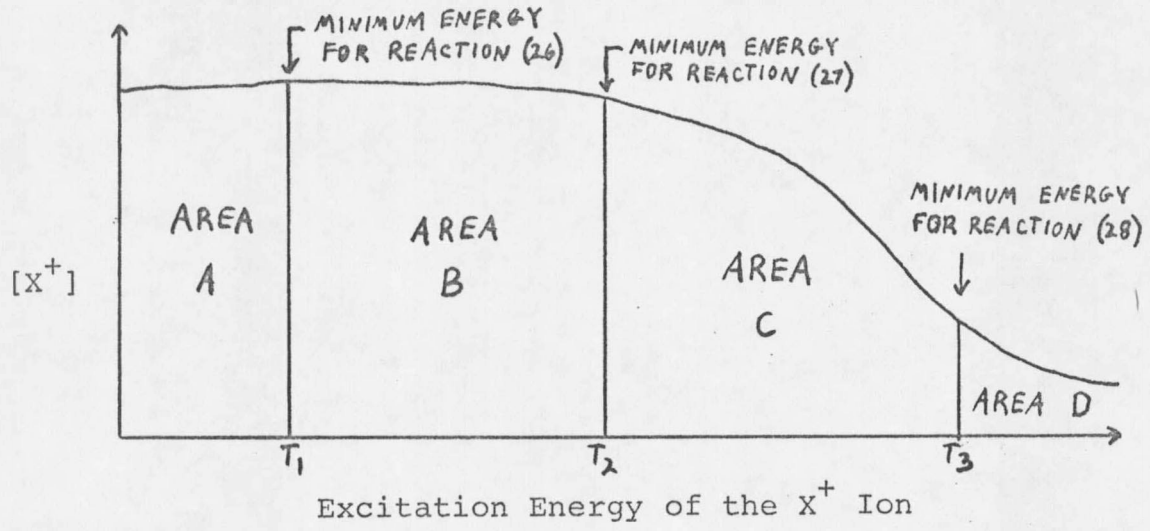


Fig. 12. Distribution of Excitation Energies in the Polymer ion, X^+.

significance of this will be demonstrated by reference to Fig. 12.

An endothermic reaction cannot normally occur without a certain minimum excitation energy. Thus, all ions in areas B, C, and D can react with propane by mechanism (26) to give CH_4. All ions in areas C and D can react by mechanism (25) and only those in area D are capable of reacting by mechanism (28). The relative heats of reactions estimated for these reactions are (where primary carbonium ions are converted to primary carbonium ion, secondary to secondary, etc.): (26) - 3, (27) + 10, and (28) + 13 $\frac{\text{kcal}}{\text{mole}}$. For the curve in Fig. 12 showing $[X^+]$ decreasing with increasing energy, one would expect reaction (26) to occur much more often than reaction (27) when the excitation energy value differences are $T_3 - T_2 = 3 \frac{\text{kcal}}{\text{mole}}$ and $T_2 - T_1 = 13 \frac{\text{kcal}}{\text{mole}}$. Since the ratio of $\frac{k_{27}}{k_{26}}$ being 0.9 conflicts with this idea, one could assume here that an activation energy of about 10-13 $\frac{\text{kcal}}{\text{mole}}$ reduces the number of X^+ ions capable of reacting with C_3H_8 by mechanism (26). However, the fact that ion-molecule reactions typically have activation energies very close to zero leads one to doubt this explanation[30].

An alternative explanation is that while mechanism (27) is only slightly exothermic, mechanism (26) is so highly exothermic that the reaction complex frequently dissociates before going to reaction products. This seems unlikely in the case of a polymer ion of high molecular weight, since so many vibrational degrees of freedom are available to dissipate the 10 kcal/mole excess energy.

Another explanation is that virtually no ions have excitation energies between T_1 and T_2. This is reasonable in the case where T_2 is equal to or slightly larger than $0 \frac{kcal}{mole}$ (then, of course, no ions are allowed to have the negative excitation energies, which would exist at values significantly lower than T_2). Since ΔH for reaction (26) has been estimated to be $3 \frac{kcal}{mole}$ or less, one can <u>a priori</u> presume that T_1 is a negative number, thus reducing the number of X^+ ions carrying energies between T_1 and T_2. For T_2 approximately equal to zero, ΔH for reaction (26) is estimated at $-13 \frac{kcal}{mole}$. This indicates that, unless our earlier ΔH_r estimates were badly in error, the product carbonium ion, X_i^+, formed is additionally stabilized by a transformation such as from primary to secondary, tertiary or allyl ion.

The knowledge that the polymer formed is highly branched supports the idea of forming secondary and tertiary ions. To show that this transformation could supply the additional 10 $\frac{\text{kcal}}{\text{mole}}$ stabilization necessary to explain the data, one can quote[31] butyl ion ΔH_f values as varying from $\frac{+218 \text{ kcal}}{\text{mole}}$ for n-butyl to $\frac{+176 \text{ kcal}}{\text{mole}}$ for tert-butyl. It is thus proposed that the heats of reaction are approximately:

Reaction (26) - 13 kcal/mole

Reaction (27) 0 kcal/mole

Reaction (28) + 3 kcal/mole

KINETICS IN THE PRESENCE OF WATER

A comparison of methane production rates in the presence and absence of water gives the ratio:

$$G_{HP} = \frac{G(CH_4)_{H_2O}}{G(CH_4)_{pure}} = \frac{\bar{X}k_{28}[CH_4] + (\bar{Y}k_{27} + \bar{Z}k_{26})[C_3H_8] + k_t}{\bar{X}k_{28}[CH_4] + (\bar{Y}k_{27} + \bar{Z}k_{26})[C_3H_8] + k_H[H_2O] + k_t}$$

Substituting experimental values of $\bar{X}k_{28}[CH_4] + k_t = 6.5 \times 10^{14}k_{26}$ and $\bar{Y}k_{27} + \bar{Z}k_{26} = .26k_{26}$, one obtains

$$G_{HP} = \frac{G(CH_4)_{H_2O}}{G(CH_4)_{pure}} = \frac{(6.5 \times 10^{14} + .26[C_3H_8]k_{26}}{(6.5 \times 10^{14} + .26[C_3H_8]k_{26} + k_H[H_2O]}$$

This can be rearranged to give

$$\frac{k_{26}}{k_H} = \frac{[H_2O]G_{HP}}{(1-G_{HP})(6.5 \times 10^{14} + .26[C_3H_8])}$$

Calculations of this ratio from the data on Table III for water pressures 1, 3, 7 and 8 mm gives the values 47, 9, 27, and 37, respectively. These values average out to $\frac{k_{26}}{k_H} = 30$ meaning that water is not an effective scavenger for the polymerizing ion X^+. Sample reactions for comparing

H_2O and C_3H_8 reactions would be

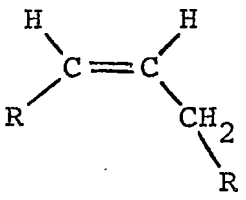
$$sec\text{-}RC_3H_6^+ + C_3H_8 \rightarrow sec\text{-}RC_5H_{10}^+ + CH_4 \quad \Delta H_r = -3 \left(-13\right) \frac{kcal}{mole} \quad (26)$$

$$sec\text{-}RC_3H_6^+ + H_2O \rightarrow RC_3H_5 + H_3O^+ \quad \Delta H_r = +14 \frac{kcal}{mole} \quad (30)$$

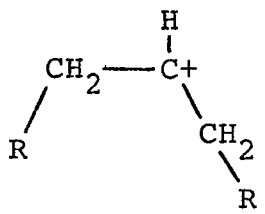
$$sec\text{-}RC_3H_6^+ + H_2O \rightarrow sec\text{-}RC_3H_7OH_2^+ \quad \Delta H_r \simeq -22 \frac{kcal}{mole} \quad (31)$$

ΔH for reaction (26) was estimated earlier from the -5 kcal/mole increment per CH_2 group. The -13 $\frac{kcal}{mole}$ is the corrected value based on previously discussed assumptions of an increase in carbonium ion stability during reaction.

