



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
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Abstract:

The kinetics of gaseous methane radiolysis at room temperature using X-rays as a high energy source was studied using as a reaction chamber a glass syringe with a stopcock attached to it. The rate of disappearance of 1,3-C¹⁴-propane and the rate of formation of C¹⁴methane was studied as a function of energy absorbed.

The G values in ultra-high purity methane as a function of propane concentration (molec/cc) were determined to be: (Formula not captured by OCR) The presence of air in all samples and the sensitivity of the reaction to the presence of water pointed to an ionic mechanism for methane formation. Since the water concentration needed to be much greater than the propane concentration in order to reduce G(CH₄) by 50%, it was concluded that the heavy ions involved in methane polymerization were the only ions which could reasonably explain why propane reacts more efficiently with a positive ion than does water. Thus, to explain the above equation for G(CH₄), the following reactions were proposed: where X⁺ is a heavy polymerizing ion. The ΔH values were estimated from theoretical ΔH_f 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 C₃H₈ the only polymerization reaction of importance proceeds by reactions (1) and (2). This apparently conflicts with previous literature studies, which indicate no dependence of CH₄ polymerization on reaction products (such as propane). These conflicts are explained by a reinterpretation of the data of previous studies.

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Chemistry

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ABSTRACT

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

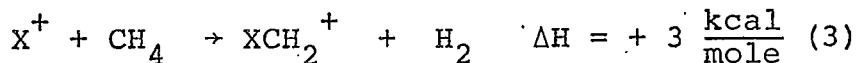
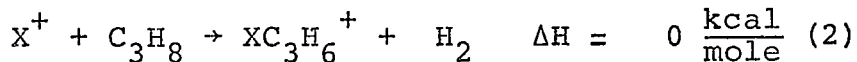
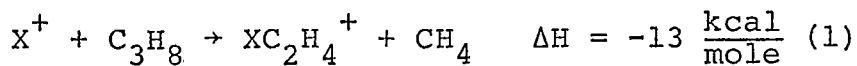
The rate of disappearance of 1,3-C¹⁴-propane and the rate of formation of C¹⁴-methane was studied as a function of energy absorbed.

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(CH₄) by 50%, it was concluded that the heavy ions involved in methane polymerization were the only ions which could reasonably explain why propane reacts more efficiently with a positive ion than does water. Thus, to explain the above equation for G(CH₄), the following reactions were proposed:



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

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

INTRODUCTION

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

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

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

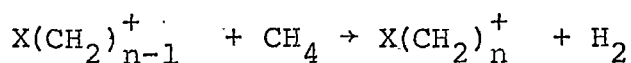
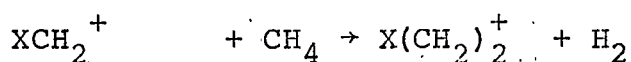
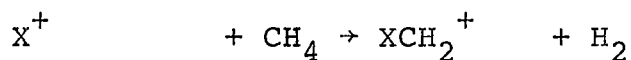
The most important initial products in methane radiolysis are C_2H_6 , H_2 and a highly branched polymer of the approximate composition $(CH_2)_{20}$.

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

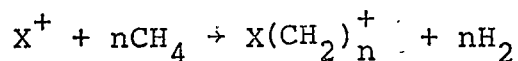
It is presently considered that methane polymerization must be initiated by such highly energetic species as

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

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



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 CH_4 molecule collides with the reaction center around X^+ . "Instantaneous" also refers to the low probability of observing the intermediate ions during mass spectrometric studies of methane radiolysis.

