



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  
© Copyright by Daniel Thomas Rogers (1973)

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<sup>14</sup>-propane and the rate of formation of C<sup>14</sup>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: (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(CH<sub>4</sub>) 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<sub>4</sub>), the following reactions were proposed: where X<sup>+</sup> is a heavy polymerizing ion. The ΔH values were estimated from theoretical ΔH<sub>f</sub> values and adjusted to give reasonable consistency with the observed G values.

(Formula not captured by OCR) (Formula not captured by OCR) This kinetic scheme predicts that at 300 ppm C<sub>3</sub>H<sub>8</sub> 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<sub>4</sub> polymerization on reaction products (such as propane). These conflicts are explained by a reinterpretation of the data of previous studies.

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

Approved:

E. W. Anacker

Head, Major Department

Reed Hurd

Chairman, Examining Committee

Henry L. Parsons

Graduate Dean

MONTANA STATE UNIVERSITY  
Bozeman, Montana

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.

## TABLE OF CONTENTS

	<u>Page</u>
VITA . . . . .	ii
ACKNOWLEDGEMENT . . . . .	iii
TABLE OF CONTENTS . . . . .	iv
LIST OF TABLES . . . . .	v
LIST OF FIGURES . . . . .	vi
ABSTRACT . . . . .	vii
INTRODUCTION . . . . .	1
THE PROBLEM . . . . .	15
EXPERIMENTAL PROCEDURES . . . . .	17
EXPERIMENTAL RESULTS AND INTERPRETATIONS . . . . .	28
KINETICS OF METHANE RADIOLYSIS . . . . .	54
KINETICS IN THE PRESENCE OF WATER . . . . .	64
INFLUENCES DUE TO VARIOUS IMPURITIES . . . . .	71
REFERENCES . . . . .	79
APPENDIX . . . . .	82

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
I. Propene Disappearance in $\text{LiAlH}_4$ Chamber . . . . .	20
II. Methane Impurity Analyses . . . . .	21
III. Effect of Water on Methane Production Rate . . . . .	40
IV. Predicted G Values in Argon Solutions Assuming Only Mechanisms (26) and (27) . . . . .	49
V. Effect of Unlabeled Propane on Kinetics . . . . .	72
VI. The Effects of Propene . . . . .	76

## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. The Sample Tube . . . . .	17
2. The Vacuum System . . . . .	18
3. The Injection Chamber . . . . .	24
4. Typical Methane Production Data (Tube 32) . . .	30
5. Typical Ethane "Production" Data (Tube 32) . .	31
6. Propane Production Rates in UHP Methane . . . .	32
7. Propane Production Rates in CP Methane and UHP Methane Plus Water . . . . .	33
8. Methane Production Rates in UHP Methane . . . .	34
9. Methane Production Rates in CP Methane . . . . .	35
10. Hexane Production Rates in UHP Methane . . . . .	36
11. Methane Production Rate Dependence on Water Pressure . . . . .	43
12. Distribution of Excitation Energies in the Polymer Ion X <sup>+</sup> . . . . .	60

## 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.

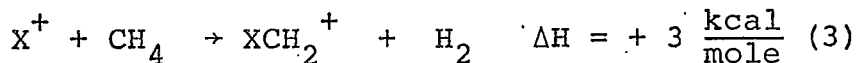
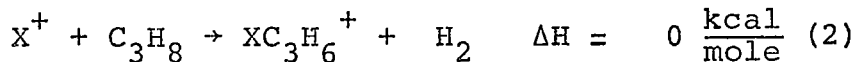
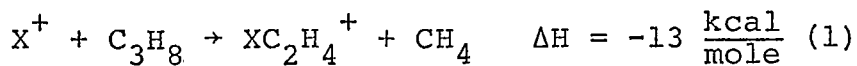
The rate of disappearance of 1,3-C<sup>14</sup>-propane and the rate of formation of C<sup>14</sup>-methane was studied as a function of energy absorbed.

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<sub>4</sub>) 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<sub>4</sub>), the following reactions were proposed:



where X<sup>+</sup> is a heavy polymerizing ion. The ΔH values were estimated from theoretical ΔH<sub>f</sub> 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  $\alpha$ -particles, electrons, X-rays and  $\gamma$ -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<sup>(1)</sup> show the primary species produced to be:  $\text{CH}_4^+$ ,  $\text{CH}_3^+$ ,  $\text{CH}_2^+$ ,  $\text{CH}^+$ ,  $\text{C}^+$ ,  $\text{H}_2^+$ ,  $\text{H}^+$ ,  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$ ,  $\text{C}$ ,  $\text{H}_2$  &  $\text{H}$  (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<sup>(2,3)</sup>. 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 ( $\text{CH}_4^+$ ,  $\text{H}_2$ , 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.

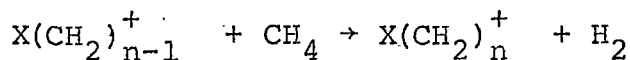
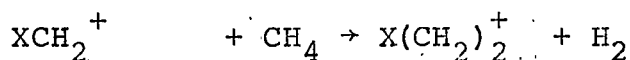
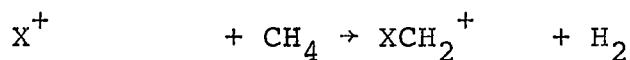
The most important initial products in methane radiolysis are  $C_2H_6$ ,  $H_2$  and a highly branched polymer of the approximate composition  $(CH_2)_{20}$ .

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<sup>(4-6)</sup>. 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.

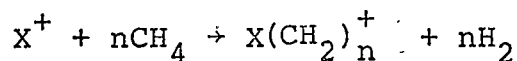
It is presently considered that methane polymerization must be initiated by such highly energetic species as

$C^+$ ,  $CH^+$  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:



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



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

not completely formed before another  $\text{CH}_4$  molecule collides with the reaction center around  $\text{X}^+$ . "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<sup>(4)</sup>. Therefore, the initiating ion,  $\text{X}^+$ , must provide this energy. Dilute methane solutions in liquid argon also give polymer. The argon excess would likely energetically deactivate the polymerizing species ( $\text{X}^+$ ,  $\text{XCH}_2^+$ , 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 electron emission is a possible explanation<sup>(5)</sup>. Auger emission (246 eV electrons from carbon<sup>(5)</sup>) 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

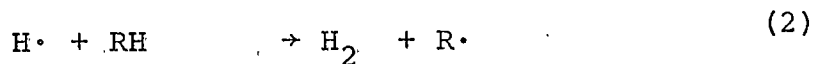
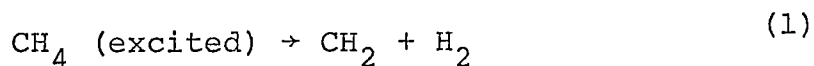
of ethane and ethylene gave polymer of molecular weight similar to that of methane. Their argument is that since ethane and ethylene samples contain twice as many carbon atoms per unit volume there would be twice as many carbon atoms in the Auger emission area as there would be for methane, one would 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 ( $\frac{-20.2 \text{ kcal}}{2 \text{ mole}}$ ) and propane ( $\frac{-24.82 \text{ kcal}}{3 \text{ mole}}$ ) have greater thermodynamic instability (as measured by enthalpies of formation,  $\Delta H_f$ ) per carbon atom than does methane ( $\frac{-17.9 \text{ kcal}}{1 \text{ mole}}$ ). 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.



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<sup>(9)</sup>. 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.

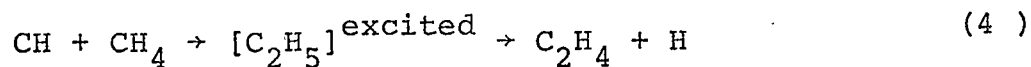
Ethane and other alkanes are formed predominantly by radical recombination



where R and R' are alkyl radicals. The radical recombination mechanism is confirmed by addition of radical scavengers such as NO or O<sub>2</sub> to the methane and noting the large reduction (85% or more) in alkane yields<sup>(10)</sup>.

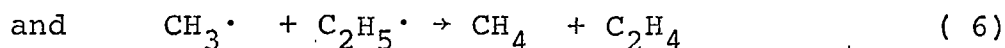
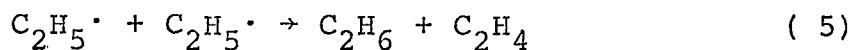
Addition of radical scavengers also increases alkene yields to detectable levels. This is understandable since alkenes are radical scavengers themselves, scavenging predominantly hydrogen atoms. Addition of another radical scavenger protects ethylene against further radical reactions.

Ethylene is formed mainly by the insertion reaction<sup>(11)</sup>.



and possibly to a lesser extent by removal of a proton from C<sub>2</sub>H<sub>5</sub><sup>+</sup><sup>(11)</sup>. It is also well known that disproportionation

reactions such as

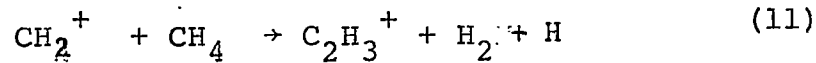
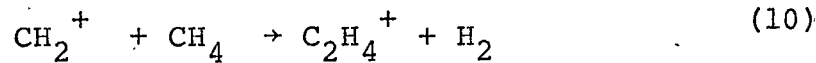
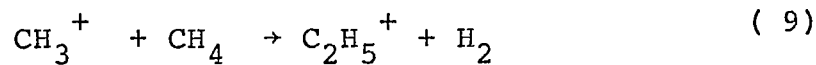
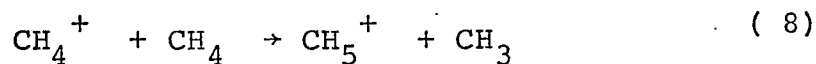


can produce ethylene.

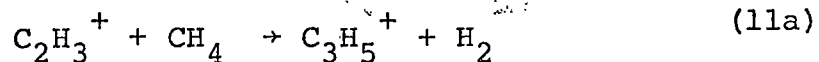
Then in the absence of scavengers we have the following mechanism for ethylene removal

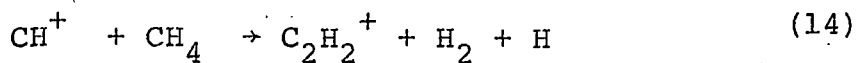
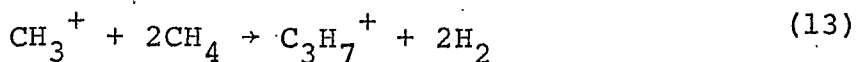
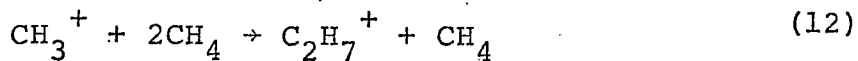


Ionic reactions are also of importance in producing small molecules. The following ionic reactions are generally considered to be the important ones occurring in methane (12)



followed by





followed by further reactions of  $\text{C}_2\text{H}_2^+$  to give probably  $\text{C}_3\text{H}_3^+$ .

