

REACTIONS OF SOLID HYDROCARBONS WITH HOT HYDROGEN
PRODUCED BY ELECTRIC FIELDS

by

MYUNGSOOK RHEE
B.S., SOGANG UNIVERSITY, 1973

A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Chemistry
KANSAS STATE UNIVERSITY
Manhattan, Kansas

1978

Approved by:


Major Professor

Document
LD
2668
.T4
1777
R52
C.2

TABLE OF CONTENTS

INTRODUCTION.....	1
LITERATURE REVIEW.....	3
Field ionization as a source of producing hydrogen ions.....	3
Production of hot hydrogen atoms.....	7
Charge of hot hydrogen species.....	9
Hot hydrogen atom reactions.....	10
Models for hydrogen atom reactions.....	13
EXPERIMENTAL METHODS.....	16
Materials.....	16
Introduction of tritium.....	16
Reaction assembly.....	17
Reactions of hydrocarbons with H ₂ by field ionization.....	21
Separation of methane from H ₂	21
Sampler.....	23
Analysis.....	25
EXPERIMENTAL RESULTS.....	29
Current from hydrogen ion species produced by field ionization.....	29
Product distributions for reactions of propene, propane and butane with field generated tritium.....	29
Yield of tritium atoms in the products.....	42
DISCUSSION	
Comparison of results.....	48
Effects of the presence of ions.....	51
Fraction of field ionized tritium ions involved in the reaction.....	52
Summary.....	53

ACKNOWLEDGEMENTS.....	55
LITERATURE CITED.....	56

INTRODUCTION

Field ionization is the phenomenon of positive ion formation at a surface where there is a large electric field directed away from the surface.

The process of field ionization can be explained theoretically on the basis of the wave properties of matter. The high electric field strength induces electron tunneling through a potential barrier in the molecule by the quantum mechanical tunnel effect. Thus it differs fundamentally from thermionic emission or photoemission where only electrons with sufficient energy to go over the potential barrier are ejected. A tungsten tip of very small radius of curvature, about 1000\AA (2), is used as an emitter in the field ionization source for production of the extremely high field strengths necessary for the field ionization. Gas atoms or molecules are field ionized in front of the tip and emitted if high electric fields of the order 10^7 to several times 10^8 V/cm are acting on them. Field ionization of hydrogen produces H_2^+ and H^+ in ratios that depend upon the field strength at the ionizing surface (5).

The phenomenon of field ionization has been applied widely in field ion microscopy and field ionization mass spectrometry. The latter has been adapted recently to the field of kinetics of unimolecular decomposition of ions in the gas phase (6,7). The application of a field ion emitter as a source of reactive chemical species has not been explored.

In this research field ionization has been used as a means of generating hydrogen ions for the study of their reactions with solid hydrocarbons. Even though there are several methods to produce hydrogen ions such as nuclear recoil of hydrogen (8) and the molecular beam method (3), the technique of field ionization was selected for two principal

reasons

1) A reaction arrangement could be operated as a closed system and thus would require only a small amount of tritium as a tracer for hydrogen; 2) the area of bare metal surfaces in the reactor is small so that difficulties arising from adsorption of the reactants on the metal surface should be small.

A thin film ($2 \times 10^{-7} \frac{\text{mol}}{\text{cm}^2}$) of hydrocarbon was condensed at 77^oK on a copper metal target which provided a conducting surface. The hydrocarbons used in the present research were propene, propane and butane. Tritium has been used as a tracer for the hydrogen.

There are several physical similarities between recoil tritium and field ionized tritium, and both similarities and differences in their chemical properties were observed in this study. The products from reactions of field ionized tritium with propene were similar to those from reactions of recoil tritium with propene. But there was little similarity in the distribution of products from propane and butane.

LITERATURE REVIEW

Field Ionization as a Source of Producing Hydrogen Ions

Kirchner (3), Inghram and Gomer (2) and Müller and Bahadur (4) developed a theory of field ionization which may be illustrated with the use of a potential diagram. The potential of an electron as a function of the distance from the ideally smooth surface of a metal is drawn in Figure 1. The surface of the metal is assumed to be ideally clean, i.e. with no adsorbed layers. For field ionization to occur the potential of the external field has to be superimposed. At a certain minimum distance from the metal surface, a valence electron of the atom is raised to the Fermi level by the effect of the external field. The potential barrier between the atom and the metal surface has then a width of only a few Å and a height of a few eV. Therefore, there exists a certain probability for penetration of the electron through this barrier due to the quantum mechanical tunnel effect. A field strength of the order 10^8 V/cm is required to ionize an atom or molecule in the ground state by field ionization.

Inghram and Gomer (5) found that field ionization of hydrogen, as shown in Figure 2, produces H_2^+ and H^+ in ratios that depend upon the field strength at the ionizing surface. The principal ion is H_2^+ , except at very high fields (over 5.5×10^8 V/cm), where H^+ predominates.

At the beginning, the number of workings in this relatively new field was very small, and it was rather slowly developed. Later, it was pointed out by Inghram and Gomer (5) that a FI (field ionization) source could be used in mass spectrometric analysis which was realized experimentally a number of years later. Müller (9, 12) designed FI microscopes first and reported on qualitative analysis of field ions in a simple mass

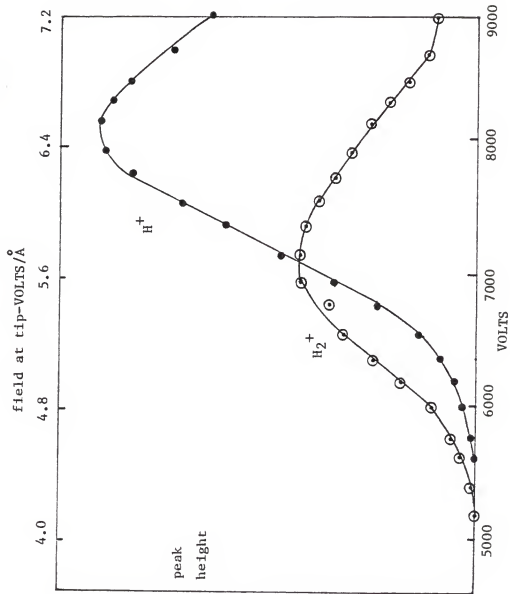


Figure 2: Peak height versus applied voltage and field for hydrogen(5)