ΔH for reaction (30) was estimated by a comparison of the following structures:



(A)



(B)

From a paper by Franklin[28] ΔH_f's can be estimated by summing up constants $\Delta H(X)$ for the various functional groups. Therefore, for A and B one obtains

$$\Delta H_f(A) = \Delta H(R + R) + \Delta H\left(\begin{matrix} H & H \\ \backslash & / \\ C=C \end{matrix}\right) + \Delta H(CH_2)$$

$$\Delta H_f(B) = \Delta H(R + R) + \Delta H(CH_2\overset{+}{C}HCH_2)$$

$\Delta H(CH_2\overset{+}{C}HCH_2)$ is taken to be the heat of formation for propane ion plus a correction of +10 kcal/mole for the fact that CH_2 rather than CH_3 groups are present. The difference is then

$$\Delta H_f(B) - \Delta H_f(A) = \Delta H(CH_2\overset{+}{C}HCH_2) - \Delta H\left(\begin{matrix} H & H \\ \backslash & / \\ C=C \end{matrix}\right) - \Delta H(CH_2) =$$

$$+187 \frac{\text{kcal}}{\text{mole}}$$

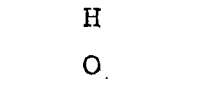
$\Delta H_f(H_3O^+) = 143 \frac{\text{kcal}}{\text{mole}}$ was obtained from a recent literature reference[32]. Where the R groups are both hydrogen, the experimental ΔH is $+16 \frac{\text{kcal}}{\text{mole}}$ rather than the $+14 \frac{\text{kcal}}{\text{mole}}$ calculated here.

ΔH for reaction (31) was determined from the reasonable approximation that the proton affinity, $P(RC_3H_6OH) \simeq 190$ of the alcohol is nearly equal to that for C_2H_5OH[33]. This gives the relation

$$RC_3H_6OH + H^+ \rightarrow RC_3H_6OH_2^+ \qquad \Delta H = -190 \frac{\text{kcal}}{\text{mole}} \quad (34)$$

from which $\Delta H_f(H^+) = 366 \frac{\text{kcal}}{\text{mole}}$ gives the result

$\Delta H_f(RC_3H_6OH_2^+) - \Delta H_f(RC_3H_6OH) = +176 \frac{kcal}{mole}$. The structure



(C)

has the heat of formation

$$\Delta H_f(C) = \Delta H(R + R) + 2\Delta H(CH_2) + \Delta H(CH) + \Delta H(\text{secondary OH})$$

Thus

$$\Delta H_f(B) - \Delta H_f(C) = \Delta H_f(RC_3H_6^+) - \Delta H_f(RC_3H_6OH) = +256 \frac{kcal}{mole}$$

gives

$$\Delta H_f(RC_2H_4OH_2^+) - \Delta H_f(RC_3H_6^+) = 176 - 256 = -80 \frac{kcal}{mole}$$

This gives ΔH_r(reaction 31) = -22 which is equal to the value calculated for both R's in (B) and (C) being hydrogen. An experimental value for both R's being hydrogen is $-17 \frac{kcal}{mole}$ (27).

One immediate realization is that reaction (30) is not likely to be important due to its large endothermicity. Therefore, for secondary or tertiary carbonium ions (which are more stable, with a smaller ΔH_f, than primary ions containing the same number of carbon atoms), the only mode of

reaction likely to slow polymerization is

$$X^+ + H_2O \rightarrow XH_2O^+ \qquad (32)$$

The $C_2H_5^+$ ion (which is a primary carbonium ion) has already been mentioned as reacting by hydrogen abstraction[25]:

$$C_2H_5^+ + H_2O \rightarrow C_2H_4 + H_3O^+ \qquad (33)$$

Less stable cations such as CH_2^+, CH_3^+ and CH_4^+ have previously been mentioned as unlikely to react with water where methane is in great excess. The same is likely for C^+ and CH^+ since these are ions which also initiate rapid polymerization in methane.

Other hydrogen deficient ions might be expected to undergo water-complexing reactions although non-reaction of $C_2H_4^+$ and $C_3H_5^+$ with 1% H_2O in methane indicate the contrary[25]. It is not clear just precisely what are the important mechanisms by which H_2O slows polymerization, but it's not unreasonable that a complexing reaction such as (32) could accomplish this end. The fact that propane can react effectively even in the presence of excess water could indicate that the H_2O complex is not highly inactivated with

respect to polymerization.

Alternatively the complex could be decomposed by the presence of excitation energy in the polymerizing ion X^+, or through a mechanism suggested by the mass spectrometric studies of Minc and Wincel[34]

$$C_4H_9^+ + H_2O \rightarrow C_3H_7^+ + \text{residue}$$

$$C_3H_7^+ + H_2O \rightarrow C_2H_5^+ + \text{residue}$$

This mechanism, which is calculated to be endothermic by 8 and 39 $\frac{\text{kcal}}{\text{mole}}$, respectively, when the residue is equated with CH_3OH, was inferred indirectly in the presence of numerous other reactions and might be in error. If this reaction occurs for excited X^+ ions, one wonders why similar reactions for CH_4 and C_3H_8 (instead of H_2O) could not slow down polymerization. Perhaps the explanation is that in our radiolysis experiments at near atmospheric pressure, the ionic reactants have less excitation energy (due to greater chances for non-reactive collisional stabilization) and the importance of these reactions is minimized. Also alkyl ions may possibly not be the ion most important in promoting polymerization.

In the absence of further experimental studies, it seems prudent to relegate polymerization slowdown to the

vague reaction, $X^+ + H_2O \xrightarrow{k_H}$ inactive products, used in the kinetic scheme.

INFLUENCES DUE TO VARIOUS IMPURITIES

In addition to the effects of water and air, the production of methane from propane could have been influenced by the presence of unlabeled propane, hexane, propene, glass walls of the sample tubes, and unspecified impurities in CP (or even UHP) methane.

Unlabeled propane was added to two different samples to determine whether competition between labeled and unlabeled propane would slow down the observed rates of radioactive methane production. The data is summarized in Table V.

One sees that methane production rates in the presence of unlabeled propane do not agree well with the predicted rates even when the activities are corrected* to 10·3 mc/mmol. This may well be due to the fact that the isopropyl iodide used in preparing this propane (by reaction with $LiAlH_4$) contained impurities which could scavenge X^+ ions. It must also be noted that sample 1 contained 3100 counts of labeled propene and that sample 2 had recently had the sample tube walls cleaned with aqueous NaOH and toluene

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*To correct for the presence of unlabeled C_3H_8, both rates and concentrations are multiplied by $([C_3H_8]_{\text{unlabeled}} + [C_3H_8]_{\text{labeled}})/[C_3H_8]_{\text{labeled}}$.

TABLE V

EFFECT OF UNLABELED PROPANE ON KINETICS

		Sample 1	Sample 2
1.	$[C_3H_8]_{labeled}$ (in molec/cc)	4.8×10^{14}	8.5×10^{14}
2.	$[C_3H_8]_{unlabeled}$ (in molec/cc)	16.2×10^{14}	32.4×10^{14}
	METHANE PRODUCTION RATES (CTS/HR)		
3.	Observed (with unlabeled C_3H_8)	1.20	1.88
4.	Predicted* (without unlabeled C_3H_8)	3.5	9.2
	METHANE PRODUCTION RATES (CORRECTED TO 10.3 mc/mmol)		
5.	Observed	5.3	9.2
6.	Predicted*	10.3	14.2

* Taken from UHP line in Fig. 8 for the corresponding $[C_3H_8]_{labeled}$.

(the significance of this with regard to decreasing $G(CH_4)$ will be discussed later). The important thing to note is that the addition of unlabeled propane can cause an apparent

decrease in $G(CH_4)$. This decrease is explained by a comparison of the theoretical rates derived in the presence and in the absence of additional unlabeled propane. The observed rate in the presence of additional unlabeled propane concentrations of $[C_3H_8]_a$ is

$$G(CH_4)_a = \frac{(\frac{100}{D})\, k_i k_{26} [C_3H_8]}{(\bar{Y}k_{27} + \bar{Z}k_{26})([C_3H_8]_a + [C_3H_8]) + \bar{X}k_{28}[CH_4] + k_t}$$

It is then seen that the decrease in G values is due to an increase in the rate of the termination reactions due to the term $(\bar{Y}k_{27} + \bar{Z}k_{26})[C_3H_8]_a$ in the denominator without an increase in the rate of methane production due to the factor $k_{26}[C_3H_8]$ in the numerator.

The presence of hexane during radiolysis could conceivably have the same effect as additional propane. However, the few radiolyses which contained radioactive hexane in amounts greater than 10% of the propane peak were done in CP methane. Since $G(CH_4)$ was so low in CP methane even effects due to the maximum ratio of $[C_6H_{14}]/[C_3H_8] = .70$ might well be attributed to experimental error. Thus, no conclusion can be formed on the effects of hexane on CH_4 formation from propane.