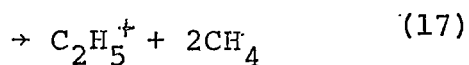
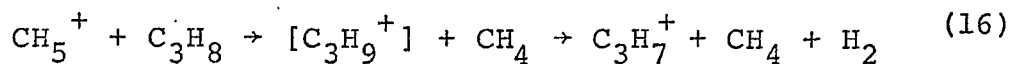
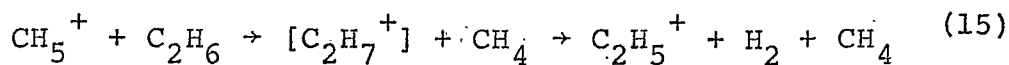
Reaction (12) involves an extra  $\text{CH}_4$  molecule to remove the excess energy which might decompose  $\text{C}_2\text{H}_7^+$  to  $\text{C}_2\text{H}_5^+$  and  $\text{H}_2$ . The intermediate ion involved in reaction (13) has not been identified. The relative intensities of the above mentioned end product ions at 1.9 mm pressure are, according to the mass spectrometric studies of Field and Munson<sup>(12)</sup>

$\text{CH}_5^+$	.452	$\text{C}_2\text{H}_6^+$	.024
$\text{C}_2\text{H}_5^+$	.349	$\text{C}_2\text{H}_7^+$	.0055
$\text{C}_3\text{H}_5^+$	.053	$\text{C}_3\text{H}_3^+$	.00036
$\text{C}_3\text{H}_7^+$	.028		

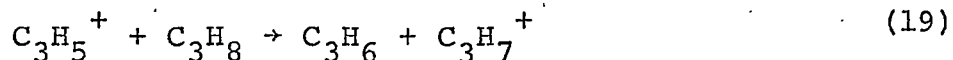
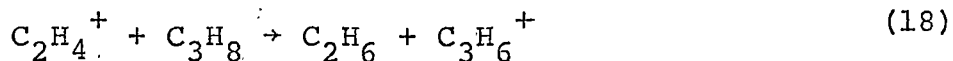
These ions can further react with other alkanes (such as ethane and propane) which may be present during radiolysis. It is found experimentally that of the five

most abundant ions just mentioned (which in comparison to their precursor ions are relatively inert toward methane).

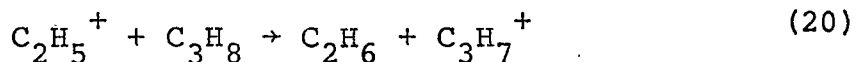
$\text{CH}_5^+$  reacts rapidly with ethane and propane<sup>(13)</sup>.



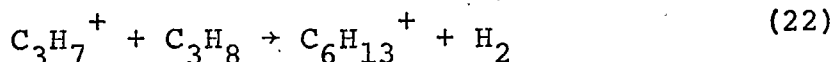
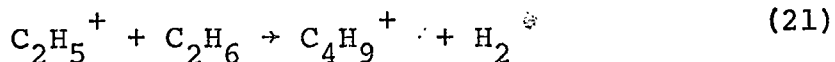
$\text{C}_2\text{H}_4^+$  and  $\text{C}_3\text{H}_5^+$  react rapidly with propane but not with ethane



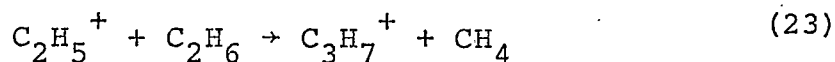
While  $\text{C}_2\text{H}_5^+$  reacts rapidly with propane by hydride transfer



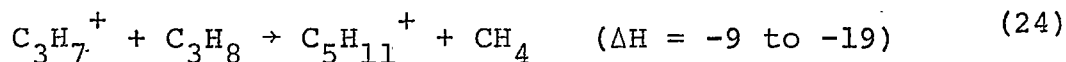
The following condensation reactions have been shown through mass spectroscopic studies to be important in radiolysis at high pressures (up to 200 mm)<sup>(6)</sup>



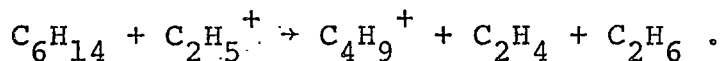
Additionally ion-cyclotron resonance studies confirmed the existence of reaction (21) and another reaction path<sup>(14)</sup>



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



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<sup>(16)</sup>




---

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

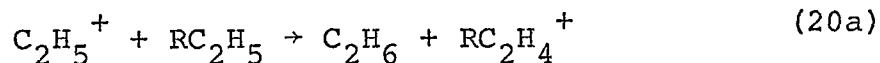
This reaction goes smoothly except when the hexane involved is 2,3-dimethyl butane. Presumably a methyl migration is necessary for the reaction only in the case of this particular hexane isomer.

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).

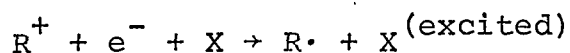
- |   |   |
|---|---|
| a. Hydride ( $H^-$ ) transfer   | $RH^+ + R'H_2 \rightarrow RH_2 + R'H^+$     |
| b. Proton ( $H^+$ ) transfer  | $RH_3^+ + R'H_2 \rightarrow RH_2 + R'H_3^+$ |
| c. $H_2^-$ transfer   | $R^+ + R'H_2 \rightarrow RH_2 + R'^+$       |
| d. $H_2$ transfer   | $R + R'H_2^+ \rightarrow RH_2 + R'^+$       |
| 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



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



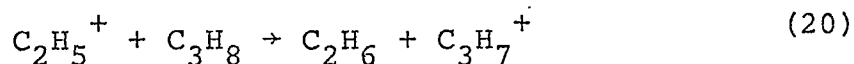
Presently no general methods have been developed for direction detection of these neutralization reactions. The best methods for studying ion reactions, which involve the use of mass spectrometer, generally elucidate only ion-molecule reactions. Thus the fate of these ions of low reactivity is seldom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

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

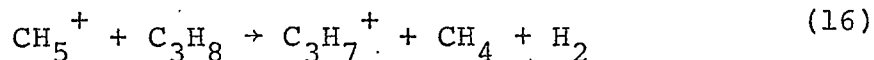
Methane radiolyses are sometimes complicated by trace impurities. Oxygen, as an impurity, has the desirable property of suppressing radical reactions so that one can study the predominantly ionic reactions which remain. However, at high radiation doses, oxidation products such as  $\text{CH}_3\text{OOH}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{HCHO}$  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  $\text{C}_6\text{H}_{13}^+$  could possibly be entirely attributed to reaction (22) in the presence of less than 1-7 ppm  $\text{C}_3\text{H}_8$  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

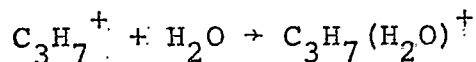


and protonation



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



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  $\text{LiAlH}_4$  chamber was prepared by pouring a diethylether suspension of  $\text{LiAlH}_4$  onto a glass wool plug and then removing the ether under vacuum.

To prepare radioactive propane samples, the  $\text{LiAlH}_4$  chamber was cooled in liquid  $\text{N}_2$  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  $10.3 \frac{\text{mc}}{\text{mmol}}$ ).

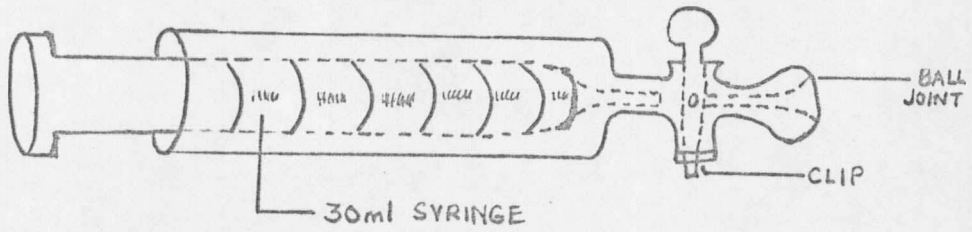
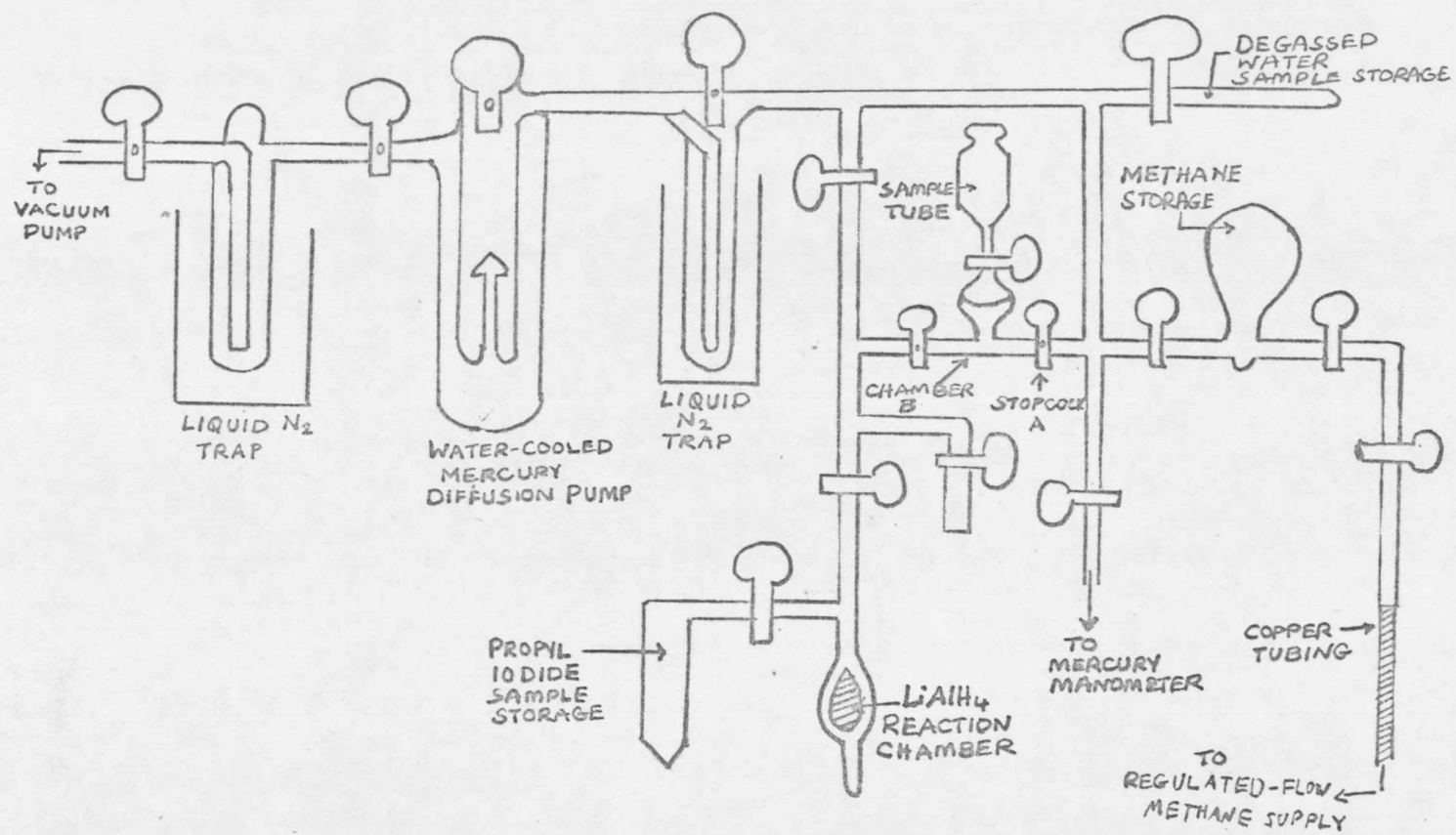


Fig. 1. The Sample Tube



19

Fig. 2. The Vacuum System

A portion of the  $\text{LiAlH}_4$  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  $[\text{C}_3\text{H}_6]/[\text{C}_3\text{H}_8]$  radioactive count ratios in consecutively filled samples.