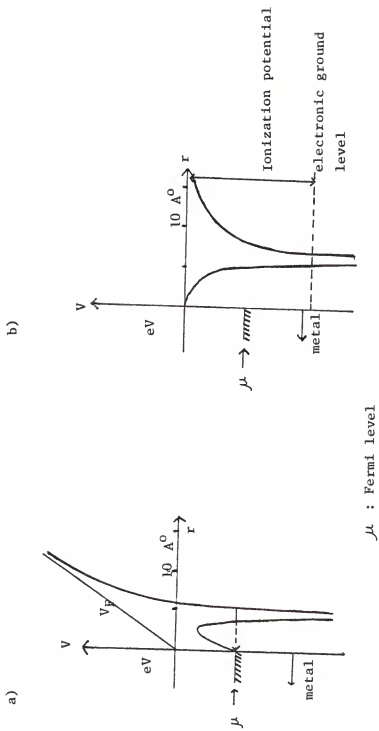


Figure 1 : Potential of hydrogen near a metal surface(5)
 a) with field b) without field

spectrometer (4). More quantitative results were obtained with a device designed by Clements and Müller (32). Field ionization mass spectrometers have been used very widely during the last ten years.

FI mass spectrometer offers an interesting new application in the field of kinetics of unimolecular reactions of ions that are produced by field ionization in the gas phase (6, 7, 10, 11, 13, 14, 15). Derrick, Falick and Burlingame reported (14) that randomization or scrambling of the hydrogen atoms and deuterium atoms in cyclohexene -3, 3, 6, 6- d_4 is observed to begin within 1×10^{-11} sec and to be completed within 1×10^{-9} sec and randomization is the result of successive 1, 3-allylic arrangements. They also reported (13) that the kinetics of ion decomposition reactions in the short time frame (10^{-11} to 10^{-9} sec) could be deduced from the analysis of the product ion translational energy distribution by a double focusing FI mass spectrometer. Mechanisms and kinetics of elimination of water from hexanol following field ionization have been studied at times from 10^{-11} to 10^{-5} sec by them (15). The essential properties of an FI source which make such study of gas phase ion reaction kinetics at 10^{-12} to 10^{-5} sec possible are the sharply defined ionization region and very high electric field by which ions are accelerated very rapidly after their formation.

There are two distinct kinds of emitters for FI which have been developed so far. They are tips and wires or sharp edges. Methods for production of fine metal tips suitable for FI have been described by Müller (17). Much higher field strengths can be obtained with tips than with wires. The highest field strength can be obtained with tungsten tips (16). Sharp edges of metal blades as emitters have been introduced by Robertson (18) and Becky (19, 1). The advantage of blades

as compared to thin wires consists in avoiding rupture which easily occurs with thin wires.

Production of Hot Hydrogen Atoms

Thermal hydrogen reactions have been studied for a long time because reactions in systems at or near thermal equilibrium can be studied with relative ease experimentally. But unfortunately thermal systems, while experimentally convenient, tend to be restricted to threshold processes. Possible reaction paths and products characterized by higher activation energies than those of threshold processes are inaccessible.

Since several techniques for production of hot atoms have been developed, reactions of hot atoms have been studied to a large extent. These techniques are summarized below.

Beam Method

This is the ideal way of studying kinetic processes of single collisions by producing a beam of the species in question and letting the beam interact with another reagent. If the surface density of the reagent is very low, the beam particles will undergo initial collision with not more than one molecule. If the beam is monoenergetic (but variable in energy), an excitation function can be determined.

By using thermal beams, reactions having zero to very low energy threshold were studied by Fite and Datz (20) and some information on excitation functions in the very low energy region (≤ 1 eV) was obtained.

The fast velocity selected molecular beam method can overcome the limitation of the recoil method (to be discussed later) where only limited information on the energy dependence of the processes are available and can provide information on the angular and energy distributions of the reaction products.

Several chemical accelerators for neutral molecular beams have been constructed, but all have the problem that the primary neutral beam was too weak to be detected. To overcome this difficulty, the radioisotope tritium has been used as the beam material by M. Menzinger and R. Wolfgang (21). They reported the energy dependence of reactions of tritium ion beams, T^+ and T_2^+ (having controlled energies between 1-200 eV) with solid cyclohexane. At high energies (≥ 30 eV) absolute yields for T^+ beams are close to those found by the nuclear recoil technique. With T_2^+ , high energy yields are about 20% lower. At lower energies, yields of both decline in comparison with that of nuclear recoil atoms.

Yencha, Menzinger and Wolfgang (22) studied the total reaction cross section for the reactions of monoenergetic tritium ions in the 1-200 eV range by a molecular beam technique with n-hexane, cyclopentane, n-butane and 1-chlorobutane and reported that T for H substitution cross sections are similar for all alkanes studied: threshold at 1.5 ± 0.5 eV, a rapid rise to a maximum at 9-12 eV, and a slow decline at higher energies.

Recently, Lagarde and Paulus (23) reported that T atoms in the 250 eV to 6 keV range were allowed to strike thick solid alkane targets of n-C₄H₁₀, i-C₄H₁₀, n-C₅H₁₂ and c-C₆H₁₂ and the yields are energy independent in this large range and results are close to those obtained in similar experiments with ionic beams or found by the nuclear recoil technique.