It is, however, interesting to speculate on the nature of hexane reactions. The consumption rate for hexane in UHP methane is the same as that for propane (see rate summary at beginning of this paper). This could indicate a similar mechanism for both hexane and propane disappearance. Quite possibly both are incorporated into polymer at the same rate. Unfortunately, no reliable $G(-C_6H_{14})$ data is available for runs in CP methane. This low reliability can be attributed to failure to sweep out the injection chamber between GC analyses. Later analyses corrected this omission and gave much more reliable data (Fig. 10). Also, no data is available concerning the effects of water on hexane consumption. Thus, whether or not hexane has both an ionic and a non-radical, non-ionic mechanism must be left to future experimentation.

It seems a reasonable conjecture, however, that hydrocarbons of structures similar to that for the hexane (2,2- or 2,3-dimethyl butane) used in this study would react with a G value of $G(RH) = 1.2 \times 10^{-15}[RH]$.

Propene is an excellent ion scavenger which can undergo a great variety of reactions in methane.[35] Some typical reactions are:

$$CH_5^+ + C_3H_6 \rightarrow CH_4 + C_3H_7^+ \quad (35)$$

$$C_2H_5^+ + C_3H_6 \rightarrow C_2H_4 + C_3H_7^+ \quad (36)$$

$$C_3H_7^+ + C_3H_6 \rightarrow C_6H_{13}^+ \quad (37)$$

The condensation reaction (37) is of particular interest since $C_3H_7^+$ could represent the polymerizing ion, X^+. In this manner C_3H_6 could be considered a scavenger which could terminate polymerization. However, the calculated $\Delta H = -20 \frac{kcal}{mole}$ for reaction (38)

$$RC_3H_6^+ + C_3H_6 \rightarrow RC_6H_{12}^+ \quad (38)$$

indicates that the production would have sufficient energy to react readily by any of mechanisms (26), (27) and (28). Thus, polymerization would not be slowed by the presence of C_3H_6.

This idea is supported by the experimental observation (Table VI) that C_3H_6 (at concentrations below $1.5 \times 10^{15} \frac{molec}{cc}$) has no measurable effect on $G(-C_3H_8)$ or $G(CH_4)$.

TABLE VI

THE EFFECTS OF PROPENE

$[C_3H_8]$	$[C_3H_6]$	$G(-C_3H_8)$	$G(-C_3H_8)^{\#}_{expected}$	$G(CH_4)$	$G(CH_4)^{*}_{expected}$
16,000	5,500	--	52	+ 8.9	+ 8.6
29,000	11,000	--	95	+13.1	+12.2
6,700	4,000	--	22	+ 4.22	+ 5.2
10,300	3,500	35.66	33	+ 8.58	+ 6.6

\# Taken from line in Fig. 6.
* Taken from line in Fig. 8.

The unirradiated glass walls of the sample tube may have effected a slowdown in methane production rates for some of the radiolyses. Even allowing for a correction of two standard deviations on these samples, $G(CH_4)$ could not always be made to agree with the expected values. One sample tube containing unlabeled propane (sample 2) had been recently cleaned with NaOH and exhibited unpredictably low $G(CH_4)$ values. Thus, although Lind[3] indicates that wall effects in gaseous radiation chemistry are largely unsubstantiated, there exists the possibility here that polymerization occurs at the container walls. Further studies will be needed to substantiate such an effect.

The substitution of CP methane for UHP methane has a profound effect (Figs. 8 and 9) on methane radiolysis. Reference to Table II shows that this effect could be due to any of a number of impurities present in CP methane. It has already been shown that propane impurities could cause a decrease in $G(CH_4)$. Other ion scavengers such as C_2H_6, CO_2 and H_2O could also slow methane production.

The pertinent question here is whether or not a sufficiently high concentration of radioactive propane could cause $G(CH_4)$ to approach the limiting value of $G(CH_4) = 1{\cdot}6$ found in UHP methane. A glance at the curve for CP methane in Fig. 9 indicates that $G(CH_4)$ is approaching approximately $0{\cdot}4$. Barring experimental uncertainty at the observed low reaction rates, this seems to say that the extremely high concentrations of propane necessary to attain $G(CH_4) = 1{\cdot}6$ will simultaneously reduce the tendency to polymerize (because propane having a lower ionization potential than methane will have less tendency to produce X^+ ions sufficiently energetic to polymerize). The ion scavenger involved apparently has a high rate of scavenging since propane concentrations which might be sufficient to cause $G(CH_4)$ to approach $1{\cdot}6$ are likely to exist only when the sample approaches 100%

propane content. It is difficult to determine the true scavenger when faced with the knowledge that propane apparently reacts 30 times faster with X^+ than does H_2O. Perhaps CO_2 at 2000 ppm (Table II) has some unique scavenging efficiency which cannot be predicted solely on the grounds of basicity. The only literature available on the effects of CO_2 is a study by Blake et al.[36] which states that large excesses of CO_2 accelerate methane polymer production. Perhaps this is due to some effect similar to that of a higher ionization potential for CO_2 than for CH_4. The lowest ionization potentials for CO_2 and CH_4 are nearly the same, making it impossible to attribute the effect to this explanation alone. However, the earlier ionization potential model for predicting $G(-C_3H_8$ to polymer) may apply better to a series of similar hydrocarbons than to a heterogenous collection of compounds. The presence of a large number of ionization potentials for a specific compound may also complicate the picture.

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APPENDIX

KEY TO APPENDIX

The description "res." after a tube number indicates that samples analyzed did not contain the usual 1.7 ml of gas sample

Some irradiations were done with ν-rays and such irradiation times were designated with (ν). All other irradiations were done with X-rays.

Temperatures are in °C.

A is the activity of the isopropyl iodide (or propane) used in preparing the samples (measured in millicuries per millimole).

UHP or CP designates the purity of the methane sample.

Irradiation times are in actual hours and minutes, although the rate constants are calculated for 55 minute hours.

Peaks analyzed in a particular tube are designated by approximate peak times in minutes and are assigned the most likely molecular identification.

The numbers in the tables are observed counts minus background for a 1.7 ml sample.

The notation "N.D." means not determined.

A second set of tables give kinetic data for each peak in each tube on which least squares treatments were performed. Rate data listed are the initial concentration of the compound $[C_3H_8]_i$ in counts followed by the rate constant K in plus or minus counts per hour for the equation

$$[C_3H_8] = [C_3H_8]_i + K(\text{time})$$

The standard deviations for $[C_3H_8]_i$ and K are also tabulated.

Footnotes used are:

* This data point not used in calculations.

R This data point not used in revised calculations.

C Contribution of CO_2 to this peak was subtracted out to give this result.

Tube 1 (Temp. = 150°, A = 4.9, CP, no additives)

Irrad. Time	1.7	2.5	4.1	7.0	8.0	15.0	33.0
0:00	134	702	47,978	202	160	584	16,309
24:59(ν)	97	779	48,838	291	262	724	15,676
49:22(ν)	78	755	49,794	267	217	458	14,791
49:22(ν)	80	824	47,111	N.D.	N.D.	433	11.920
189:49(ν) + 1:30	88	770	47,566	420	190	591	13,179
189:49(ν) + 3:20	137	856	50,728	354	238	615	13,327
189:49(ν) + 3:20	68	791	44,473	400	174	543	12,088
189:49(ν) + 5:10	81	209	11,735	105	33	240	10,966
189:49(ν) + 7:00	35	163	11,697	86	22	275	7,054
189:49(ν) + 9:50	64	164	10,697	74	44	227	6,464

Tube 1 (Temp. = 75°)	1.9	4.2	4.7	13.0	15.0
0:00	77	111	620	20,902	27,236
24:59(ν)	103	44	621	19,546	29,039

Tube 1 res. (Temp. = 75°)	1.9	4.2	4.7	13.0	15.0
189:49(ν) + 1:30	---	---	66	2,067	3,530
189:49(ν) + 3:20	---	---	33	2,388	4,570
189:49(ν) + 5:10	---	---	27	520	860

Tube 2 (Temp. 150°, A = 4.9, CP, no additives)

Irrad. Time	1.7	2.5	4.1	7.3	8.1	15.7	33.5
0:00	∿ 0	410	28,846	174	143	640	22,443
24:27(ν)	∿ 0	382	26,237	111	58	467	19,119
49:26(ν)	31	300	25,638	33	∿ 0	405	16,444
121:49(ν)	16	458	27,679	<355	162	486	18,756
262:16(ν)	∿12	456	27,001	150	186	503	16,840
403:12(ν)	40	500	27,314	N.D.	N.D.	465	15,638
516:52(ν)	60	430	25,795	143	143	324	11,970
516:32(ν) + 1:50	37	418	23,636	134	104	442	13,027

Tube 2 (Temp. = 126°)

	1.5	3.0	5.5	11.2	13.0	28.9
516:32(ν) + 1:50	37	309	15,983	69	52	273

Tube 2 (Temp. = 75°)

	1.9	4.2	4.6	13.0	15.0	16.5
49:26(ν)	N.D.	∿ 0	346	7338	15,368	N.D.
121:49(ν)	∿ 0	42	373	8721	18,022	N.D.