TABLE I  
PROPENE DISAPPEARANCE IN  $\text{LiAlH}_4$  CHAMBER

<u>Time (Hrs.)*</u>	<u><math>[\text{C}_3\text{H}_6]/[\text{C}_3\text{H}_8]</math></u>
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

<u>Compound</u>	<u>CP Grade</u>	<u>Ultra High Purity</u>
Methane	99.1 %	99.98 %
O <sub>2</sub>	50 ppm	8-10 ppm
N <sub>2</sub>	6000 ppm	40-50 ppm
C <sub>2</sub> H <sub>6</sub>	1200 ppm	20-30 ppm
CO <sub>2</sub>	2000 ppm	40-50 ppm
C <sub>3</sub> H <sub>8</sub>	300 ppm	5 ppm
H <sub>2</sub> O	not listed	4-6 ppm

In order to add known amounts of air to the samples, air was admitted (passing through a CaCl<sub>2</sub> 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  $305 m\mu$  was used to calculate the change in  $Fe^{+2}$  concentration using the equation in Radiation Chemistry of Gases<sup>(3)</sup> 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  $5.3 \times 10^{17}$  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

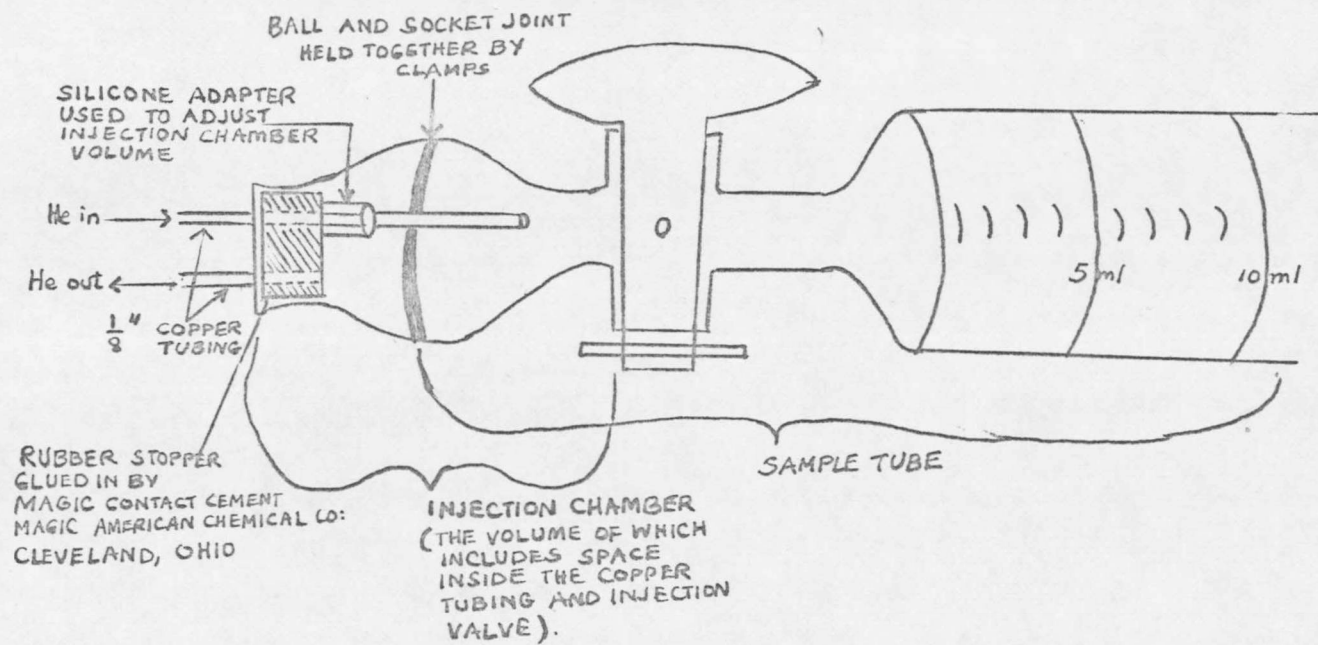


Fig. 3. The Injection Chamber

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 ( $3.7 \times 10^5$  dpm/ml) injected with 10  $\mu$ l 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):

<u>ml toluene</u>	<u>counts</u>
$7.85 \times 10^{-3}$	501
$8.7 \times 10^{-3}$	653

From this a typical  $10.3 \frac{\text{curie}}{\text{mole}}$  propane sample of C counts was determined to have a concentration of

$$[\text{C}_3\text{H}_8] = 9.8 \times 10^{10} \text{ C } \frac{\text{molec}}{\text{cc}} \pm 10\%$$

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<sup>(23)</sup>. 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

---

\*Meyers and Schmidt-Bleek<sup>(24)</sup> 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.

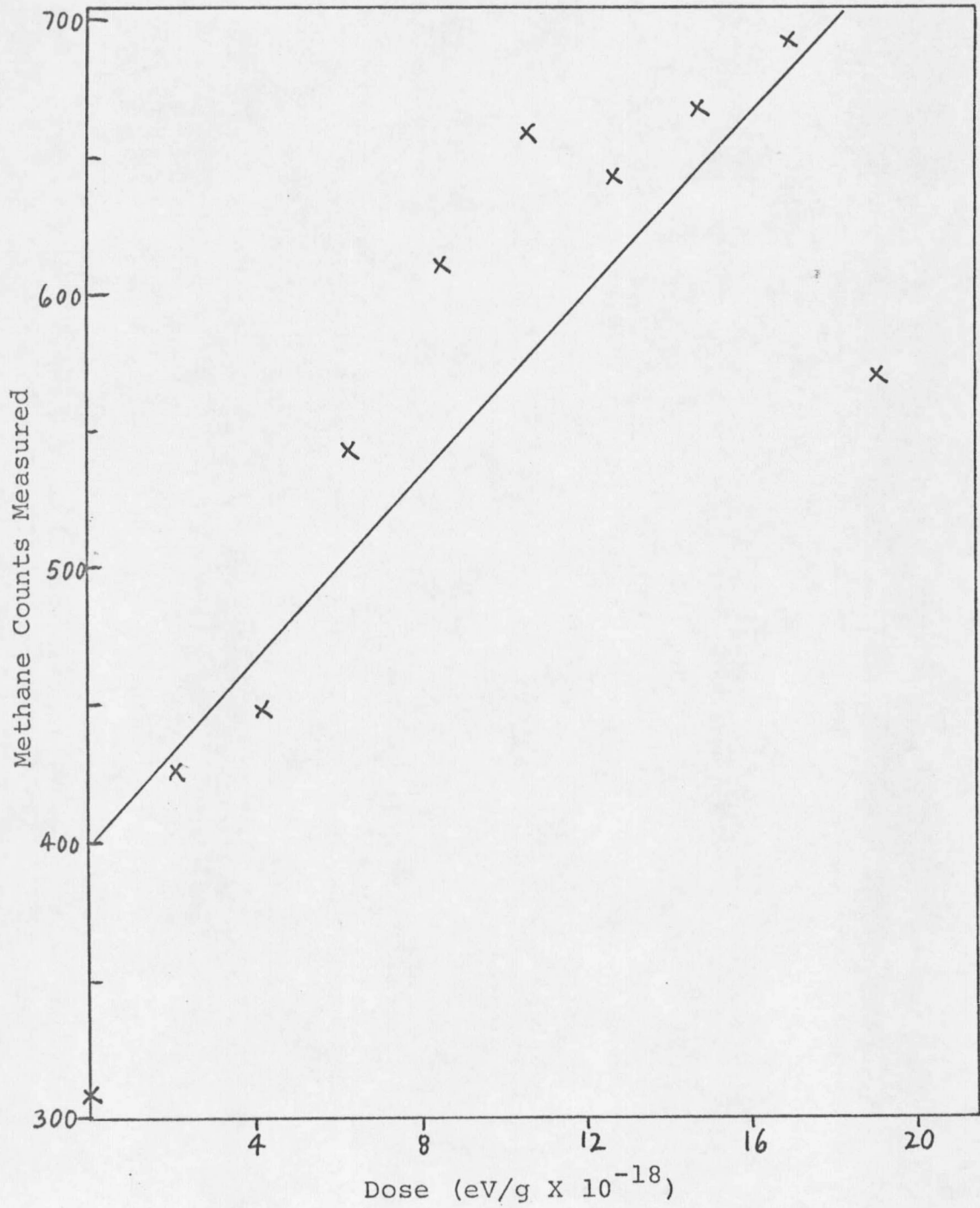


Fig. 4. Typical Methane Production Data  
(Tube 32)