Photodissociation (24,25)

This method can produce hot atoms of well defined initial energy so that it can provide good information on energy dependence. But this photodissociation technique is limited to relatively low energies (<3 eV)

and there is the further limitation that the system should absorb light only in that mode which leads to the production of hot atoms. Because of these limitations, not very many investigations using this method have been done.

Nuclear Recoil Techniques

This method is extremely simple and hot atoms of essentially all energies are available so that the method may be appropriate for studies over the entire chemical energy range. So the great majority of hot atom studies have been made using nuclear recoil techniques, even though this technique is limited by the lack of direct control over the reaction energy. But not all elements have radioisotopes of suitable life time which is another limitation in this method.

For the production of tritium atoms the useful nuclear processes are the neutron irradiation of either helium 3 which gives tritium of 2.7 MeV recoil energy or lithium 6 which gives tritium with 0.19 MeV recoil energy.

Charge of Hot Hydrogen Species

Most nuclear transformations which provide enough recoil energy to be potentially useful for hot atom studies are more or less likely to yield the hot species as an ion. These hydrogen ions have a very high energy of the order of several keV or higher, so many charge exchange collisions can take place before the species reach the hot chemical reaction region. During this collision stage, energy is lost leading to ionization and electronic excitation of the medium. So the equilibrium or average charge of the recoil species gradually decreases until it becomes neutral. Wolfgang (26) explained that for atoms where

the ground state and the excited states are well separated (hydrogen case), the expectation would be that the species reaching the hot chemical reaction region would be in its ground state. But if the excited state lies close to the ground states it becomes less likely that only the ground state species will reach the chemical energy range (carbon case).

In most of hot tritium experiments, an assumption has frequently been made that the products of recoil tritium reactions are normally in the ground electronic state but have high vibrational and/or rotational energy.

In 1975, Fee and Markowitz (27) proposed the possibility of ion molecule reactions in recoil tritium chemistry.

For the molecular beam method, the same charge exchange collision was suggested as had been proposed for tritium recoil. Menzinger and Wolfgang (21) proposed the efficient charge transfer of high energy hydrogen at the surface of target to form hot tritium atoms, so hydrogen ions T^+ , T_2^+ , produced by high energy beams react as hot atoms in the electronic ground state as in the case of nuclear recoil tritium.

Hot Hydrogen Atom Reactions

Thermal hydrogen atoms have relatively low energy compared to hot hydrogen atoms, so reaction pathways are fairly simple. The present research work has been a study of hot hydrogen atoms reactions, so a survey of the thermal hydrogen atom reactions was not emphasized.

Thermal hydrogen atoms mainly undergo abstraction of H with saturated hydrocarbons and abstraction and addition with unsaturated hydrocarbons.

Hot atom reactions have been developed mostly for hot hydrogen, and reasonably complete reaction mechanisms have been proposed. Hot hydrogen atom reactions have been developed mainly in the saturated, unsaturated and aromatic hydrocarbon compounds, halocarbon, oxygen-containing carbon compounds and inorganic compound systems.

Our interest is in hydrocarbon systems, and the reactions of hot hydrogen atom with hydrocarbons are summarized below. Only a few general types of reaction are needed to interpret all of the experimental works which have been done so far.

1. Abstraction of atom: $T + RH \rightarrow R + HT$

This threshold reaction is the most common hot reaction studied so far.

2. Substitution of atom: $T + RH \rightarrow RT + H$

This reaction is of comparable importance to abstraction in hot hydrogen reactions.

3. Substitution of radicals or groups: $T + R_1 - R_2 \rightarrow R_1T + R_2$

This is a less efficient type of reaction than substitution of atom. The hot atom preferentially combines with the small alkyl group.

4. Substitution for 2H: $T + RCH_3 \rightarrow RCH_2\cdot + H_2$

The radical produced may dissociate more to form a smaller alkyl radical and an unsaturated hydrocarbon.

5. Addition to unsaturated double bonds:



The intermediate radical R^* is highly excited and usually decomposes.

The reactions of the recoil tritium atoms with the saturated hydrocarbons propane and butane in the gas phase were studied by Urch and Wolfgang (28) and propane by Lee, Musgrave and Rowland (29). The result was that abstraction of hydrogen atoms occurred more than substitution of hydrogen atoms in various ratios. Wolfgang and Chang (30) studied the reaction of recoil tritium with n-butane. They studied the magnitude of temperature effects on hot atom reactions and reported that hot hydrogen reaction yields are very weakly dependent on such temperature effects.

Most of hot hydrogen chemistry studies have been done in the gas phase simply because the condensed systems are more complex and control of the experimental variables are more difficult.

In 1968, Menzinger and Wolfgang (31) studied the reaction of recoil tritium with n-butane in the solid phase and obtained the same result as their previous work (28) in the gas phase. They reported that phase effects of recoil tritium reactions play only a minor part in hot hydrogen atom reactions and reported on a simple method for the determination of absolute yields or products formed by reactions of recoil tritium in the solid phase. Previously, results had been expressed only on a relative basis.

For propene, Lee and Rowland (8) and Lee, Musgrave and Rowland (29) reported that recoil tritium reacted with propene principally by substitution of T for H and T for CH_3 , in contrast to the result of the thermal hydrogen reactions which reacted by addition more than by substitution.

In 1971, Mahan and Garland (33) reported that in the reaction of recoil tritium with propene, a decreasing $\text{HT}/\text{C}_3\text{H}_5\text{T}$ ratio was observed

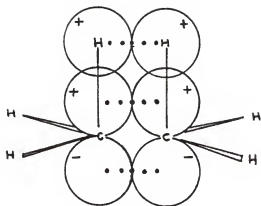
with increasing pressure and observed a product distribution similar to Lee and Rowland (8) and Lee, Musgrave and Rowland (29).