Tube 2 (Temp. = 75°) res.

	1.9	4.2	4.6	13.0	15.0	16.5
262:16(ν)			33	1032	2306	240
516:52(ν)			100	1146	2768	211
516:52(ν) + 1:50			52	836	1886	211

Tube 3 (Temp. = 150°, A = 4.9, CP, no additives)

Irrad. Time	2.0	2.6	4.2	7.1	8.1	15.1	32.0
0:00	32	168	10,228	67	65	321	10,297
0:15	24	162	9,643	N.D.	52	261	9,821
2:05	21	181	8,747	N.D.	44	181	7,682
2:05	950	793	13,138	N.D.	N.D.	N.D.	N.D.
3:55							
3:55							
3:55	681	489	12,694	42	61	218	7,106
3:55	340	400	14,090	N.D.	92	260	8,823
5:45	722	522	11,653	N.D.	90	204	6,486
7:35	518	441	9,706	N.D.	5	106	4,578
9:25	--2239--		3,300	56	N.D.	45	2,622
11:15	∿ 0	∿ 0	67	∿ 0	∿ 0	∿ 0	269

Tube 3 res. (Temp. = 75°)

	4.7	14.5	17.0
0:15	30	1351	46

Tube 4 (Temp. 150°, A = 4.9, CP, no additives)

Irrad. Time(ν)	2.1	2.5	4.1	5.2	7.5	14.0	30.0
0:00	N	62	3126	N.D.	N.D.	22	2751
47:41(ν)	--1276--		3204	N.D.	N.D.	N.D.	2122
47:41(ν)	N.D.	N.D.	N.D.	N.D.	N.D.	14	1936
47:41(ν)	36	64	3771	103	21	40	3240
47:41(ν) + 1:50	95	68	3636	N.D.	N.D.	N.D.	2943
47:41(ν) + 3:40	90	94	3712	N.D.	N.D.	N.D.	3091
47:41(ν) + 5:30	150	100	3789	106	N.D.	70	2454
47:41(ν) + 7:20	∿ 0	10	432	∿ 0	∿ 0	∿ 0	298
47:41(ν) + 7:20	∿ 0	∿ 0	405	∿ 0	∿ 0	∿ 0	258
47:41(ν) + 9:10	∿ 0	∿ 0	353	∿ 0	∿ 0	∿ 0	270
47:41(ν) +11:00	∿ 0	∿ 0	254	∿ 0	∿ 0	∿ 0	145

Tube 5 (Temp. = 150°, A = 4.9, CP, no additives)

Irrad. Time	1.9	2.5	4.1	7.1	7.9	11.3	15.0	31.5
0:00	--183--		19,571	411	150		49	590
0:00	59	96	21,014	195	141		0	596
1:50	42	183	20,221	170	180		N.D.	446
3:40	74	116	20,133	213	207	30	24	569
5:30	37	126	19,278	180	167	100	25	453
7:20	72	151	22,805	211	156	111	34	606
11:00	57	125	19,218	216	155	255	N.D.	547
12:50	--227--		15,336	194	130	50	69	335
14:40	--252--		13,340	40	56	60	N.D.	199
18:20	--226--		13,753	--271--		82	N.D.	366

Tube 5 (Temp. = 75°)

	1.8	2.6	3.7	4.5	12.7	14.2
0:00	15	N.D.	64	51	14,005	3506
1:50	N.D.	N.D.	39	41	12,125	3077
7:20	28	8	28	66	11,283	3112
18:20	47	57	33	49	9,296	2529

Tube 6 (Temp. = 150°, A = 4.9, CP, no additives)

Irrad. Time	2.0	2.6	4.1	7.0	8.0	11.0	15.0	31.0
0:00		64	7810	77	51			400
1:50	21	37	7808	60	70			380
3:40	32	40	7820	--91--			39	422
5:30		13	7697	50	59			417
7:20		10	8681	12	~ 0	20		455
11:00	11	25	7276	86	70	48	~ 0	437
12:50	--100--		5726	150	83			172
14:40		46	5169	42	35			200
18:20		46	5360	36				290
20:10		50	5520					262

Tube 6 (Temp. = 75°)

	13.0	14.5
0:00	5451	1561
1:50	4892	1409
5:30	4842	1395
20:10	2921	990

Tube 7 (Temp. = 150°, A = 4.9, CP, no additives)

Irrad. Time	1.55	2.25	3.6	5.25	27.0
0:00	23	23	1854	11	256
1:50		37	2243		368

Tube 7 (Temp. = 75°)

	2.0	4.4	13.8
0:00	32	55	2051
1:50	18	16	1743

Tube 8 (Temp. = 150°, A = 0.7, CP, no additives)

Irrad. Time	1.6 CH_4	2.0 CO_2	2.3 C_2H_4+ C_2H_6	4.2 C_3H_6 +C_3H_8	7.0 i-C_4H_{10}	11.3 i-C_3H_7OH	14.6 C_5H_{12}
0:00	300	1728	667	33,395	9756	25,411	772

Tube 8 (Temp. = 120°)

	1.8 CH_4	2.3 CO_2	3.0 C_2H_4+ C_2H_6	7.0 C_3H_6+ C_3H_8	9.0 ---	13.5 i-C_4H_{10}	16.0 ---	25 i-C_3H_7OH	30 C_5H_{12}	35 ---
0:00	238	1988	397	36,411	166	13,038	669	39,537	374	892
1:50	274	1895	432	34,244	268	9,427	860	32,222	268	590
3:40	240	1980	580	35,134	218	10,766	668	43,010	296	614
7:20	200	2030	507	34,210	222	9,452	658	27,104	197	689
11:00	273	1541	213	28,595	158	7,688	374	21,846	98	718
14:40	173	1167	225	20,450	164	5,933	393	12,927	60	468
14:40	155	1389	312	25,900	146	7,185	560	18,480	∿ 0	282

Tube 9 (Temp. 150°, A = 10.3, CP, no additives)

Irrad. Time	2.25 min.	3.1	5.0	8.5	37.5
	CH_4	$C_2H_4+C_2H_6$	C_3H_8	$i\text{-}C_4H_{10}$	C_6H_{14}
0:00	869	112	24,605	140	7678
1:50	844	91	23,004	135	6120
1:50	947	134	23,187	130	6138
5:30	928	136	23,496	171	6698
9:10	935	93	23,878	140	6878
12:50	997	167	23,627	183	5973
16:30	966	130	23,407	142	6760
20:10	986	113	23,348	170	6123
23:50	931	166	22,369	165	6747
27:30	912	120	22,400	120	5520
31:10	1023	124	22,749	110	5735

Tube 10 (Temp. = 160°, A = 10.3, CP, no additives)

Irrad. Time	2.2	3.0	4.55		7.2	39.5
	CH_4	$C_2H_4+C_2H_6$	C_3H_8		$i\text{-}C_4H_{10}$	C_6H_{14}
0:00	N.D.	70	5353		∿ 0	2753
0:00	194	27	5677		29	3472
1:50	184	33	4970		31	2854
5:30	221	50		--5519--		3543
5:30	200	∿ 0	5392		21	3243
9:10	169	48	5578		39	3115
12:50	167	∿ 0	5500		46	3220
16:30	258	18		--6597--		3760
20:10	210	∿40	5345		∿46	3042
23:50	215	47	5037		∿ 0	2380
27:30	223	8	5302		15	2804
31:10	190	29	5160		0	2228
34:50	208	23	5308		37	(no data)

Tube 10 (Temp. = 75°)

	2.9	22.5
	CH_4	$C_2H_4+C_2H_6$
34:50	250	5223

Tube 11 (Temp. = 150°, A = 10.3, CP, no additives)

Irrad. Time	2.3	5.1	39.0
	CH_4	C_3H_8	C_6H_{14}
0:00	46	1892	2772
0:00	36	1828	2152
3:40	88	1863	2753
7:20	46	1985	2700
11:00	53	1874	2938
14:40	60	1874	2603
18:20	77	1908	2445
22:00	77	1792	2505
25:40	91	1825	2380
29:20	90	1833	2190
33:00	90	1908	2380
36:40	51	1745	2117
40:20	78	1821	2265

Tube 11 (Temp. = 75°)

	3.0	23.5
40:20	64	1775

Tube 12 (Temp. = 150°, A = 10.3, CP, no additives)