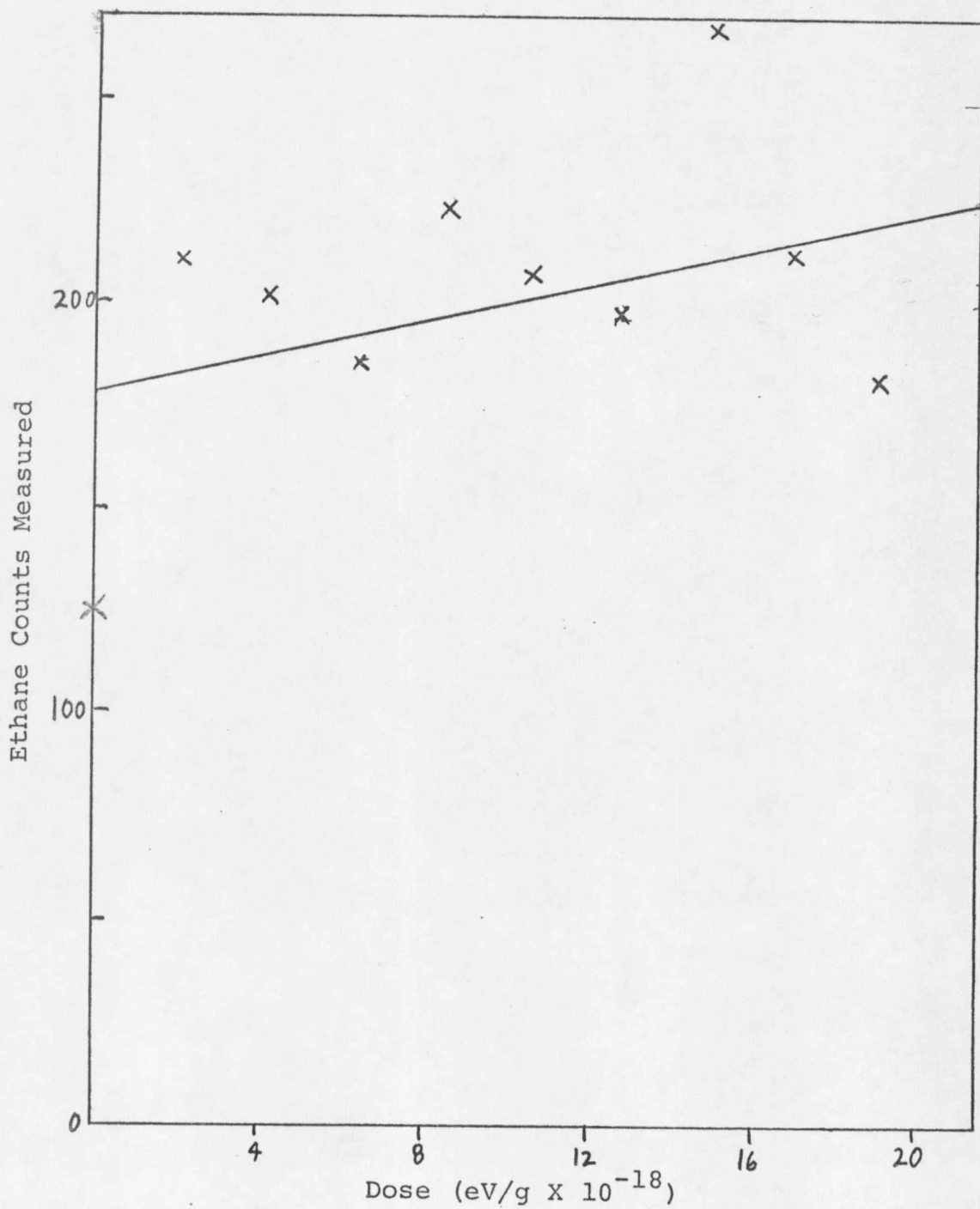


Fig. 5. Typical Ethane "Production" Data  
(Tube 32)

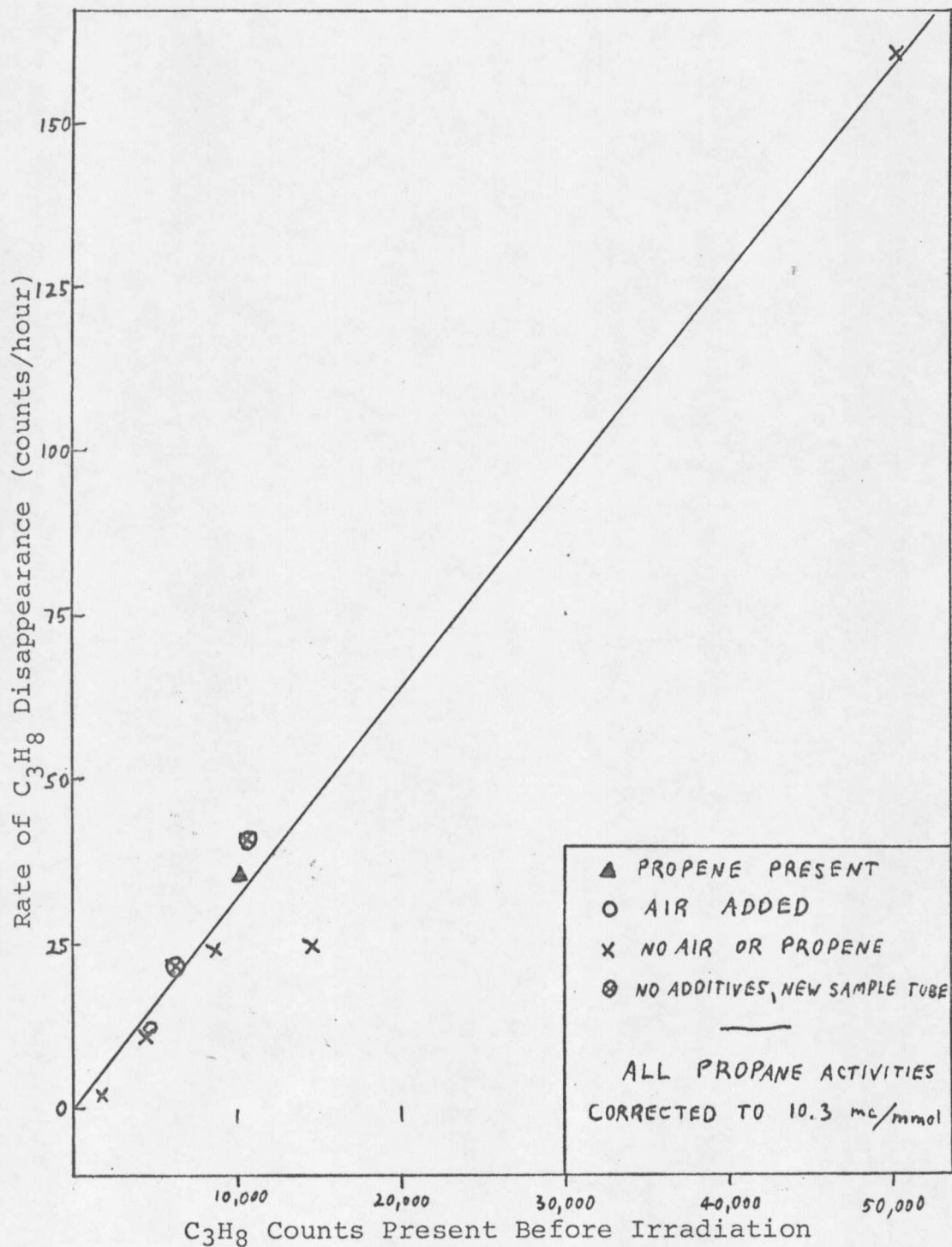


Fig. 6. Propane Production Rates in UHP Methane

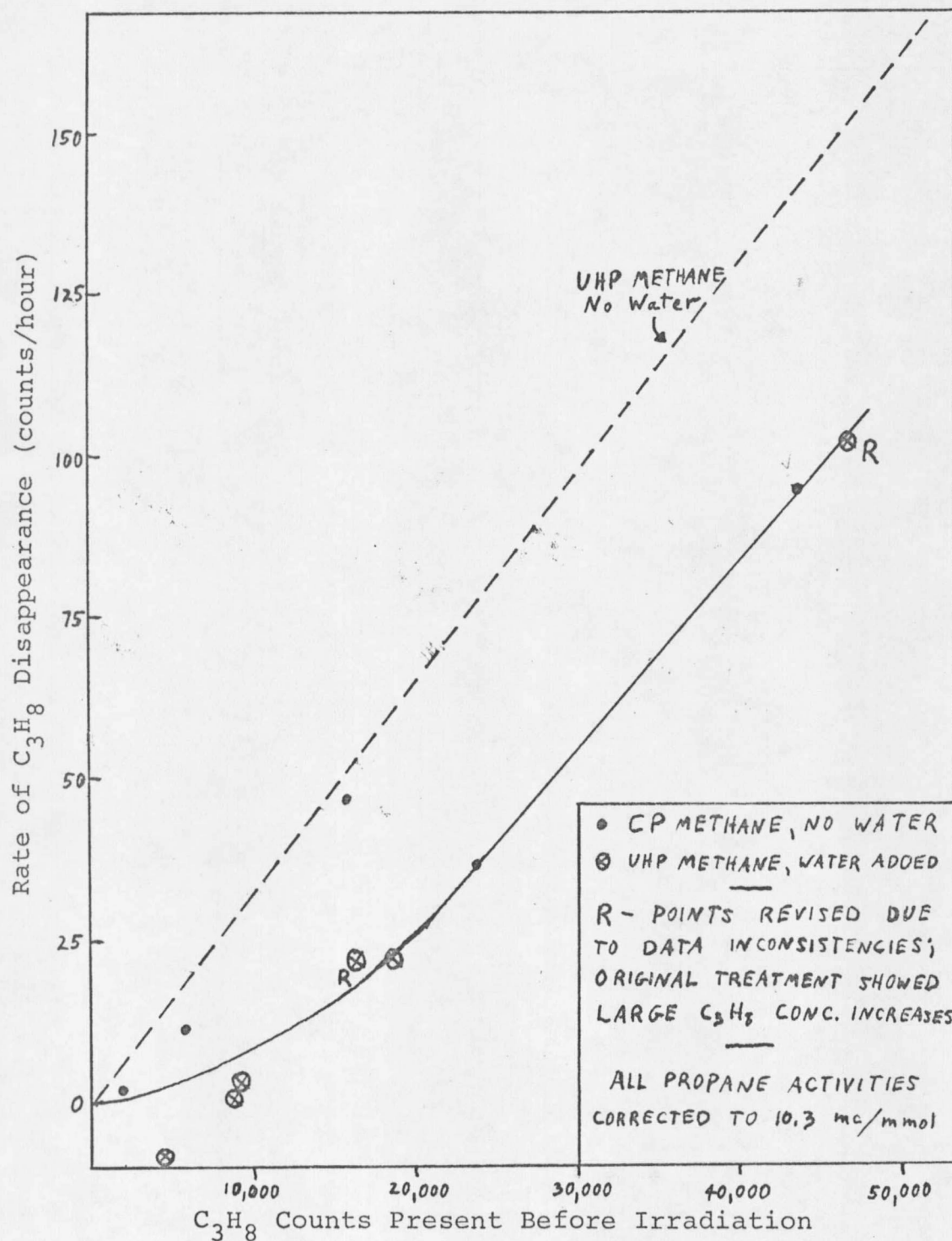


Fig. 7. Propane Production Rates in CP Methane and UHP Methane plus Water.