Models for Hydrogen Atom Reactions

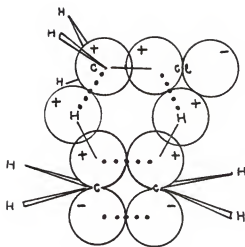
For hot hydrogen atom reactions with saturated hydrocarbons, it has been found so far that abstraction and substitution are the main reactions and with unsaturated hydrocarbons, addition to the double bond is also of comparable importance. Wolfgang and Rosenberg (34) supported these experimental results with a kinetic theory model of hot reactions which provided a satisfactory description for the entire range of data.

Wolfgang rejected the possibility of an internally equilibrated reaction complex because of the difficulty in conceiving of any reasonable electronic structure that would allow the tritium atom of several eV energy to be bound to give a long lived collision complex. And this was supported by the detailed theoretical calculation of Karplus, Porter and Sharma (35).

Cipollini and Stocklin (36) have reported enhanced yields of ethylene from ethane when recoil tritium reacts with an equimolar mixture of ethane and methyl chloride. Such large yields of ethylene had not been observed in the reaction of recoil tritium with ethane. In 1972, Urch (37) explained this remarkable result by proposing that a collision complex undergoes unimolecular decomposition $C_2H_5T \rightarrow C_2H_3T + H_2$ via a high activation energy route where four orbitals interact in phase in a cyclic manner. The addition of methyl chloride permits the in-phase cyclic interaction of six orbitals and has a lower activation energy than the preceding activated complex.



complex containing a 4-membered
cyclic unit



complex with methyl chloride
containing a 6-membered
cyclic unit

For unsaturated systems, substitution and abstraction seem to follow the same pattern as in alkanes, but large yields of certain specific degraded alkenes are found. Wolfgang postulated that there could be an excited radical sufficiently long-lived which undergoes unimolecular decomposition later.

Highly excited radicals from the addition of hydrogen to unsaturated double bonds undergo reactions in such a way to reduce the instability associated with the lone electrons. All the reactions of radicals are described well by Watkins (39). Through these radical reactions, there would be products having more carbon atoms than reactant hydrocarbons in the reaction of hot hydrogen with unsaturated hydrocarbons.

The reaction of methane with H was studied theoretically by K. Niblaens, Roos and Siegbahn (40) recently in 1977. This theoretical study might be regarded as an archetype for the corresponding reactions of higher homologs and substituted hydrocarbons. This theoretical calculation gave results of 13.5 kcal/mol and 36.6 kcal/mol for the threshold energies of abstraction and substitution, respectively, by predicting a CH_5^* activated complex to have several thermodynamically stable configurations with respect to the isolated reactants H and CH_4 . These theoretical threshold energies fall in the same regions as the corresponding kinetically determined activation energies which are 10-12 kcal/mol and 35-40 kcal/mol, respectively.

In cyclo-compounds, unimolecular decomposition of the excited intermediate, i.e. ring opening, have been reported after the substitution of T for H reaction. Izawa, Lee and Rowland (41) reported the decomposition of highly excited $\text{c-C}_3\text{H}_5\text{T}^*$ molecules to either of $\text{C}_2\text{H}_3\text{T}$ plus CH_2CO or of $\text{c-C}_3\text{H}_5\text{T}^*$ plus CO. Su and Tang (42) reported the ring opening of 1,1-dimethylcyclopropane after substitution of H reaction.

In 1973, Malcome-Lawes (43) predicted that HT produced by a high energy abstraction process may undergo dissociation on collision with surrounding molecules, and attempted to relate a wide range of apparently conflicting experimental results to a crude but simple model of the reactions of recoil tritium atoms.

EXPERIMENTAL METHODS

Materials

The gaseous hydrocarbons which have been used as reactants are propene, propane and butane. Besides them, many other low molecular weight hydrocarbons have been used for the identification of the tritium labeled products. The gaseous hydrocarbons were obtained from Matheson Co. and were research grade with a reported purity of 99.98 mol%. They were directly used without any further purification. Liquid hydrocarbons, 2,3-dimethylbutane, 4-methyl-1-pentene, 1-hexane (all from Aldrich Chemical Company), n-hexane (Fisher Scientific Company, certified reagent) and 2-methylpentane (Pfaltz and Bauer) were used for the identification of the products in the propene reaction with hydrogen.

Molecular sieve was used for the separation of methane and hydrogen from the other hydrocarbon products which were condensable at 77°K.

Linde Molecular Sieve 5A, 30/60 mesh, chromatograph grade, was used for this purpose.

Introduction of Tritium

Carrier free tritium was obtained from New England Nuclear Corporation. It was in a small ampule (about 2cc volume) containing a break seal. A glass tube extended beyond this seal. A small glass rod was placed in the glass tubing next to the break seal. A side arm was connected to the vacuum system. Before breaking the seal, the glass tube was evacuated through a side arm by high vacuum system. Then the side arm was sealed off. Tritium was introduced into the vacuum system

through a palladium thimble. Tritium will not diffuse through palladium at room temperature, but it will slowly diffuse through at temperatures above 200°C . Indirect heating of the thimble was accomplished by applying about 30V through a nichrome coil which surrounded the glass tube containing the thimble.