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

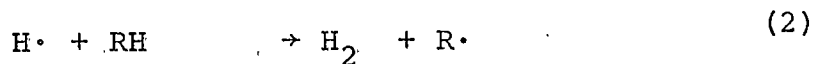
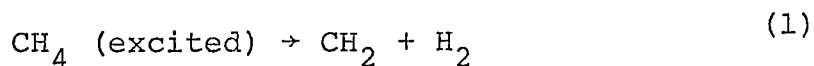
of ethane and ethylene gave polymer of molecular weight similar to that of methane. Their argument is that since ethane and ethylene samples contain twice as many carbon atoms per unit volume there would be twice as many carbon atoms in the Auger emission area as there would be for methane, one would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

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

Methane seems to be an ideal medium for polymerization. The unusually high ionization potential of methane (12.5 eV) makes methane an excellent source of high energy ions as compared to other hydrocarbons. Also since methane in comparison to the heavy n-alkanes does not have its carbon atoms previously committed to a particular set of

carbon-carbon bonds, it can form a more highly-branched polymer than the heavy n-alkanes. Thus, on these two counts methane seems to be the n-alkane most likely to polymerize. Observations bear this out. Ethane and propane have polymer formulas corresponding to the incorporation of 11 and 5 hydrocarbon molecules, respectively. One should note that both ethane ($\frac{-20.2 \text{ kcal}}{2 \text{ mole}}$) and propane ($\frac{-24.82 \text{ kcal}}{3 \text{ mole}}$) have greater thermodynamic instability (as measured by enthalpies of formation, ΔH_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⁽⁹⁾. Studies indicate that steel walls of the

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

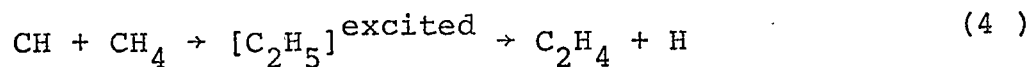
Ethane and other alkanes are formed predominantly by radical recombination



where R and R' are alkyl radicals. The radical recombination mechanism is confirmed by addition of radical scavengers such as NO or O₂ to the methane and noting the large reduction (85% or more) in alkane yields⁽¹⁰⁾.

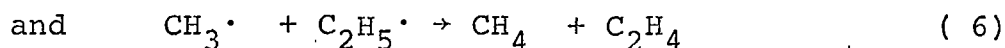
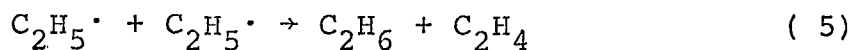
Addition of radical scavengers also increases alkene yields to detectable levels. This is understandable since alkenes are radical scavengers themselves, scavenging predominantly hydrogen atoms. Addition of another radical scavenger protects ethylene against further radical reactions.

Ethylene is formed mainly by the insertion reaction⁽¹¹⁾.



and possibly to a lesser extent by removal of a proton from C₂H₅⁺⁽¹¹⁾. It is also well known that disproportionation

reactions such as

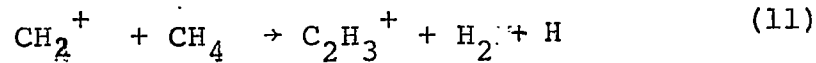
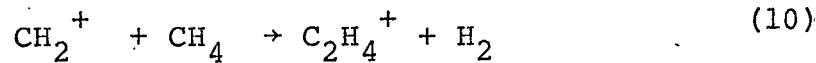
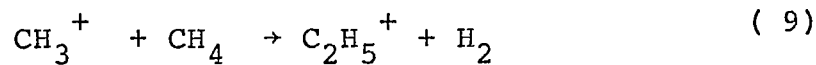
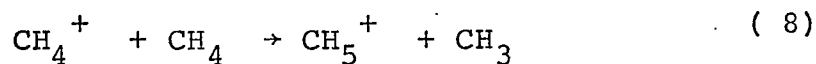


can produce ethylene.

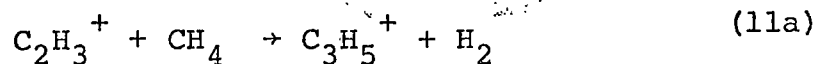
Then in the absence of scavengers we have the following mechanism for ethylene removal