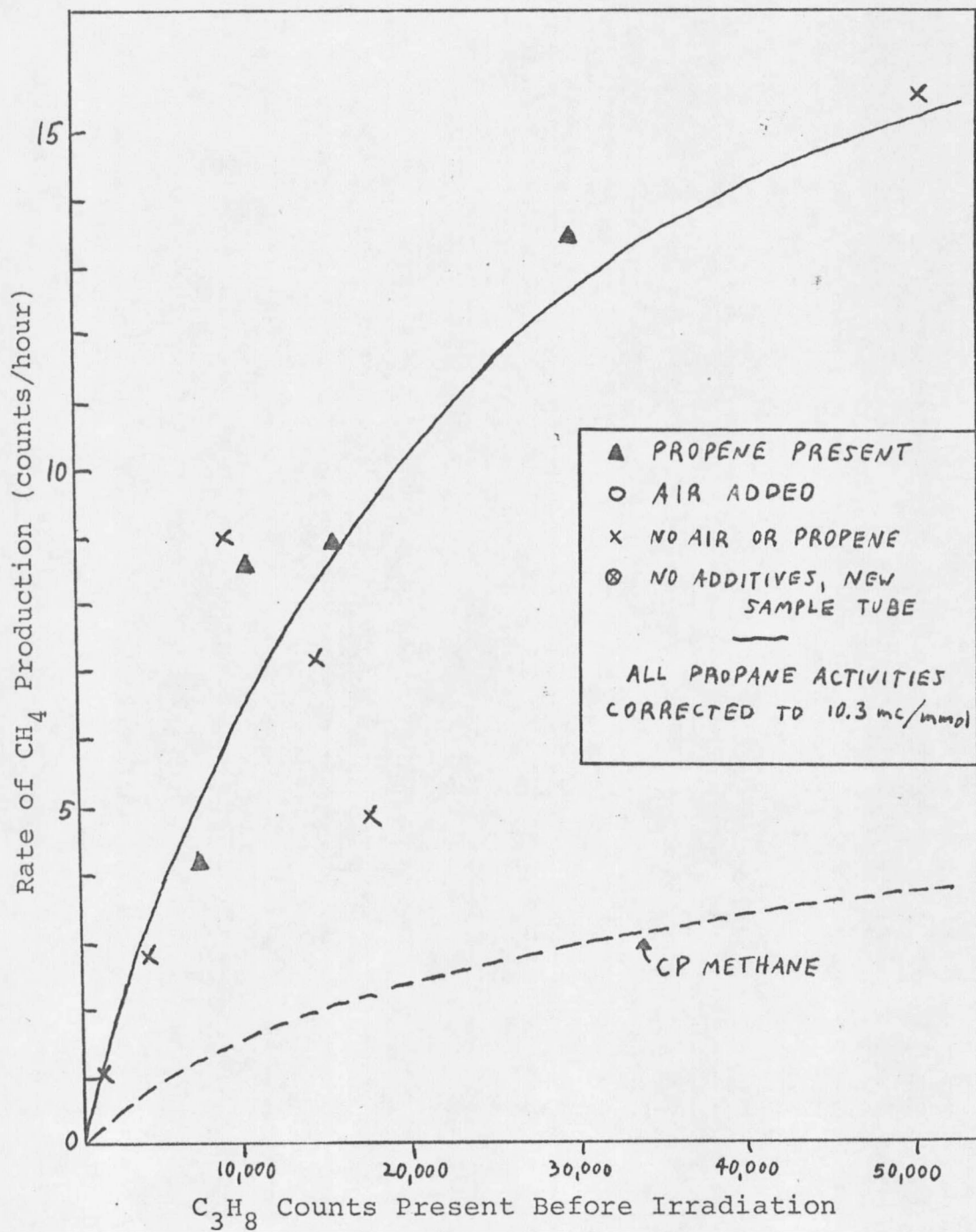


Fig. 8. Methane Production Rates in UHP Methane.

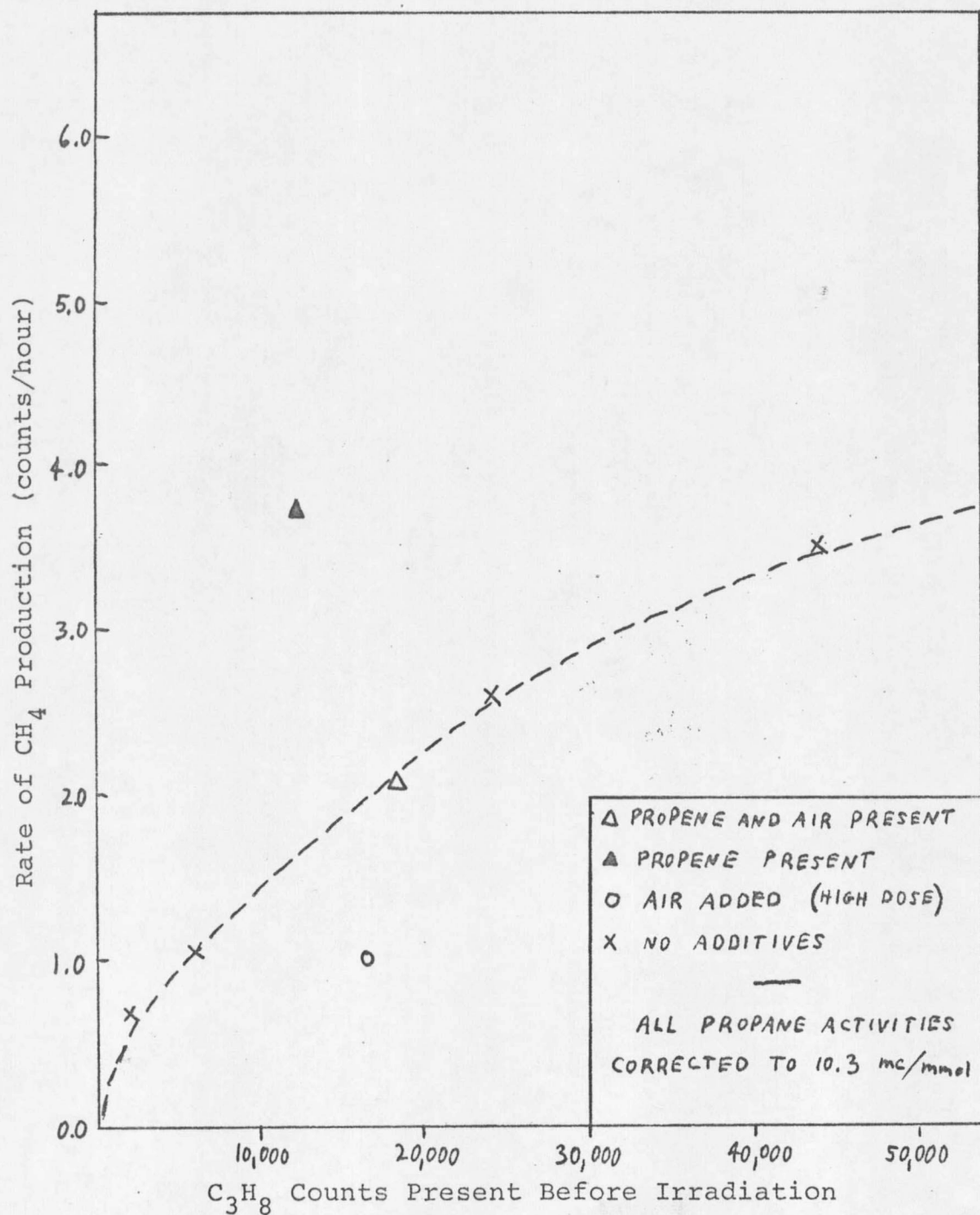


Fig. 9. Methane Production Rates in CP Methane

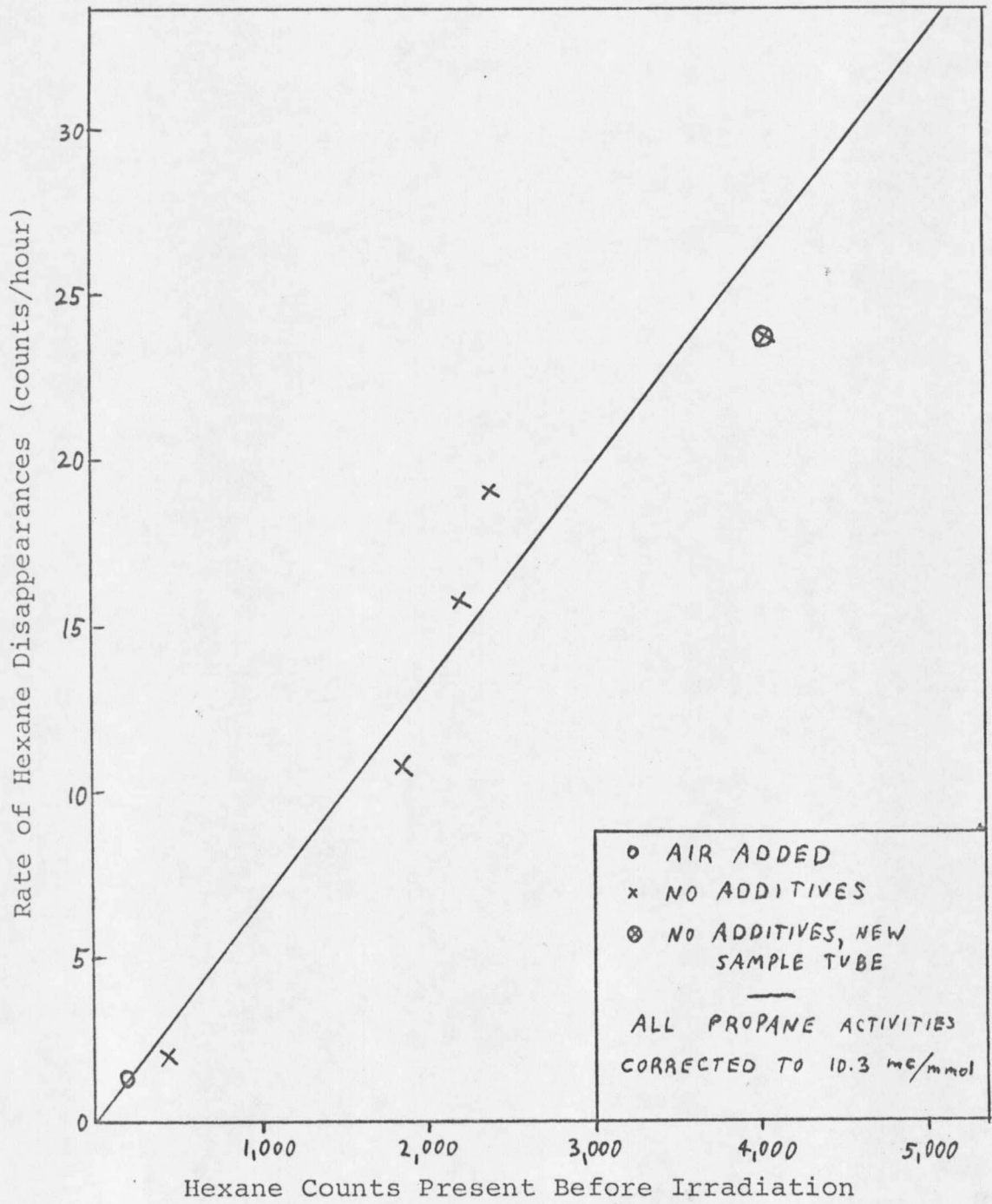


Fig. 10. Hexane Production Rates in UHP Methane

Of these, only  $\text{CH}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $i\text{-C}_3\text{H}_7\text{OH}$ , and  $\text{C}_6\text{H}_{14}$  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 known to be present in the mixture.