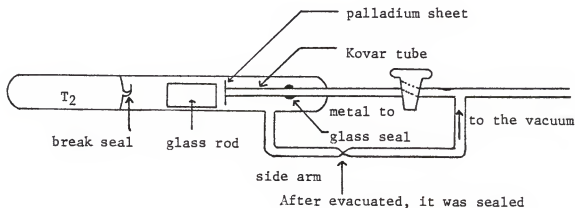


Figure 3 : Tritium supply

Reaction Assembly

Field ionization source (Tip as FI emitter)

There are two main methods for tip production. The first consists in dipping a wire of the metal concerned with a diameter of about 0.1mm, periodically into a molten salt such as NaNO_2 or into a solution of etchant. The second method consists in electrolytic etching of the wire in molten salts or in aqueous solutions of salts with a few volt AC or DC applied. Because there is a large variation in the treatment possible in the second method, the first method mentioned above was used in the present work. Tungsten tips were prepared by chemically

etching the end of 10 mil tungsten wires with molten sodium nitrite. Several minutes of etching time are required, so the periodic dipping into the molten salt NaNO_2 was made by hand. The tip wire has to be inserted as nearly vertically as possible into the etching bath. The etching process was examined by microscopic inspection from time to time. The optical microscope at 30 times magnification was used to examine it. The tip should show a long slender taper to get a high electric field. If it is too tapered we might get a high electric field, but the tip easily bends or folds after use several times. Then it has to be sharpened again. After it has been used for a long time, it needs cleaning which can be done by chemical etching. After having gained some experience from observations in the optical microscope, the quality of the tip could be judged well.

A couple of tips were made and used for the whole work. The radius of the tip which was used for the last part of the work was 5000\AA as measured by an electron microscope. The tip was soldered (with gold solder) to the bridge of tungsten leads in the tip supporter.

Reaction Vessel

The reaction vessel whose diameter is 0.8 inch and length is 10 inches was made of Pyrex glass. There was a tip as a field ionization source and a target where a thin film of hydrocarbon reactant was condensed at 77°K . A diagram of the reaction vessel is shown in Figure 4. A copper target (disc of area 7 cm^2) was positioned at a distance of 2 cm from the end of the tip. The tungsten tip was connected to the positive pole of a high voltage DC power supply (HIPOTRONICS Atomic Accessories Company) which had a variable output up to 25 kV.

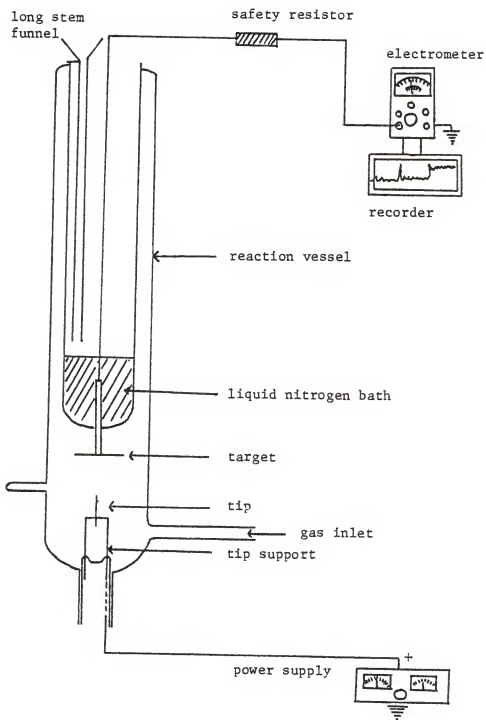


Figure 4 : Reaction assembly

The target was attached to the end of the sealed glass tube inside the reaction vessel with a wire which passes through the sealed glass tube to the electrometer (610B, Keithley Instruments which has the range of $10^{-1} \sim 10^{-12}$ Amperes) to measure the current of positive ions (atomic hydrogen ions or molecular hydrogen ions). Liquid nitrogen was introduced into the sealed glass tube inside the reaction vessel to cool the target at 77°K . The electrometer was connected to a recorder (Atomic Accessories Inc.) to record the current during the reaction.

Pressure Measurement

The pressure of the system was monitored using a Pirani gauge (Consolidated Vacuum Corporation, Model GP-210). The Pirani gauge was calibrated against a McLeod Gauge (Consolidated Vacuum Corporation, Type GM-100A) primary standard. A mercury diffusion pump was used to evacuate to a pressure of less than 10^{-4} torr. A cold trap with liquid N_2 was used between the mercury diffusion pump and reaction vessel to maintain this vacuum and keep mercury out of the reaction vessel.

Reactant Gases Introduction

The proper quantity of the gas (~ 30 mtorr) from the storage reservoir was introduced and measured by Pirani gauge to monitor the pressure. Before transfer, the gas in the storage reservoir was condensed so that gas could be evaporated slowly and the pressure of the gas could be under control. Prior to transferring the sample to the reaction vessel, the target of the reaction vessel was cooled by liquid N_2 . Then the reactant sample was transferred rapidly to the target of the reaction vessel. In this way, a homogeneous layer of reactant ($2 \times 10^{-7} \frac{\text{mol}}{\text{cm}^2}$)

probably resulted. A diagram of the reaction system is shown in Figure 5.

Reactions of Hydrocarbons with H_2 by Field Ionization

A small amount of tritium, about 1 mtorr, was allowed to enter the system through the indirect heating of the palladium thimble for a couple of minutes. When the tritium pressure reached the desired magnitude, 10~18 kV voltage was applied from the power supply to the tip where the tritium gas was ionized into atomic or molecular ions. The reaction time from the instant the voltage was applied to the tip until it was manually shut off was measured. Reactions were normally carried out for five minutes.