Irrad. Time	2.3	3.25	5.2	9.0	10.0	19.0	40.5
	CH_4	C_2H_4+ C_2H_6	C_3H_6+ C_3H_8	C_4H_{10}	C_2H_5OH	C_5H_{12}	C_6H_{14}
0:00	100	275	7325	203	97	100	2218
1:50	135	238	7879	132	59	75	2345
5:30	95	288	7544	122	82	135	2126
9:10	154	250	7634	182	96	95	2538
12:50	125	250	7300	112	98	55	2253
16:30	177	364	7431	158	81	74	2357
20:10	133	316	7011	137	95	127	2090
23:50	184	304	7391	148	106	138	2373
27:30	85	301	7412	203	66	201	2249
31:10	180	267	7513	157	57	93	2123
34:50	202	307	6856	136	57	93	2198
38:30	193	232	6972	142	87	268	2093

Tube 12 (Temp. = 75°)

	3.05 CH_4	4.2 CO_2	6.55 C_2H_4	7.6 C_2H_6	21.6 C_3H_6	23.65 C_3H_8
38:30	209	52	152	221	1348	5378

Tube 13 (Temp. = 150°, A = 4.9, CP, no additives)

Irrad. Time	2.3 CH_4	3.3 C_2H_4+ C_2H_6	5.3 C_3H_6+ C_3H_8	8.9 C_4H_{10}	10.1 C_2H_5OH	19.0 C_5H_{12}	40.5 C_6H_{14}
0:00	702	1443	9650	795	265	248	3059
0:00	743	1589	9701	789	246	247	2987
1:50	776	1538	9306	756	210	196	2494
5:30	750	1666	9413	731	340	225	2820
9:10	671	1550	9129	737	264	220	2834
12:50	823	1477	9509	450	317	210	2934
16:30	693	1593	9661	763	263	297	3193
16:30	744	1676	9388	730	257	256	2295
20:10	787	1650	9599	836	214	302	3167

Tube 13 res. (Temp. - 75°)

	2.9 CH_4	7.45 C_2H_4+C_2H_6	22.4 C_3H_6	24.0 C_3H_8
12:50	66	87	123	1002

Tube 13+ (Temp. = 150°, A = 4.9, CP, air added)

	2.3 CH_4	3.3 C_2H_4+ C_2H_6	5.3 C_3H_6+ C_3H_8	8.9 C_4H_{10}	10.1 C_2H_5OH	~14	19.0 C_5H_{12}	40.5 C_6H_{14}
0:00	760	1501	8387	596	264	94	188	2421
0:00	807	1430	9165	758	180	30	274	2611
1:50	696	1669	8966	750	250	93	280	3097
5:30	808	1474	8732	808	219	69	256	2730

Tube 14 (Temp. = 150°, A = 4.9, CP, no additives)

Irrad. Time	2.4 CH_4	3.4 C_2H_6	5.5 C_3H_8	9.5 $i\text{-}C_4H_{10}$ $+C_2H_5OH$	19 C_5H_{12}	40.5 C_6H_{14}
0:00	186	265	7901	308	154	3301
1:50	215	268	8236	233	118	4070
1:50	247	377	8195	330	235	3604
1:50	188	260	7674	349	163	2908
5:30	190	268	6996	328	139	2516
9:10	212	308	7205	288	120	2881
18:20	179	255	7189	290	158	2553
29:20	130	180	4826	212	94	1641
33:00	290	251	6584	300	128	2258
49:30	203	250	6052	220	121	2002
73:20	282	277	6321	302	132	1690
91:40	225	238	5763	242	76	1372

Tube 14 (Temp. = 75°)

	3.0 CH_4	7.5 C_2H_6	24.1 C_3H_8
0:00	172	246	8063

Tube 15 (Temp. 150°, A = 4.9, CP, no additives)

Irrad. Time	2.4 CH_4	3.4 C_2H_6	5.5 C_3H_8	9.1 $i\text{-}C_4H_{10}$	10.4 C_2H_5OH	~42 C_6H_{14}
0:00	50	124	7224	60	56	566
0:00	56	120	7294	65	111	538
1:50	45	136	7231	86	86	464
5:30	50	132	7113	74	77	487
9:10	61	129	6738	70	89	437
12:50	51	134	6754	68	102	452
16:30	27	115	5844	71	53	393
20:10	47	132	6276	58	79	335
23:50	58	147	6845	85	85	403

Tube 15 (Temp. = 75°)

	3.1 CH_4	7.7 C_2H_6	24.4 C_3H_8
23:50	51	172	7145
23:50	60	154	6745

Tube 16 (Temp. = 150°, A = 4.9, CP, no additives)

Irrad. Time	2.4	3.4	5.5	8.9	10.2	420
	CH_4	C_2H_6	C_3H_8	$i\text{-}C_4H_{10}$	C_2H_5OH	C_6H_{14}
0:00	719	1451	20,565	129	181	3133
1:50	788	1458	20,903	149	233	3204
5:30	735	1403	20,833	184	264	3327
9:10	740	1485	19,974	166	218	2946
12:50	803	1525	21,378	161	273	3250
16:30	788	1509	20,568	123	210	3079
20:10	785	1419	18,423	115	224	2445
23:50	737	1496	18,889	125	193	2513
27:30	776	1497	19,365	167	214	2620
31:10	837	1478	20,275	210	214	2768

Tube 16 (Temp. = 75°)

	3.0	7.6	24.1
	CH_4	C_2H_6	C_3H_8
0:00	714	1535	21,713

Tube 17 (Temp. = 150°, A = 4.9, UHP, no additives)

Irrad. Time	2.4 CH_4	3.4 C_2H_6	5.5 C_3H_8	42.6 C_6H_{14}
0:00	130	309	4089	926
1:50	170	282	4384	1141
5:30	150	284	4189	1016
9:10	159	286	4174	991
12:50	173	294	4063	844
16:30	211	270	4238	892
20:10	222	248	3781	814
23:50	259	269	4016	910
27:30	204	253	3990	805

Tube 17 (Temp. = 75°)

	3.1 CH_4	7.8 C_2H_6	25.0 C_3H_8
0:00	100	236	4000
27:30	195	266	3977

Tube 18 (Temp. = 150°, A = 4.9, UHP, no additives)

Irrad. Time	2.4 CH_4	3.4 C_2H_6	5.5 C_3H_8	43.0 C_6H_{14}
0:00	208	334	5181	1880
1:50	227	354	5108	1874
5:30	245	349	4776	1685
9:10	220	316	4931	1892
12:50	242	339	4998	1970
16:30	249	344	4962	1909
20:10	255	317	4233	1534
23:50	262	349	4554	1522
27:30	235	292	4519	1621
31:10	252	352	4436	1510
34:30	232	294	4204	1381
38:10	224	331	4486	1535

Tube 18 (Temp. = 75°)

	3.0 CH_4	7.7 C_2H_6	24.35 C_3H_8
38:10	218	276	3950

Tube 19 (Temp. = 150°, A = 4.9, UHP, no additives)

Irrad. Time	2.4	3.4	5.5	43.0
	CH_4	C_2H_6	C_3H_8	C_6H_{14}
0:00	135	205	3086	2196
3:40	140	173	3082	2169
7:20	163	171	2804	2003
11:00	106	182	2835	2262
14:40	127	154	2832	2124
18:20	144	184	2929	2216

Tube 19 (Temp. = 75°)

	3.15	7.8	25.0
	CH_4	C_2H_6	C_3H_8
0:00	121	228	2939

Tube 20 (Temp. = 150°, A = 4.9, UHP, no additives)

Irrad. Time	2.4 CH_4	3.4 C_2H_6	5.5 C_3H_8	42.0 C_6H_{14}
3:40	59	61	937	1099
7:20	55	60	888	1049
11:00	47	63	778	1051
14:40	78	51	844	975
18:20	45	29	941	956

Tube 20 (Temp. = 75°)

	3.2 CH_4	7.85 C_2H_6	25.55 C_3H_8
0:00	50	48	866

Tube 21 (Temp. = 150°, A = 10.3, UHP, no additives)

Irrad. Time	2.4	3.5	5.7	16.0	16.0+	44.0
	CH_4	C_2H_4+ C_2H_6	C_3H_6+ C_3H_8	C_3H_7OH	ox. prod.	C_6H_{14}
0:00	29	514	22,133	23	109	59
1:50	46	522	21,497	249	175	70
5:30	119	536	20,422	342	367	66
9:10	123	515	19,380	584	436	48
12:50	175	538	18,160	779	491	24
16:30	280	496	17,802	988	646	48
20:10	303	507	16,356	1062	716	32
23:50	329	409	15,682	1020	772	46
27:30	347	415	14,589	993	761	39
31:10	385	476	15,803	1152	977	32