A reaction observed in samples containing propene was apparently the conversion of  $\text{C}_3\text{H}_6$  to isopropanol ( $i\text{-C}_3\text{H}_7\text{OH}$ ). 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:

<u>In UHP methane</u>		(99.98% pure)
$G(-\text{C}_3\text{H}_8)$	$= 1.18 \times 10^{-15}$	$[\text{C}_3\text{H}_8]$
$G(-\text{C}_6\text{H}_{14})$	$= 1.16 \times 10^{-15}$	$[\text{C}_6\text{H}_{14}]$
$G(\text{CH}_4)$	$= 0.64 \times 10^{-15}$	$[\text{C}_3\text{H}_8]$ at low $[\text{C}_3\text{H}_8]$
$G(\text{CH}_4)$	$\approx 1.6$	at high $[\text{C}_3\text{H}_8]$

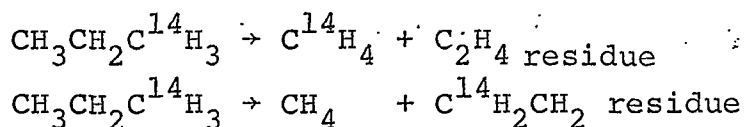
In CP methane (99.1% pure)

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

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

$$G (CH_4) \approx 0.4 \text{ at high } [C_3H_8]$$

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:

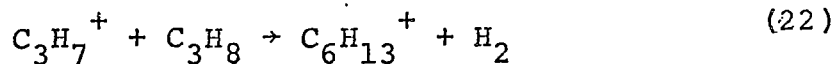


The term " $C_2H_4$  residue" implies that  $C_2H_4$  is not necessarily the molecular form of the product. In fact, it is most likely that the other carbon atoms are incorporated into polymer (as will be seen later).

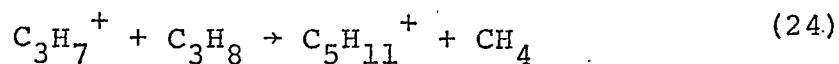
The counts/hour rates for hexane were divided by two since each hexane molecule is presumed to have been prepared through a condensation of two propane molecules (giving twice as much activity per molecule) while preparing propane samples in the  $LiAlH_4$  chamber.

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  $\Delta G$  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<sup>(19)</sup> 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



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



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.)	<u>Scavenged Rate</u> <u>Unscavenged</u> 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  $4.8 \times 10^{16}$  molec  $\text{H}_2\text{O}/\text{cc}$ . If propane reacted with the ion of interest (i.e., the one responsible for  $\text{CH}_4$  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 if water competes with propane, it does so inefficiently in our experiments.

Literature values <sup>(13,25)</sup>, on the other hand, indicate that water reacts with  $\text{CH}_5^+$  or  $\text{C}_2\text{H}_5^+$  (the two major ions present during methane radiolysis) roughly 10 times faster than with  $\text{C}_3\text{H}_8$ . Then since  $\text{C}_3\text{H}_7^+$  ions are produced almost exclusively by reactions of  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$ , 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  $\text{CH}_4$  for methane reactive ions such as  $\text{C}^+$ ,  $\text{CH}^+$ ,  $\text{CH}_2^+$ ,  $\text{CH}_3^+$ ,  $\text{CH}_4^+$ , and  $\text{C}_2\text{H}_3^+$ .

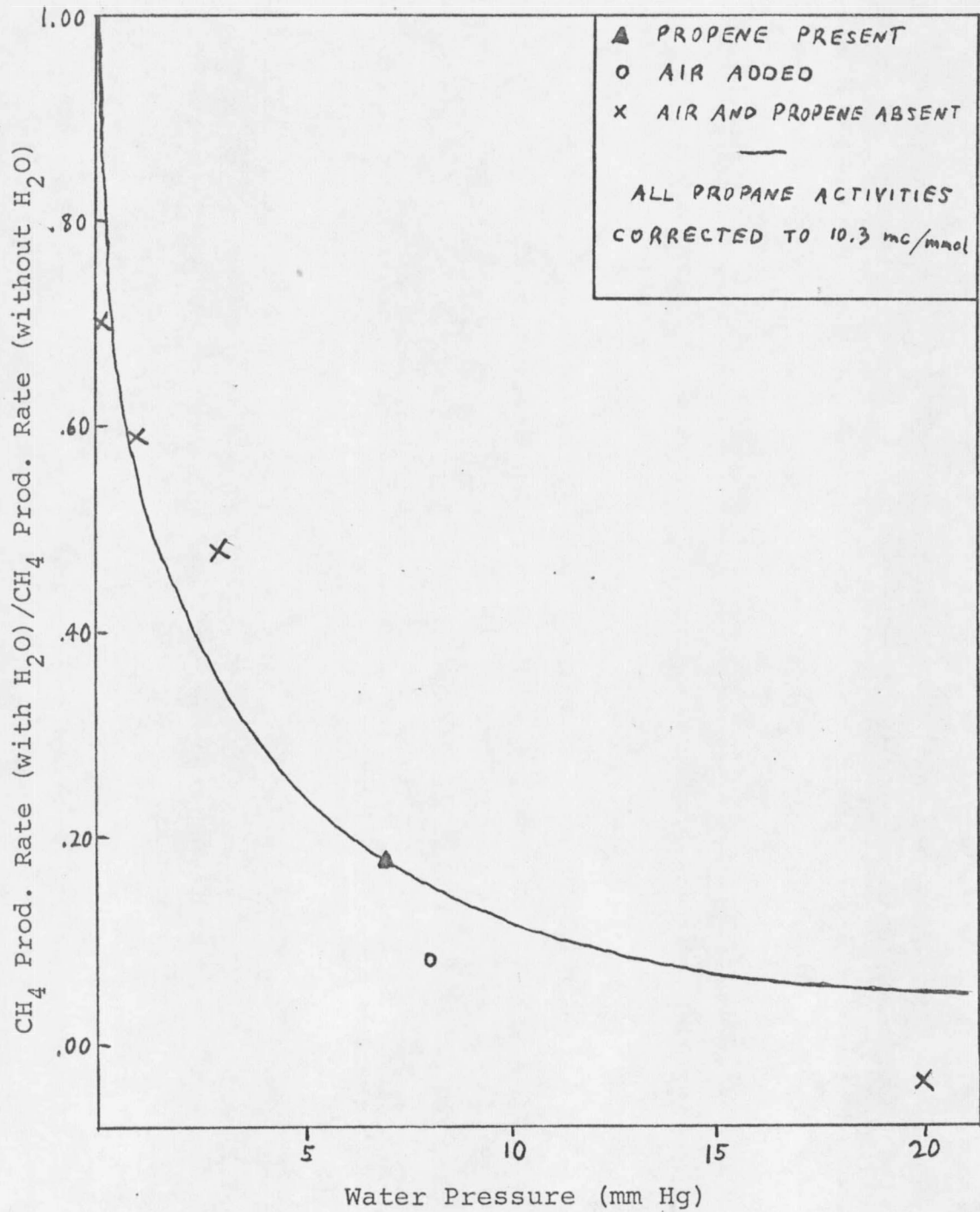
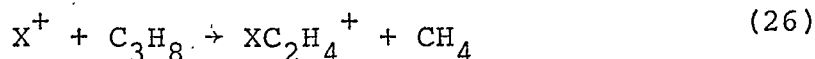


Fig. 11. Methane Production Rate Dependence on Water Pressure

A mass spectrometric study<sup>(25)</sup> 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  $\text{CH}_4^+$ ,  $\text{CH}_3^+$  and  $\text{CH}_2^+$ . 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<sup>(26)</sup> list reaction cross sections for methane reactions with  $\text{CH}_4^+$ ,  $\text{CH}_3^+$ ,  $\text{CH}_2^+$  and  $\text{CH}^+$  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  $\text{H}_2\text{O}$  at low concentrations ( $\text{C}^+$ , which was not mentioned, seems likely to fit into this category too). The logical conclusion is then that  $\text{H}_2\text{O}$  reacts with some of the heavier polymerizing ions. At 1.5 mm pressure of  $\text{H}_2\text{O}$  and approximately 620 mm pressure of  $\text{CH}_4$ , 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 ( $G = 1.6$ )\*,



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

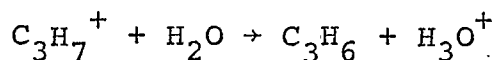
---

\*Obtained from the leastsquares curve fit in Fig. 8

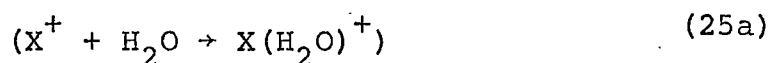
$$G(CH_4) = \frac{1.6[C_3H_8]}{[C_3H_8] + 2.5 \times 10^{15}}$$

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



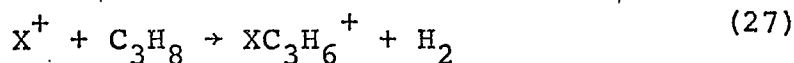
Later calculations will show the endothermicity of this reaction for heavy alkyl ions. The complexing reaction



(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  $\Delta H_f$  by 10 kcal/mole<sup>(28)</sup> to apply equally to the  $R^+$  ion considered here.