Separation of Methane from H_2

Methane and H_2 could not be condensed in the regular trap at 77°K in which all the other products could be condensed. A separation method based on molecular size difference was used. Methane and H_2 both were adsorbed at 77°K on molecular sieve LMS 5Å(44) which has a pore opening that will permit molecules with a diameter of less than 5Å to be adsorbed. Tritium gas was used as a source of tritium ions and had a very high radioactivity compared to that of tritium labeled products. Care was needed to avoid an overlap and masking of the methane peak by the tritium in the radio-gas-chromatography. There was no attempt to separate tracer tritium from diatomic hydrogen species as reaction products. So tritium had to be removed from other products as much as possible. For the separation of methane from H_2 , several trials were done to find an optimum temperature. Mixtures of organic solvents and liq N_2 were used to obtain different temperatures. It was found

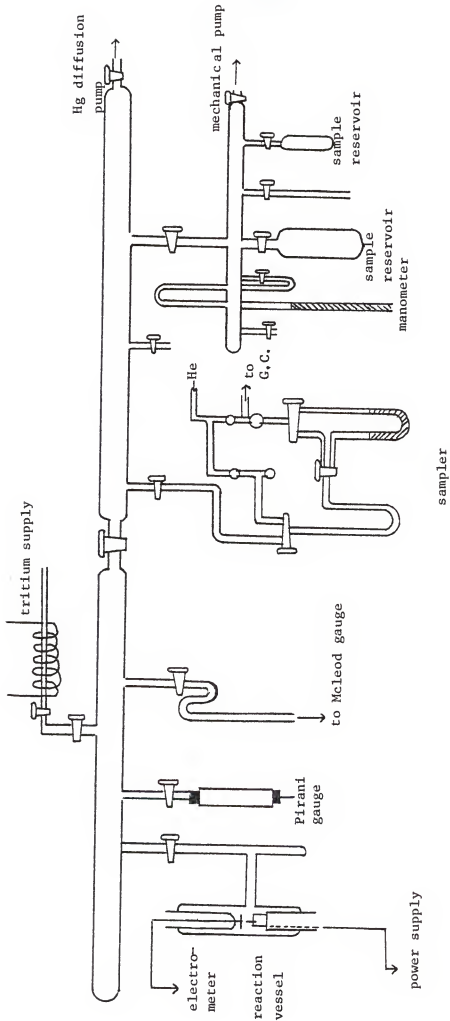


Figure 5 : Reaction system

that the optimum temperature, which could be obtained from a mixture of liq N_2 and Freons, was about $128^{\circ}K$. A mixture of 25% Freon 12 and 75% Freon 11 was cooled by addition of liq N_2 slowly and stirring continuously until it became pasty and cloudy just before the f.p. At this temperature, methane can be condensed but not hydrogen.

Approximately 3 cm^3 of molecular sieve (LMS 5A 30/60 mesh chromatograph grade) was packed in the U-type glass tube and a little glass wool was plugged in tightly enough on top of molecular sieve at both sides so that the molecular sieve would remain stationary when the pressure was changed.

The capacity of molecular sieve to separate molecules could be restored by regeneration or reactivation of the molecular sieve. The design and operation of the regeneration cycle has a direct influence on the adsorptive capacity and efficiency of the molecular sieve. Since the molecular sieve has a finite capacity for the adsorbate molecules, regeneration had to be done completely. The LMS 5A bed was heated with electrical heating overnight under the high vacuum. Before use in the next adsorption cycle, the bed was cooled in order to increase the bed capacity.

Sampler

In order to transfer the reaction products to the gas chromatograph, a sampler was used which consisted of two U-tubes. One of the U-tubes was used to collect the condensable reaction products at $77^{\circ}K$ for transfer to the gas chromatograph. The other U-tube contained activated molecular sieve 5A and served as a trap for hydrogen and methane when immersed in liquid N_2 and as a trap for methane only at $128^{\circ}K$ when immersed in a mixture of liquid N_2 , Freon 11 and Freon 12. A diagram of the sampler is shown in Figure 6.

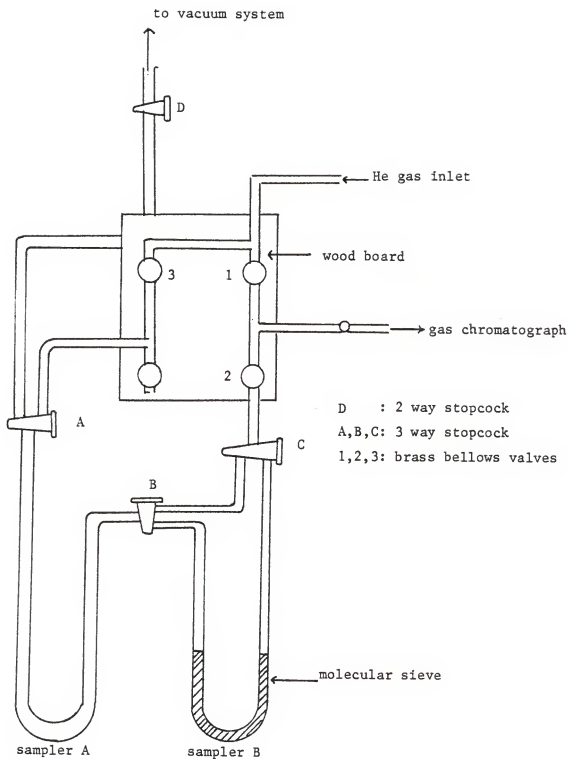


Figure 6 : The sampler

When the sampler was not in use, helium gas was flowed through 1 to the gas chromatograph. All products came into the sampler through D and A. All reaction products condensable at 77⁰K were trapped in sampler A. Methane and hydrogen kept travelling to sampler B and methane could be trapped at 128⁰K but not hydrogen. Since it took quite a long time to trap methane at this temperature (1×10^{-6} mol for 10 min, and took longer at a lower pressure), it was required to watch the pressure decrease carefully. When a pressure reading by the Pirani gauge was about 1 mtorr and the pressure didn't decrease any more, the hydrogen-tritium gas was pumped out as much as possible.

Analysis

The sampler was connected to a radio-gas-chromatograph system for analysis. The products from the reactions were separated by a gas chromatograph (CENCO #70130) and their radioactivities were counted by an ionization chamber and electrometer (Cary Vibrating Reed Electrometer, Model 31). The signal from the vibrating reed electrometer was recorded on a recorder (Varian Associates Graphic Recorder, Model G-14) equipped with an integrator for measuring the peak area. The signal from the thermal conductivity detector of the gas chromatograph was also recorded on a recorder (Honeywell, Electronic 19).