Tube 21 (Temp. = 75°)

	3.25	4.6	7.3	8.1	24.5	25.5
	CH_4	CO_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8
0:00	8	16	132	285	6388	17,074
16:30	220	73	154	243	3624	15,700
31:10	283	68	179	211	1562	12,598

Tube 22 (Temp. = 150°, A = 10.3, UHP, no additives)

Irrad. Time	2.5 CH_4	3.4 C_2H_4+ C_2H_6	5.7 C_3H_6+ C_3H_8	15.7 C_3H_7OH	15.7+ ox. prod.	43.5 C_6H_{14}
0:00	80	795	40,803	∿ 0	∿ 0	116
1:50	75	876	39,049	282	263	91
5:30	186	833	39,607	620	595	241
9:10	286	862	36,460	736	788	250
12:50	329	886	34,575	914	807	225
16:30	363	948	35,171	1256	1095	234
20:10	458	881	32,166	1378	964	202
23:50	534	905	32,771	1493	1158	205
27:30	567	830	30,217	1370	1128	120
31:10	589	831	29,785	1396	1111	146
34:50	672	951	30,429	1705	1539	198

Tube 22 (Temp. = 75°)

	3.2 CH_4	4.6 CO_2	7.1 C_2H_4	8.0 C_2H_6	14.1 HCHO	23.0 C_3H_6	25.0 C_3H_8
0:00	13	13	308	335	∿ 0	9630	25,572
16:30	343	70	407	414	∿ 0	6704	29,067
34:50	524	116	297	393	152	3536	24,824

Tube 23 (Temp. = 150°, A = 10.3, UHP, no additives)

Irrad. Time	2.5 CH_4	3.5 C_2H_4+ C_2H_6	5.9 C_3H_8	∿ 15+ i-C_3H_7OH	44.0 C_6H_{14}
0:00	74	180	54,556	110	1898
1:50	111	184	48,351	276	1851
5:30	184	264	48,878	253	1741
9:10	258	241	48,508	307	1721
12:50	339	266	46,097	358	1674
16:30	411	354	46,243	434	1736
20:10	464	375	46,599	453	1662
23:50	508	350	46,365	547	1636
27:30	589	342	46,962	566	1592
31:10	662	354	41,275	582	1331
34:50	681	430	46,138	646	1458
38:30	791	421	45,053	682	1460

Tube 23 (Temp. = 75°)

	3.3 CH_4	4.6 CO_2	7.2 C_2H_4	8.0 C_2H_6	25.5 C_3H_8
0:00	59	8	∿ 0	174	49,307
42:10	830	55	119	353	48,332

Tube 24 (Temp. = 150°, A = 10.3, UHP, .17 mm air added)

Irrad. Time	2.5 CH_4	3.5 C_2H_6	5.65 C_3H_8	∿ 16 $i\text{-}C_3H_7OH$	44.0 C_6H_{14}
0:00	43	40	4046	26	209
1:50	19	44	4688	23	212
5:30	43	62	4616	45	184
9:10	94	19	4752	4	234
12:50	90	59	4728	22	185
16:30	104	47	3887	110	125
20:10	120	66	4566	35	118
23:50	134	62	4635	46	187
27:30	147	52	4096	42	144
31:10	154	70	4288	115	168
34:50	165	75	3756	79	175

Tube 24 (Temp. = 75°)

	3.3 CH_4	8.0 C_2H_6	26.0 C_3H_8
0:00	42	N.D.	5085
34:50	144	28	4385

Tube 25 (Temp. = 150°, A = 10.3, UHP, 20 mm water added)

Irrad. Time	2.5 CH_4	3.5 C_2H_6	5.6 C_3H_8	10.0 C_2H_5OH	16.0 $i\text{-}C_3H_7OH$	44 C_6H_{14}
0:00	105	89	16,327	112	170	1111
1:50	125	86	18,732	101	56	1515
5:30	94	79	18,551	87	70	1587
9:10	84	100	17,763	108	66	1510
12:50	108	82	17,862	99	49	1461
16:30	99	96	18,324	86	117	1569
20:10	79	72	18,332	98	100	1557
23:50	95	71	17,974	97	99	1623
27:30	104	89	17,443	108	100	1499
31:10	102	74	17,661	103	103	1367
34:50	85	86	16,673	107	131	1211
38:30	97	82	16,649	105	97	1124

Tube 25 (Temp. = 75°)

	3.3 CH_4	8.0 C_2H_6	25.0 C_3H_8
0:00	127	98	19,084
38:30	92	86	17,566

Tube 26 (Temp. = 150°, A = 0.7, UHP, no additives)

Irrad. Time	2.85 CO_2	3.4 C_2H_4+ C_2H_6	5.5 C_3H_6+ C_3H_8	9.8 C_2H_5OH	15.5 $i\text{-}C_3H_7OH$	20.7 C_5H_{12}	44 C_6H_{14}
0:00	588	301	15,032	4229	6077	320	164
1:50	528	290	14,325	3985	5373	312	81
5:30	623	141	13,777	3771	5160	373	86
9:10	572	208	13,570	3924	5319	287	87
12:50	624	242	14,349	4381	7238	444	178
16:30	645	201	13,897	3841	5653	470	140
20:10	644	179	14,518	4098	6221	474	129
23:50	570	169	13,117	3446	5197	362	85
27:30	634	158	13,906	3821	5765	350	69
31:10	501	237	12,530	3301	4892	237	112
34:50	597	155	12,882	3329	5103	304	88

Tube 26 (Temp. = 75°)

	4.5 CO_2	7.0 C_2H_4	8.0 C_2H_6	23.0 C_3H_6+C_3H_8
0:00	651	146	33	15,714
34:50	565	96	33	13,150

Tube 27 (Temp. 150°, A = 10.3, UHP, no additives)

Irrad. Time	2.5 CH_4	3.4 C_2H_4+ C_2H_6	5.7 C_3H_8+ C_3H_6	16.0 $i\text{-}C_3H_7OH$	45.0 C_6H_{14}
0:00	398	431	10,985	30	171
1:50	385	439	10,495	74	151
5:30	431	386	10,425	41	168
9:10	353	314	7,962	172	128
12:50	444	395	9,194	308	205
16:30	480	359	8,963	471	192
20:10	487	325	7,934	485	136
23:50	493	303	7,784	595	156
27:30	500	318	6,910	649	142

Tube 27 (Temp. = 75°)

	3.2 CH_4	4.6 CO_2	7.1 C_2H_4	8.0 C_2H_6	23.2 C_3H_6	25.4 C_3H_8
0:00	391	∿ 0	265	97	4000	6915
1:50	387	∿ 0	285	127	4091	6444
20:10	451	42	186	134	1788	6191
27:30	434	54	138	144	1128	5827

Tube 28 (Temp. = 150°, A = 10.3, UHP, 1 mm H_2O added)

Irrad. Time	2.5 CH_4	3.5 C_2H_4+ C_2H_6	5.7 C_3H_6+ C_3H_8	9.0 i-C_4H_{10} +C_2H_5OH	15.5 i-C_3H_7OH	44.0 C_6H_{14}
0:00	210	474	8510	367	19	359
1:50	200	540	9788	425	46	504
5:30	142	507	8549	381	158	443
9:10	261	557	9813	488	88	485
12:50	272	550	9725	470	110	571
16:30	243	453	9479	442	168	550
20:10	253	497	8995	410	129	479
23:50	293	469	8885	379	159	419
27:30	288	436	8949	371	169	481

Tube 28 (Temp. = 75°)

	3.2 CH_4	4.5 CO_2	7.2 C_2H_4	8.1 C_2H_6	23.8 C_3H_6	25.8 C_3H_8
0:00	169	5	246	335	637	9484
5:30	164	4	147	333	364	7784
20:10	279	36	146	359	306	8693
27:30	295	30	122	349	197	8903

Tube 29 (Temp. = 150°, A = 10.3, UHP, no additives)

Irrad. Time	2.5 CH_4	3.6 C_2H_6	5.7 C_3H_8	9.6 $i\text{-}C_4H_{10}$ + C_2H_5OH	∿ 44 C_6H_{14}
0:00	129	142	4399	217	410
3:40	127	135	4249	191	402
7:20	153	144	4290	289	457
11:00	131	152	4444	262	351
14:40	184	164	4238	183	393
18:20	186	161	4318	194	378
22:00	190	147	3966	189	371
25:40	184	175	4055	164	366
29:20	180	138	3676	181	327
33:00	253	241	4043	193	359
36:40	224	155	4168	154	344