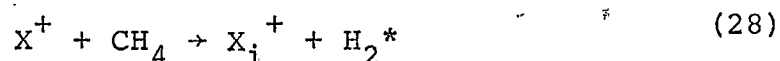
The other mechanism should incorporate propane ( $G = 1.4$ ) by a reaction such as



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<sup>(4,5,29)</sup> 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



Thus, if one postulates the same polymer yields in the presence as well as in the absence of  $C_3H_8$ . ( $G(\text{polymer}) = .08$  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  $G(-C_3H_8 \text{ to polymer})$  can be calculated as follows:

$$G(-C_3H_8 \text{ to polymer}) = G(\text{Reaction 26}) + G(\text{Reaction 27})$$

$$G(\text{Reaction 26})/G(\text{Reaction 27}) = 1.6/1.4 = 1.143$$

$$G(\text{Carbon to polymer}) = 2G(\text{Reaction 26}) + 3G(\text{Reaction 27})$$

Solving gives

$$G(-C_3H_8 \text{ to polymer}) = .405 (G(\text{carbon to polymer}))$$

Thus for methane  $G(\text{carbon to polymer}) = 1.6$  gives

$$G(-C_3H_8 \text{ to polymer}) = .65$$

---

\*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 ( $G(\text{polymer}) = .20$ ) would give  $G(-\text{C}_3\text{H}_8 \text{ to polymer}) = 1.86$ . 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<sup>(4)</sup> are  $G(-\text{C}_2\text{H}_6 \text{ to } \text{C}_{23}\text{H}_{46}) = 0.2$  and  $G(-\text{C}_3\text{H}_8 \text{ to } \text{C}_{16}\text{H}_{32}) = 0.15$  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

$$G(\text{polymer from } \text{C}_2\text{H}_6) = \left( \frac{2 \text{ carbon atoms}}{\text{ethane molecule}} / \frac{23 \text{ carbon atoms}}{\text{polymer molecule}} \right) \\ \times \frac{0.2 \text{ ethane molecules}}{100 \text{ eV}} \\ = .017$$

$$G(\text{polymer from } \text{C}_3\text{H}_8) = (3/16) \times 0.15 = .028$$

Thus a value for  $G(-\text{C}_3\text{H}_8 \text{ to polymer})$  might be  $(.028/.017) \times 0.2 \times 16 \times .405 = 2.14$  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 ( $\text{IP}(\text{C}_2\text{H}_6) = 11.65 \text{ eV}$ ,  $\text{IP}(\text{C}_3\text{H}_8) = 11.21 \text{ eV}$ <sup>(15)</sup>)

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 <sub>3</sub> H <sub>8</sub> to polymer)
CH <sub>4</sub> - Ar	.08	1.6	0.65
C <sub>2</sub> H <sub>6</sub> - Ar	.20	4.6	1.86
C <sub>3</sub> H <sub>8</sub> - Ar	>.33	>5.3	>2.14

Since the G(-C<sub>3</sub>H<sub>8</sub> to polymer) values represent maximum rates in the various solutions, one asks the question as to why the particular hydrocarbon (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> or C<sub>3</sub>H<sub>8</sub>) 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  $\text{Ar}^+$  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  $G(-\text{C}_3\text{H}_8 \text{ to polymer})$  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<sup>(4)</sup> on solid methane indicating the contrary may well not apply to room temperature gases or liquid argon solutions. The present liquid argon studies<sup>(5)</sup> 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.

---


$$\begin{aligned}
 & *8.5 \text{ Mrad} \times \frac{6.24 \times 10^{19} \text{ eV/g}}{\text{Mrad}} \times \frac{16gCH_4}{6.02 \times 10^{23} \text{ molec } CH_4} \\
 & \times \frac{2.1 \text{ molec } C_2H_6}{100 \text{ eV}} \times 10^6 = 300 \text{ ppm ethane}
 \end{aligned}$$

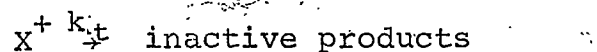
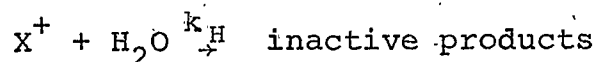
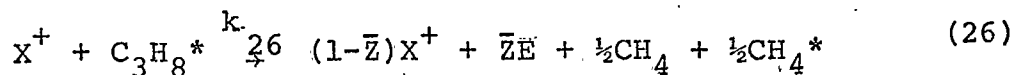
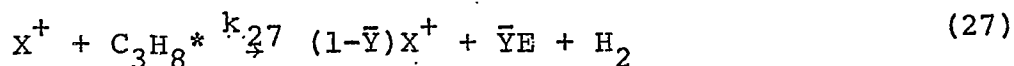
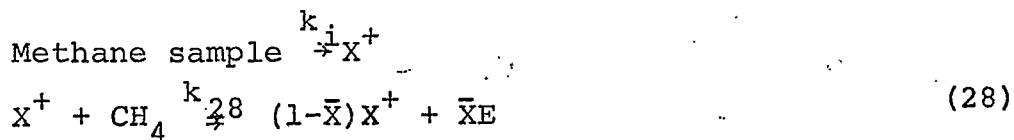
There may be a literature clue as to the reason for an increase in polymerization rates at higher temperatures. Davis et al. <sup>(4)</sup> give gas chromatograms of propane polymer produced at  $-196^{\circ}\text{C}$  in the solid phase. They suggest that coarse structure in the chromatogram may indicate 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  $G(-\text{C}_3\text{H}_8 \text{ to polymer})$ . 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  $G(-\text{C}_3\text{H}_8)$  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  $5 \times 10^{15}$  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.



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:

$$\begin{aligned} \frac{d[CH_4^*]}{dt} &= 1/2 k_{26}[X^+][C_3H_8^*] \\ - \frac{d[C_3H_8^*]}{dt} &= (k_{27} + k_{26})[X^+][C_3H_8^*] \end{aligned}$$

To convert to G values the rate constant,  $k_i$ , must be divided by the dose rate D (in  $\frac{eV}{cc \cdot sec}$ ) 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  $G(\text{CH}_4)$  equation can be evaluated in the absence of water from the equation

$$G(\text{CH}_4) = \left(\frac{100}{D}\right) \frac{k_i k_{26} [\text{C}_3\text{H}_8]}{(\bar{Y}k_{27} + \bar{Z}k_{26}) [\text{C}_3\text{H}_8] + \bar{X}k_{28} [\text{CH}_4] + k_t}$$

$$= \left(\frac{100 k_i k_{26} [\text{C}_3\text{H}_8]}{D(\bar{Y}k_{27} + \bar{Z}k_{26})}\right) \left/ \left( [\text{C}_3\text{H}_8] + \frac{\bar{X}k_{28} [\text{CH}_4] + k_t}{(\bar{Y}k_{27} + \bar{Z}k_{26})} \right) \right.$$

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

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

$$\frac{\bar{X}k_{28} [\text{CH}_4] + k_t}{\bar{Y}k_{27} + \bar{Z}k_{26}} = 2.5 \times 10^{15} \frac{\text{molec}}{\text{cc}}$$

From this the best value for  $G(\text{CH}_4)$  at low concentrations is  $G(\text{CH}_4) = 0.64 \times 10^{-15} [\text{C}_3\text{H}_8]$ . At very high concentrations of propane one obtains  $G(\text{CH}_4) = 1.6$ .

The value  $\frac{100 k_i}{D}$  is actually  $G(\text{X}^+)$  or the rate of formation of polymerizing ions. In estimating the rate of formation of  $\text{C}^+$ ,  $\text{CH}^+$  and  $\text{CH}_2^+$  ions from Melton and Rudolph<sup>(1)</sup> one finds that 12% of the ions are of this type. With

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

$$G(\text{C}^+, \text{CH}^+, \text{CH}_2^+) = \frac{100}{29.4} \times .12 = .41 \frac{\text{molecules}}{100 \text{ eV}}$$

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

$$\frac{k_{26}}{(0.9\bar{Y} + \bar{Z})k_{26}} = 3.9 \text{ or } (0.9\bar{Y} + \bar{Z}) = .26, \text{ indicating that}$$

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

$$\frac{\bar{X}k_{28}[\text{CH}_4] + k_t}{.26k_{26}} = 2.5 \times 10^{15} \frac{\text{molec}}{\text{cc.}}$$

$$\text{or } \frac{\bar{X}k_{28}[\text{CH}_4] + k_t}{k_{26}} = 6.5 \times 10^{14} \frac{\text{molec}}{\text{cc.}}$$

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

$$G(\text{C to polymer}) = 100k_i/D + k_{28}[X^+][\text{CH}_4] + 3k_{27}[X^+][\text{C}_3\text{H}_8] + 2k_{26}[X^+][\text{C}_3\text{H}_8]$$

Substituting  $[X^+] = \frac{G(\text{CH}_4)}{k_{26}[\text{C}_3\text{H}_8]}$  gives

$$G(\text{C to polymer}) = 100k_i/D + \frac{k_{28}G(\text{CH}_4)[\text{CH}_4]}{k_{26}[\text{C}_3\text{H}_8]} + \frac{3k_{27}G(\text{CH}_4)}{k_{26}} + 2G(\text{CH}_4)$$

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

$$v = 1 + \left( \frac{k_{28}[\text{CH}_4]}{k_{26}[\text{C}_3\text{H}_8]} + \frac{3k_{27}}{k_{26}} + 2 \right) \frac{G(\text{CH}_4)}{100k_i/D}$$

If one calculates  $v$  for polymerization at its maximum,  $G(\text{CH}_4) = 1.6$  (by realizing that methane cannot effectively compete with propane at these high propane concentrations

giving  $\frac{k_{28}[\text{CH}_4]}{k_{26}[\text{C}_3\text{H}_8]} = 0$ ), we find that the polymer chain length is  $v = 19$ , this is a reasonable value compared to  $v = 20$  in methane and  $v = 16$  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  $G(\text{CH}_4)$  approaches zero, we get the equation  $G(\text{C to polymer}) = \frac{100k_i}{D} + \frac{k_{28}G(\text{CH}_4)[\text{CH}_4]}{k_{26}[\text{C}_3\text{H}_8]}$ . In this limit calculus

then gives

$$\frac{dG(\text{CH}_4)}{d[\text{C}_3\text{H}_8]} = \frac{k_{26} \left( G(\text{C to polymer}) - \frac{100k_i}{D} \right)}{k_{28}[\text{CH}_4]}$$

With the knowledge that  $\frac{dG(\text{CH}_4)}{d[\text{C}_3\text{H}_8]} = .64 \times 10^{-15} \frac{\text{cc}}{100\text{eV}}$  and

$[\text{CH}_4] = 2 \times 10^{19} \frac{\text{molec}}{\text{cc}}$ , one uses the presumed value  $\frac{100k_i}{D} =$

.41 calculated earlier and the literature value  $G(-\text{CH}_4 \text{ to}$

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

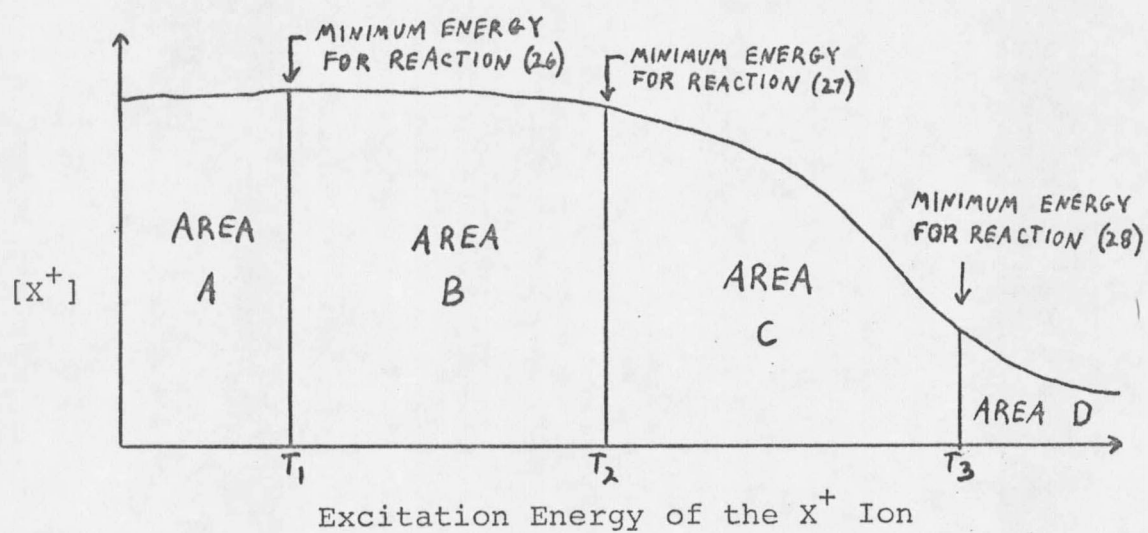


Fig. 12. Distribution of Excitation Energies in the Polymer ion,  $X^+$ .