Two procedures were used to analyze the products. One procedure was to analyze all the radioactive products including the products which have more carbon atoms than reactants. A ten foot column of 40% silver nitrate in ethylene glycol on Chromosorb P in series with a fifteen foot

column of 15% isoquinoline on Chromosorb P was used at room temperature to separate the products. The products trapped in sampler A were transferred to the gas chromatograph with a stream of helium gas flowing via 3, A, sampler A, B, C and 2. Heating the sampler with a heat gun immediately after removing the liquid N_2 bath was required to transfer the products in a short time to the gas chromatograph. It was found that there were products having more carbon atoms than the reactant with this column, but products between C_1 and C_4 could not be separated or identified well enough to analyze them because of the close retention times among them. The second procedure involved conditions allowing a separation of $C_1 - C_4$ hydrocarbons. A twelve foot Poropak Q column was used to separate and identify hydrocarbons having less or equal number of carbons, including hydrogen, than the reactant. From sampler B, products were transferred to a twelve foot Poropak Q column at room temperature ($23^{\circ}C$). After these products passed through the chromatograph, the temperature was then increased to $102^{\circ}C$ and products in a sampler A were transferred to the gas chromatograph. Several hours were required for butane to pass through the twelve-foot column of Poropak Q, so a six-foot Poropak Q column was used for butane identification.

The helium gas flow rate was $25 \sim 35$ ml/min. After passing through the chromatograph the helium stream containing the separated gas chromatographic samples was passed through the ionization chamber. A

stream of nitrogen gas was introduced from a side arm to serve as a purge gas in order to eliminate hold-up of the samples in the detector which would have caused overlap of peaks. The nitrogen gas also enhanced the sensitivity of the ionization detector. The ionization chamber capacity was 30 ml. A positive potential of 67V from a battery was supplied to the cylinder of the ionization chamber. The nitrogen gas flow rate was 20 ml/min.

The radio-gas-chromatograph diagram for the analysis is shown in Figure 7.

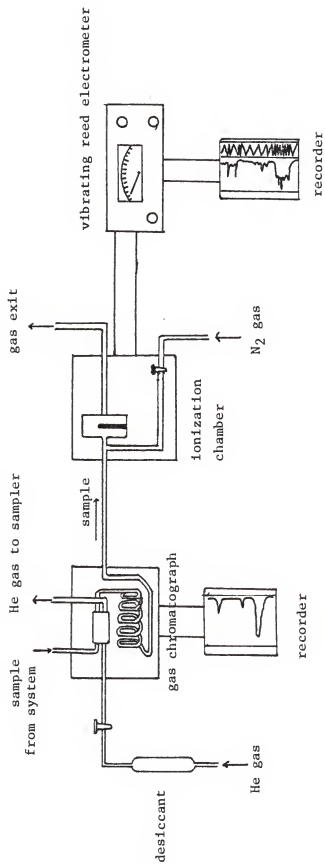


Figure 7 : Radio-gas chromatograph for analysis.

EXPERIMENTAL RESULTS

Current from hydrogen ion species produced by field ionization

The gaseous tritium used in my research was analyzed by radio-gas-chromatography and found to have a mole ratio of HT to T₂ 1:1.75. But it is not known what the relative yields of H⁺, HT⁺, T⁺ and T₂⁺ produced by field ionization were even though the relative amount of HT and T₂ was known. These four hydrogen ion species might all be involved in the reactions with solid hydrocarbons but reactions of H⁺ do not give labelled products directly.

Throughout the reactions for propene, propane and butane, the ion current was fairly constant but there was no consistency between the amount of products and the current. Figure 8 is an example of this lack of consistency. The higher current produced a smaller amount of products.

Product distributions for reactions of propene, propane and butane with field generated tritium

Propene

Propene was the first compound used as a target for the beam of field generated tritium particles.

In Table 1 are gas chromatographic retention times of several pertinent hydrocarbons which were obtained with the use of a ten foot column of 40% silver nitrate in ethylene glycol on Chromosorb P in series with a fifteen foot column of 15% isoquinoline on Chromosorb P at the room temperature with a He flow rate of 25 ml/min.

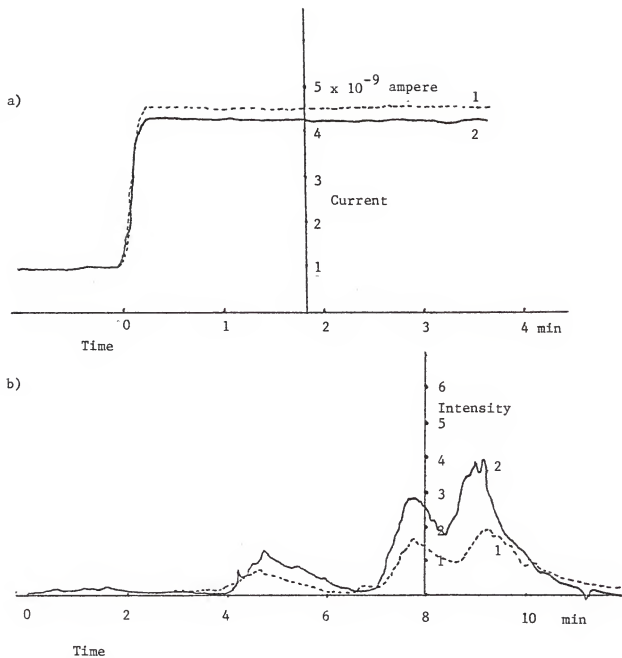


Figure 8 : a) Current for the reactions 1 & 2 of propene with hydrogen
b) Chromatograms for the reactions 1 & 2 of propene with hydrogen

compound	retention time (minutes)	compound	retention time (minutes)
hydrogen	6.0	2, 3-dimethylbutane	17.0
ethane	6.5	2-methylpentane	18.5
propane	7.0	n-hexane	25.5
ethene	10.0	4-methyl-1-pentene	28.0
propene	12.0	1-hexene	45.0

Table 1 : Retention times of some hydrocarbons.