Tube 29 (Temp. = 75°)

	3.2 CH_4	8.2 C_2H_6	25.5 C_3H_8
0:00	135	111	3789
22:00	162	140	4123

Tube 30 (Temp. = 150°, A = 0.7, UHP, no additives)

Irrad. Time	2.3 CH_4	2.8 CO_2	3.4 C_2H_4+ C_2H_6	5.5 C_3H_6+ C_3H_8	9.7 i-C_4H_{10} +C_2H_5OH	15.8 C_3H_7OH	20.8 C_5H_{12}
0:00	675	240	135	2296	867	795	121
3:40	596	281	143	2414	972	837	72
7:20	613	283	146	2190	915	638	108
11:00	636	206	133	2101	850	640	101
14:40	607	269	124	2166	736	645	93
18:20	665	293	100	2058	794	743	152
22:00	634	234	148	1783	703	641	121
25:40	673	231	144	1857	727	772	131
29:20	633	305	96	1735	671	763	147
33:00	570	287	138	1852	752	892	207
36:40	648	285	138	1598	659	691	142

Tube 30 (Temp. = 75°)

	3.0 CH_4	4.5 CO_2	7.1 C_2H_4	8.1 C_2H_6	23.5 C_3H_6	25.9 C_3H_8
0:00	626	301	45	44	2070	284
22:00	673	312	67	35	1718	223
36:40	618	323	72	29	1432	275

Tube 31 (Temp. = 75°, A = 10.3, UHP, no additives)

Irrad. Time	3.4 CH_4	20.5 C_3H_6	22.0 C_3H_8
0:00	~ 0	602	1707
3:40	21	494	1434
7:20	16	501	1614
11:00	19	375	1417
14:40	33	335	1425
18:20	37	356	1345
22:00	48	238	1322
25:40	31	156	1149
29:20*	8	39	423
33:00	41	111	849

Tube 32 (Temp. = 75°, A = 10.3, UHP, 1.2 mm air added)

Irrad. Time	3.1	4.3	6.5	7.3	20.5	22.0
	CH_4	CO_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8
0:00	308	19	--244--		3574	9,738
3.40	426	N.D.	150	210	3804	10,398
7:20	448	N.D.	190	201	3083	10,258
11:00	543	14	127	185	2767	9,878
14:40	610	32	218	223	2590	9,577
18:20	659	N.D.	188	207	2842	9,790
22:00	642	36	192	198	2246	9,361
25:40	667	53	151	268	2432	9,497
29:20	692	86	179	212	2286	9,472
33:00	570	44	207	181	2378	8,415

Tube 33 (Temp. = 75°, A = 10.3, UHP, 7 mm H_2O added)

Irrad. Time	3.1	4.3	6.5	7.3	20.5	22.0
	CH_4	CO_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8
0:00*	--35--		42	67	2537	30,960
3:40^R	89	37	78	124	3112	42,290
7:20^R	84		70	125	2538	40,050
11:00^R	84		66	102	2430	39,823
14:40	107		75	90	2770	45,369
18:20	143		94	90	2497	45,846
22:00	128	14	74	114	1885	42,554
25:40	156	44	89	86	2100	45,278
29:20	168	52	80	83	1943	43,656
33:00	141	43	92	120	1715	43,300

Tube 34 (Temp. = 75°, A = 10.3, UHP, no additives)

Irrad. Time	3.1	6.5	7.5	22.0
	CH_4	C_2H_4	C_2H_6	C_3H_8
0:00	87		38	14,867
3:40	124		53	14,453
7:20	150	11	53	13,474
11:00	172	25	62	13,942
14:40	217	38	35	14,622
18:20	273	58	53	14,992
22:00	263	27	76	14,491
25:40	300	30	75	13,784
29:20	291	16	78	14,075
33:00	365	23	91	12,968

Tube 35 (Temp. = 150°, A = 10.3, UHP, 3mm H_2O added)

Irrad. Time	3.0 CH_4	6.4 C_2H_4	7.1 C_2H_6	21.5 C_3H_8
0:00	73		62	17,126
3:40	94		65	15,689
7:20^R	92		57	10,380
11:00	125		52	15,126
14:40	147		47	16,370
18:20	186		79	17,050
22:00	224	22	51	16,413
25:40	178	~ 0	59	15,900
29:20	221		59	16,016
33:00	226	17	70	14,999

Tube 36 (Temp. = 150°, A = 10.3, UHP, .055 mm water added)

Irrad. Time	2.4	3.4	5.4	~ 40
	CH_4	C_2H_6	C_3H_8	C_6H_{14}
0:00	148	43	8900	296
3:40	175	67	9191	333
7:20	202	76	8963	337
11:00	203	62	8572	313
14:40	227	81	9358	326
18:20	288	77	9050	302
22:00	265	75	8852	334
25:40	274	69	8713	248
29:20	264	80	8896	274
33:00	287	114	9224	301

Tube 37 (Temp. 150°, A ≒ 10.3, UHP, 2.3 mm air and 8 mm water added)

Irrad. Time	2.4	3.4	5.4	∿ 40
	CH_4	C_2H_6	C_3H_8	C_6H_{14}
0:00	10	28	4746	410
3:40	15	55	4885	486
7:20	23	45	4793	442
11:00	7	36	4993	444
14:40	30	44	4693	492
18:20	∿ 0	41	5074	427
22:00	16	47	4954	438
25:40	17	34	4873	388
29:20	31	46	5163	504
33:00	24	49	5089	419

Tube 38 (Temp. = 75°, A = 10.3, UHP, .05 mm unlabeled propane added)

Irrad. Time	2.9	6.4	6.9	∿ 20	∿ 22
	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
0:00	177	113	55	3116	4413
3:40	191	99	65	2775	4873
7:20	176	93	41	2578	4974
11:00	217	89	60	2741	5142
14:40	174	69	107	2245	4730
18:20	216	89	69	2572	4644
22:00	207	89	94	2110	4790
25:40	199	65	67	1909	4609
29:20	228	84	57	1566	4193

Tube 39 (Temp. = 75°, A = 10.3, UHP, .065 mm water added)

Irrad. Time	2.9	4.1	6.4	6.9	∿ 20	∿ 22
	CH_4	CO_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8
0:00	839	20	321	364	14,414	26,432
3:40	861	16	354	270	13,856	27,596
7:20	930	27	306	385	13,445	27,109
11:00	894	36	317	347	11,316	26,354
14:40	876	33	346	283	10,456	27,026
18:20	921	49	337	295	11,514	25,168
22:00	938	36	365	322	10,752	25,130
25:40	914	34	356	311	10,035	25,537
29:20	999	57	339	389	9,510	25,117

Tube 40 (Temp. = 75°, A = 10.3, UHP, no additives)

Irrad. Time	2.8	7.5	20
	CH_4	C_2H_6	C_3H_8
0:00	439	124	17,695
3:40	463	134	15,694
7:20	545	159	19,256
11:00	507	159	17,923
14:40	476	211	18,169
18:20	502	148	15,474
22:00	603	199	18,151
25:40	572	202	17,952
29:20	625	133	16,694
33:00	619	206	17,925

Tube 41 (Temp. = 75°, A = 10.3, UHP, .1 mm unlabeled propane added)

Irrad. Time	2.8	7.5	20
	CH_4	C_2H_6	C_3H_8
0:00	164	63	8410
3:40	151	61	8767
7:20	161	49	8039
11:00	196	74	8829
14:40	200	67	8208
18:20	116	74	8670
22:00	190	65	8277
25:40	203	63	8279
29:20	237	71	7776
33:00	223	76	7788

Tube	C_3H_8	C_3H_6	CH_4	C_6H_{14}	$i\text{-}C_3H_7OH$
8	37,526	-823.04	261	- 4.76	40,612 -1537.15
	4.4%	19.7%	9.4%	50.1%	- 7.7% 19.8%
9	23,828	-36.81	901	+ 2.62	6809 -27.63
	1.1%	36.5%	2.5%	45.7%	4.0% 52.6%
10	5,689	+11.6	182	+ 1.10	N.D.
	--	--	--	--	
11	1,895	- 1.85	54	+ .70	2690 -10.47
	1.4%	58.1%	15.6%	48.0%	3.9% 39.9%
12	7,623	- 13.25	111	+ 1.78	2322 - 2.72
	1.6%	37.9%	15.6%	39.9%	2.9% 75.4%
13	9,483	+ 0.11	732	+ 1.00	2852 + 1.17
	1.1%	6891.4%	3.6%	185.5%	5.8% 998.3%
14	7,543	-22.03	199	+ 0.47	3153 -20.48
	4.0%	31.7%	8.6%	84.9%	6.0% 21.5%
15	7,209	-36.37	51	- 0.14	524 - 6.51
	2.6%	36.1%	10.7%	277.6%	3.7% 20.8%