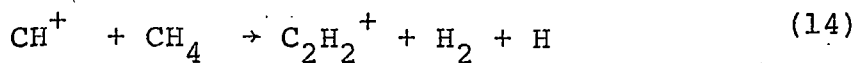
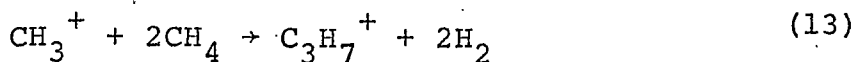
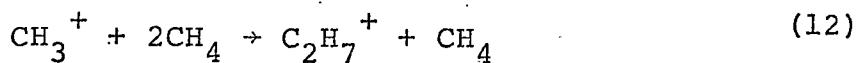


Ionic reactions are also of importance in producing small molecules. The following ionic reactions are generally considered to be the important ones occurring in methane (12)



followed by





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

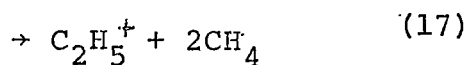
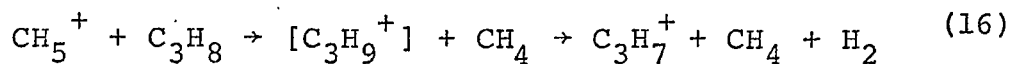
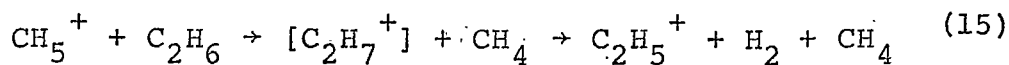
Reaction (12) involves an extra CH_4 molecule to remove the excess energy which might decompose C_2H_7^+ to C_2H_5^+ and H_2 . The intermediate ion involved in reaction (13) has not been identified. The relative intensities of the above mentioned end product ions at 1.9 mm pressure are, according to the mass spectrometric studies of Field and Munson⁽¹²⁾

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

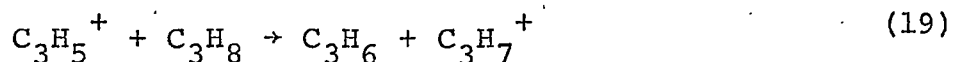
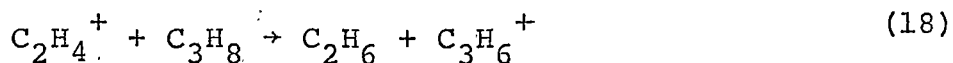
These ions can further react with other alkanes (such as ethane and propane) which may be present during radiolysis. It is found experimentally that of the five

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

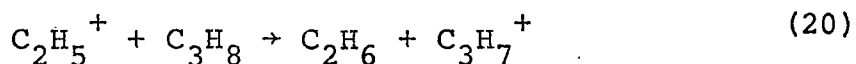
CH_5^+ reacts rapidly with ethane and propane⁽¹³⁾.



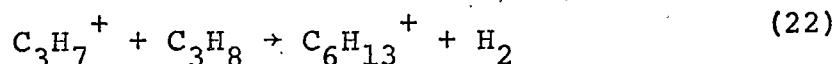
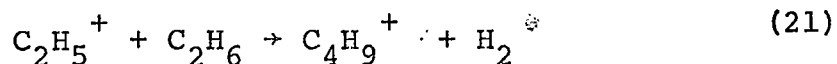
C_2H_4^+ and C_3H_5^+ react rapidly with propane but not with ethane



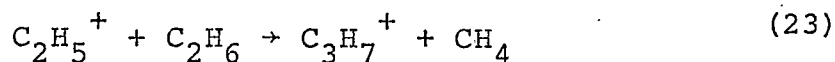
While C_2H_5^+ reacts rapidly with propane by hydride transfer



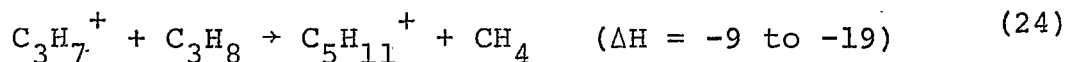
The following condensation reactions have been shown through mass spectroscopic studies to be important in radiolysis at high pressures (up to 200 mm)⁽⁶⁾



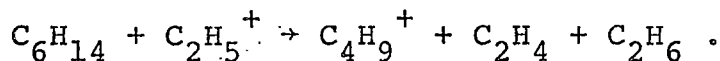
Additionally ion-cyclotron resonance studies confirmed the existence of reaction (21) and another reaction path⁽¹⁴⁾



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



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



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

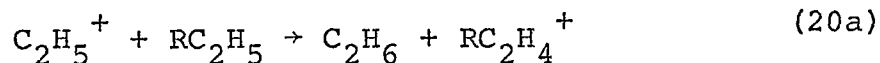
This reaction goes smoothly except when the hexane involved is 2,3-dimethyl butane. Presumably a methyl migration is necessary for the reaction only in the case of this particular hexane isomer.