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  $\text{CH}_4$ . 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  $[\text{X}^+]$  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  $\text{X}^+$  ions capable of reacting with  $\text{C}_3\text{H}_8$  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  $0 \frac{\text{kcal}}{\text{mole}}$  (then, of course, no ions are allowed to have the negative excitation energies, which would exist at values significantly lower than  $T_2$ ). Since  $\Delta H$  for reaction (26) has been estimated to be  $3 \frac{\text{kcal}}{\text{mole}}$  or less, one can a priori 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,  $\Delta H$  for reaction (26) is estimated at  $-13 \frac{\text{kcal}}{\text{mole}}$ . This indicates that, unless our earlier  $\Delta H_r$  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<sup>(31)</sup> butyl ion  $\Delta H_f$  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:

$$G_{HP} = \frac{G(\text{CH}_4)_{\text{H}_2\text{O}}}{G(\text{CH}_4)_{\text{pure}}} = \frac{\bar{X}k_{28}[\text{CH}_4] + (\bar{Y}k_{27} + \bar{Z}k_{26})[\text{C}_3\text{H}_8] + k_t}{\bar{X}k_{28}[\text{CH}_4] + (\bar{Y}k_{27} + \bar{Z}k_{26})[\text{C}_3\text{H}_8] + k_H[\text{H}_2\text{O}] + k_t}$$

Substituting experimental values of  $\bar{X}k_{28}[\text{CH}_4] + k_t = 6.5 \times 10^{14}$

$10^{14}k_{26}$  and  $\bar{Y}k_{27} + \bar{Z}k_{26} = .26k_{26}$ , one obtains

$$G_{HP} = \frac{G(\text{CH}_4)_{\text{H}_2\text{O}}}{G(\text{CH}_4)_{\text{pure}}} = \frac{(6.5 \times 10^{14} + .26[\text{C}_3\text{H}_8]k_{26})}{(6.5 \times 10^{14} + .26[\text{C}_3\text{H}_8]k_{26} + k_H[\text{H}_2\text{O}]}$$

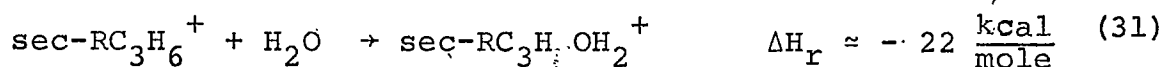
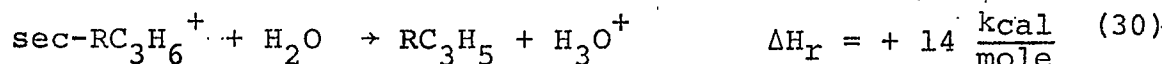
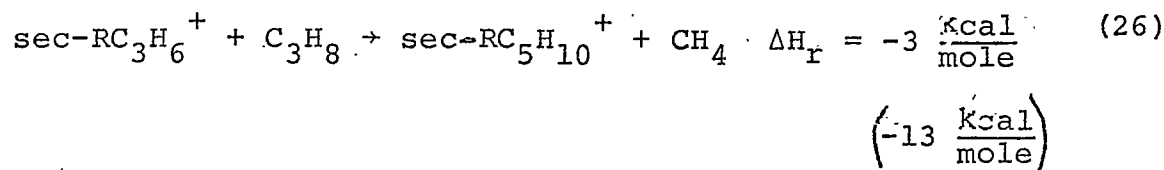
This can be rearranged to give

$$\frac{k_{26}}{k_H} = \frac{[\text{H}_2\text{O}]G_{HP}}{(1-G_{HP})(6.5 \times 10^{14} + .26[\text{C}_3\text{H}_8])}$$

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

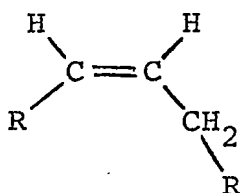
$\frac{k_{26}}{k_H} = 30$  meaning that water is not an effective scavenger for the polymerizing ion  $X^+$ . Sample reactions for comparing

H<sub>2</sub>O and C<sub>3</sub>H<sub>8</sub> reactions would be

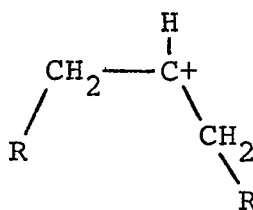


$\Delta H$  for reaction (26) was estimated earlier from the  $-5 \text{ kcal/mole}$  increment per CH<sub>2</sub> group. The  $-13 \frac{\text{kcal}}{\text{mole}}$  is the corrected value based on previously discussed assumptions of an increase in carbonium ion stability during reaction.

$\Delta H$  for reaction (30) was estimated by a comparison of the following structures:



(A)



(B)

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

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

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

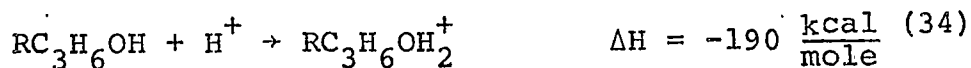
$\Delta H(CH_2 \overset{+}{CH} CH_2)$  is taken to be the heat of formation for propane ion plus a correction of +10 kcal/mole for the fact that  $CH_2$  rather than  $CH_3$  groups are present. The difference is then

$$\Delta H_f(B) - \Delta H_f(A) = \Delta H(CH_2 \overset{+}{CH} CH_2) - \Delta H\left(\begin{array}{c} H & H \\ \diagdown & / \\ C & = & C \\ / & \diagdown \end{array}\right) - \Delta H(CH_2) =$$

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

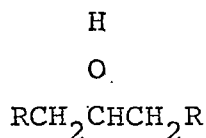
$\Delta H_f(H_3O^+) = 143 \frac{\text{kcal}}{\text{mole}}$  was obtained from a recent literature reference<sup>(32)</sup>. Where the R groups are both hydrogen, the experimental  $\Delta H$  is +16  $\frac{\text{kcal}}{\text{mole}}$  rather than the +14  $\frac{\text{kcal}}{\text{mole}}$  calculated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

$\Delta H$  for reaction (31) was determined from the reasonable approximation that the proton affinity,  $P(RC_3H_6OH) \approx 190$  of the alcohol is nearly equal to that for  $C_2H_5OH$ <sup>(33)</sup>. This gives the relation



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

$$\Delta H_f(\text{RC}_3\text{H}_6\text{OH}_2^+) - \Delta H_f(\text{RC}_3\text{H}_6\text{OH}) = +176 \frac{\text{kcal}}{\text{mole}} . \quad \text{The structure}$$



(C)

has the heat of formation

$$\Delta H_f(\text{C}) = \Delta H(\text{R} + \text{R}) + 2\Delta H(\text{CH}_2) + \Delta H(\text{CH}) + \Delta H(\text{secondary OH})$$

Thus

$$\Delta H_f(\text{B}) - \Delta H_f(\text{C}) = \Delta H_f(\text{RC}_3\text{H}_6^+) - \Delta H_f(\text{RC}_3\text{H}_6\text{OH}) = +256 \frac{\text{kcal}}{\text{mole}}$$

gives

$$\Delta H_f(\text{RC}_2\text{H}_4\text{OH}_2^+) - \Delta H_f(\text{RC}_3\text{H}_6^+) = 176 - 256 = -80 \frac{\text{kcal}}{\text{mole}}$$

This gives  $\Delta H_r$ (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

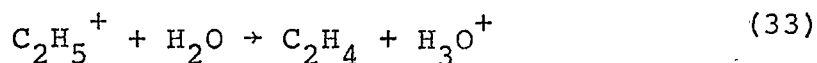
$$-17 \frac{\text{kcal}}{\text{mole}} \quad (27)$$

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  $\Delta H_f$ , than primary ions containing the same number of carbon atoms), the only mode of

reaction likely to slow polymerization is



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

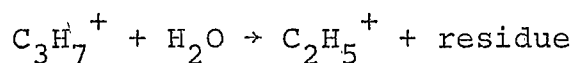
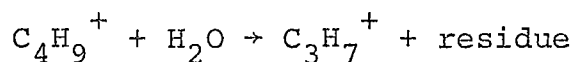


Less stable cations such as  $CH_2^+$ ,  $CH_3^+$  and  $CH_4^+$  have previously been mentioned as unlikely to react with water where methane is in great excess. The same is likely for  $C^+$  and  $CH^+$  since these are ions which also initiate rapid polymerization in methane.

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<sup>(25)</sup>. 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<sup>(34)</sup>



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  $10 \cdot 3$  mc/mmol. This may well be due to the fact that the isopropyl iodide used in preparing this propane (by reaction with  $\text{LiAlH}_4$ ) contained impurities which could scavenge  $\text{X}^+$  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

---

\*To correct for the presence of unlabeled  $\text{C}_3\text{H}_8$ , both rates and concentrations are multiplied by  $\frac{[\text{C}_3\text{H}_8] \text{ unlabeled} + [\text{C}_3\text{H}_8] \text{ labeled}}{[\text{C}_3\text{H}_8] \text{ labeled}}$ .

TABLE V

EFFECT OF UNLABELED PROPANE  
ON KINETICS

	Sample 1	Sample 2
1. $[C_3H_8]$ labeled (in molec/cc)	$4.8 \times 10^{14}$	$8.5 \times 10^{14}$
2. $[C_3H_8]$ unlabeled (in molec/cc)	$16.2 \times 10^{14}$	$32.4 \times 10^{14}$

## 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  $G(\text{CH}_4)$ . 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  $[\text{C}_3\text{H}_8]_a$  is

$$G(\text{CH}_4)_a = \frac{\left(\frac{100}{D}\right) k_1 k_{26} [\text{C}_3\text{H}_8]}{(\bar{Y}k_{27} + \bar{Z}k_{26}) ([\text{C}_3\text{H}_8]_a + [\text{C}_3\text{H}_8]) + \bar{X}k_{28} [\text{CH}_4] + k_t}$$

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  $(\bar{Y}k_{27} + \bar{Z}k_{26}) [\text{C}_3\text{H}_8]_a$  in the denominator without an increase in the rate of methane production due to the factor  $k_{26} [\text{C}_3\text{H}_8]$  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  $G(\text{CH}_4)$  was so low in CP methane even effects due to the maximum ratio of  $[\text{C}_6\text{H}_{14}]/[\text{C}_3\text{H}_8] = .70$  might well be attributed to experimental error. Thus, no conclusion can be formed on the effects of hexane on  $\text{CH}_4$  formation from propane.





























































































