Tube	C_3H_8		C_3H_6	CH_4		C_6H_{14}		$i\text{-}C_3H_7OH$	
16	20,845	-44.92		743	+ 1.69	3263	-20.63		
	2.2%	52.6%		2.5%	55.3%	3.8%	30.5%		
17	4,256	-11.36		133	+ 4.22	1032	- 7.37		
	--	--		--	--	--	--		
18	5,098	-19.29		231	+ 0.35	1918	-11.20		
	7.0%	21.1%		3.6%	98.6%	3.5%	24.8%		
19	3,035	-10.74		139	- 0.36	2136	+ 1.88		
	7.7%	62.0%		10.9%	343.5%	3.9%	368.0%		
20	888	- 0.90		58	- 0.12	1134	- 9.00		
	9.3%	691.2%		27.3%	959.4%	1.7%	16.2%		
21	(21,665	-214.94)		21[C]	+ 8.9[C]	61	- 0.91	379	+ 54.66
	(1.7%	8.7%)		--	--	10.3%	35.2%	--	--
22	(39,987	-294.13)		77[C]	13.1[C]	180	+ 0.28	583	+ 70.93
	(1.5%	9.5%)		--	--	18.8%	536.6%	--	--
23	50,321	-160.44		79[C]	+15.5[C]	1863	-10.72	188	+ 12.24
	2.2%	28.8%		10.2%	2.3%	1.9%	13.8%	10.2%	6.4%

Tube	C_3H_8		C_3H_6		CH_4		C_6H_{14}		i-C_3H_7OH	
24	4,592	-12.38			35	+ 3.67	202	- 1.45	19	+ 1.68
	4.1%	69.0%			19.9%	8.5%	8.6%	54.6%	85.9%	44.2%
25	18,127	-21.64			104	- 0.31	1502	- 3.66	88	+ 0.43
	2.2%	74.7%			6.0%	82.6%	6.3%	106.5%	20.6%	171.0%
26	14,573	- 41.98					125	- 0.79	5,896	- 14.30
	2.0%	31.4%					15.9%	114.6%	6.2%	116.4%
27	10,694	-121.85			381	+ 4.22	167	- 0.43	- 8	22.6
	3.5%	17.7%			4.7%	24.3%	9.3%	210.4%	388.5%	7.5%
28	9,235	- 3.27			191	+ 3.47	457	+ 1.38	59	+ 4.06
	3.5%	568.2%			10.3%	32.6%	8.5%	162.2%	36.7%	30.5%
29	9,389	-11.07			123	+ 2.66	418	- 2.01		
	2.2%	37.6%			8.8%	17.3%	3.5%	30.6%		
30	2,367	- 18.12			635	- 0.18			717	+ 0.76
	2.2%	17.3%			3.1%	469.2%			7.3%	289.8%
31	1,688	-19.80	577	-13.66	10	+ 1.05				
	3.4%	14.5%	3.6%	7.6%	47.9%	23.1%				

Tube	C_3H_8		C_3H_6		CH_4		C_6H_{14}		i-C_3H_7OH
32	10,280	-35.66	3508	-39.33	402	+ 8.58			
	2.0%	27.3%	4.5%	18.8%	11.0%	24.1%			
33	46,969[R]	-101.37[R]	3075	-37.16	70	+ 2.60			
	4.2%	72.6%			15.5%	18.6%			
34	14,608	-24.50			95	+ 7.20			
	2.4%	67.6%			11.4%	7.0%			
35	16,494[R]	-21.83[R]			74	+ 4.59			
	2.9%	98.6%			15.8%	11.9%			
36	8,968	+ 0.20			166	+ 3.76	328	- 1.17	
	1.7%	3493.0%			7.4%	15.2%	4.8%	62.3%	
37	4,771	+ 8.63			12	+ 0.31	449	- 0.22	
	1.5%	39.1%			49.1%	86.6%	5.2%	498.2%	
38	4,877	-10.58	3062	-41.26	179	+ 1.20			
	3.5%	85.7%	3.7%	14.5%	5.5%	43.3%			
39	27,269	-69.09	14118	-151.11	852	+ 3.51			
	1.4%	29.3%	3.0%	14.7%	2.2%	27.5%			

Tube	C_3H_8	C_3H_6	CH_4	C_6H_{14}	i-C_3H_7OH
40	17,479 + 0.82		448 + 4.85		
	4.2% 4232.0%		4.6% 20.2%		
41	8,646 -18.98		150 + 1.88		
	2.1% 45.4%		11.7% 43.6%		

Tube	CO_2	C_2H_4	C_2H_6	$i\text{-}C_4H_{10}$	C_2H_5OH	C_5H_{12}
8	2096 - 46.29	(499 - 14.27	)	11,829 -332.94		782 -21.10
	5.4% 23.8%	(14.3% 48.8%	)	5.6% 19.5%		5.7% 9.6%
9		(117 + 0.58	)	151 - 0.35		
		(10.6% 115.2%	)	7.9% 182.0%		
10		N.D.		N.D.		
11						
12		(276 + 0.33	)	155 - 0.13	89 - 0.36	75 + 2.29
		(7.5% 258.3%	)	10.3% 492.9%	10.4% 104.9%	36.8% 49.4%
13		(1528 + 4.24	)	741 - 0.83	270 - 0.51	219 + 2.32
		(2.5% 63.0%	)	8.3% 519.2%	8.7% 323.3%	7.3% 48.6%
14		280 - 0.47		(3.00 - 0.5%	)	156 - 0.68
		6.2% 86.3%		(5.6% 66.7%	)	8.5% 45.4%
15		126 + 0.39		69 + 0.13	85 - 0.24	
		3.8% 85.1%		7.7% 297.2%	12.3% 302.7%	

Tube	CO_2	C_2H_4	C_2H_6	$i\text{-}C_4H_{10}$	C_2H_5OH	C_5H_{12}
16			1453 + 1.19	69 + 0.55	230 - 0.44	
			1.5% 91.9%	12.2% 161.9%	7.2% 189.3%	
17			298 - 1.47			
			-- --			
18			343 - 0.60			
			3.2% 73.7%			
19			189 - 1.08			
			6.4% 92.1%			
20			75 - 1.83			
			13.0% 40.3%			
21		(539 - 2.83)				
		(3.5% 34.0%)				
22		(845 + 1.50)				
		(3.2% 82.2%)				
23		(201 + 5.57)				
		(8.3% 12.4%)				

Tube	CO_2	C_2H_4	C_2H_6	$i\text{-}C_4H_{10}$	C_2H_5OH	C_5H_{12}
24		40 + 0.80 17.4% 39.6%				
25		88 - 0.19 5.3% 96.9%			99 + 0.10	
26	594 - 0.04 4.5% 3083.8%	250 - 2.34 10.2% 49.5%		4181 - 19.30 3.4% 33.2%		370 - 0.68 11.7% 288.8%
27		420 - 4.02 4.3% 26.1%				
28		530 - 2.23 4.3% 58.9%		423 - 0.60 6.5% 264.2%		
29			137 + 1.14 11.1% 56.3%	239 - 1.87 8.0% 43.1%		
30	250 + 0.75 7.2% 101.0%	136 - 0.35 7.6% 177.7%		919 - 6.66 3.4% 19.7%		88 + 1.93 17.0% 32.9%
31						

Tube	CO_2	C_2H_4	C_2H_6	$i\text{-}C_4H_{10}$	C_2H_5OH	C_5H_{12}
32		146 + 1.45	177 + 1.34			
		12.1% 57.2%	11.4% 70.5%			
33		69 + 0.55	116 - 0.63			
		8.3% 46.5%	9.8% 81.3%			
34			39 + 1.25			
			16.5% 24.2%			
35			58 + 0.10			
			10.1% 263.4%			
36			54 + 1.11			
			13.5% 31.2%			
37			40 + 0.15			
			12.1% 147.2%			
38		103 - 0.94	60 + 0.54			
		6.5% 37.3%	21.3% 124.6%			
39	19 + 0.97	323 + 0.90	327 + 0.19			
	25.7% 26.0%	3.5% 65.7%	8.8% 807.0%			

Tube	CO_2	C_2H_4	C_2H_6	$i\text{-}C_4H_{10}$	C_2H_5OH	C_5H_{12}
40			140 + 1.52			
			12.6% 54.5%			
41			60 + 0.36			
			7.1% 55.3%			

Rogers, Daniel T

A mechanism for the disappearance of propane during methane radiolysis