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).

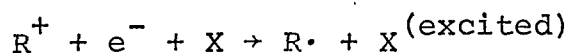
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|---|---|
| a. Hydride (H^-) transfer | $RH^+ + R'H_2 \rightarrow RH_2 + R'H^+$ |
| b. Proton (H^+) transfer | $RH_3^+ + R'H_2 \rightarrow RH_2 + R'H_3^+$ |
| c. H_2^- transfer | $R^+ + R'H_2 \rightarrow RH_2 + R'^+$ |
| d. H_2 transfer | $R + R'H_2^+ \rightarrow RH_2 + R'^+$ |
| 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^(3,6). Electron neutralization of ions in the gas phase is reasonable only if another molecule X can remove the ionization energy excess that exists:



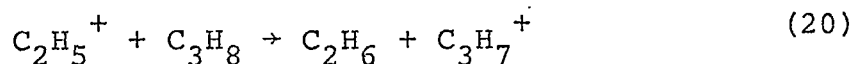
Presently no general methods have been developed for direction detection of these neutralization reactions. The best methods for studying ion reactions, which involve the use of mass spectrometer, generally elucidate only ion-molecule reactions. Thus the fate of these ions of low reactivity is seldom 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).

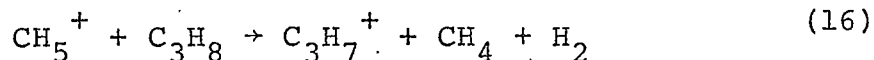
Methane radiolyses are sometimes complicated by trace impurities. Oxygen, as an impurity, has the desirable property of suppressing radical reactions so that one can study the predominantly ionic reactions which remain. However, at high radiation doses, oxidation products such as CH_3OOH , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and HCHO can be formed (18). These in turn may scavenge the ionic reactions one is trying to study. Traces of ethane (20 ppm) and higher hydrocarbons typically present in highly pure methane may introduce confusion as to whether methane or some other hydrocarbon is the direct source of certain ions (19). Because of such impurities, the observations of heavy ions cannot be readily attributed to ion-molecule reaction sequences involving methane incorporation only. For example, the production of $\text{C}_6\text{H}_{13}^+$ could possibly be entirely attributed to reaction (22) in the presence of less than 1-7 ppm C_3H_8 impurity (19).

THE PROBLEM

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

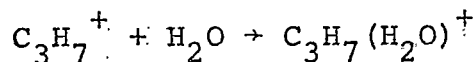


and protonation



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 LiAlH_4 chamber was prepared by pouring a diethylether suspension of LiAlH_4 onto a glass wool plug and then removing the ether under vacuum.

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

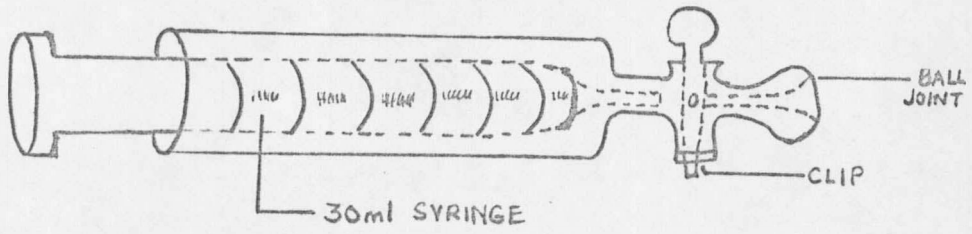


Fig. 1. The Sample Tube