A representative overall product distribution for the reaction of propene with field generated tritium is shown in Figure 9. The first peak, which represents ethane, propane and hydrogen was analyzed in more detail and is shown in Figure 10. The ratio of amount of ethane to that of propane was 1.55:1.

As was explained in the experimental part, there was no attempt to separate residual tritium from diatomic hydrogen as a reaction product, so all of the tritium was pumped out after the products were transferred to the sampler. The hydrogen peak shown is what was left over after the pumping operation. The same procedure was applied to reactions with propane and butane.

The ratio of amount of each peak to that of propene was calculated and is given in Table 2. The ratio of ethane and propane to propene were calculated from the ethane-propane peak and the previously determined ratio of ethane to propane of 1.55:1.

Propane

A representative product distribution of the reaction of propane with field generated tritium is shown in Figure 11. The emphasis was to make the separation of products complete including products having more carbon atoms than the reactant propane. The later might be the result of combinations and other reactions of intermediates, such as radicals, produced in the primary reaction. But at this stage, no attempt was made to identify all products separately except the first few peaks which represent the products having less or equal carbon atoms than the reactant propane.

Peak A represents ethane, propane or hydrogen and peaks B and C represent ethene and propene, respectively. The ratio of amount of each peak to that of the first peak was calculated and appears in Table 3.

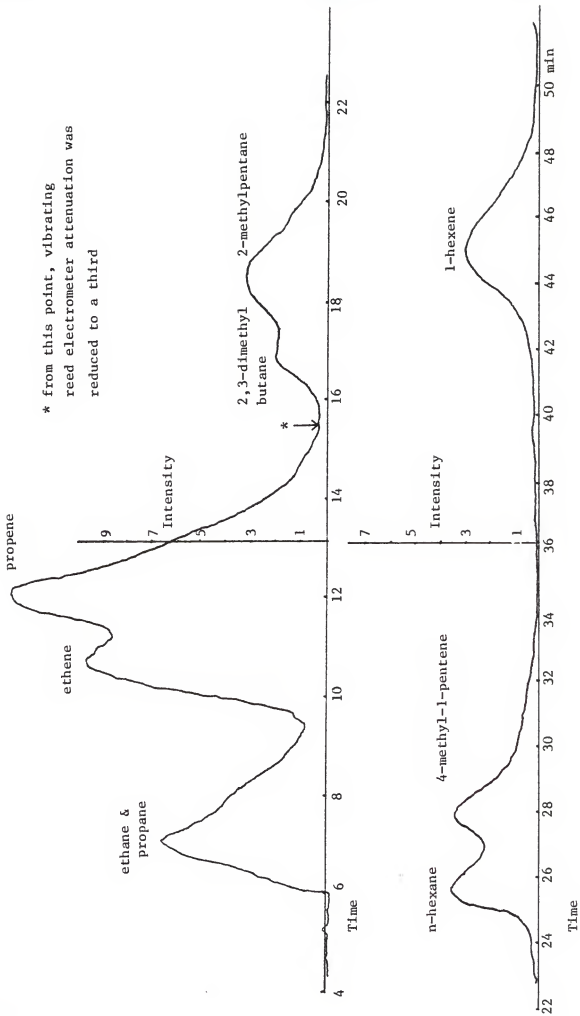


Figure 9 : Chromatogram of products from the reaction of propene and field generated tritium

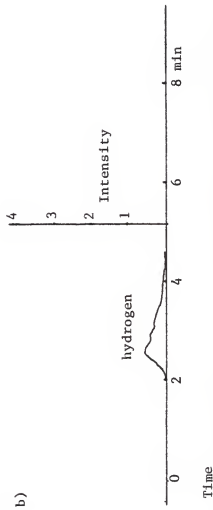
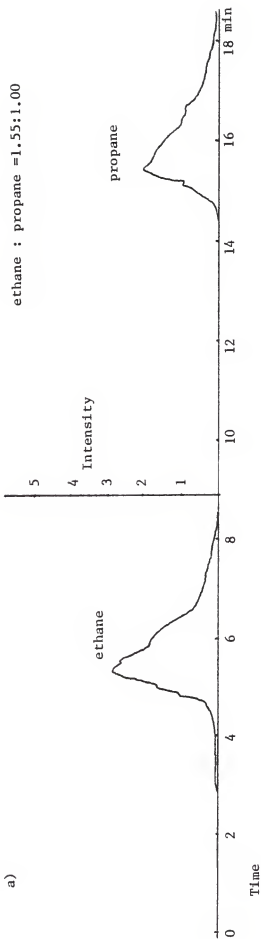


Figure 10: Chromatograms of parts of the products from the reaction of propene with field generated tritium.

a) 12 foot-Poropak Q at 10¹°C from liquid nitrogen trap

b) 12 foot-Poropak Q at 23°°C from molecular sieve trap of 123°K

peak reaction	ethane & propane	ethene	propene	2, 3-dimethylbutane & 2-methylpentane	n-hexane	4-methyl-1 -pentene	1-hexene
1	0.35	0.82	1.00	0.38			
2	0.12	0.78	1.00	0.56			
3	0.38	0.82	1.00	0.50			
4	0.28	0.61	1.00	0.78	0.29		
5	0.25	0.90	1.00	0.78	0.39	0.48	
6	0.39	0.75	1.00	0.32	0.31	0.25	0.26
7	0.27	0.85	1.00	0.34	0.20	0.24	0.27
average	0.29	0.79	1.00	0.53	0.32	0.32	0.27

$$\text{ethane} = 0.29 \times \frac{1.55}{1.55 + 1.0} = 0.18, \quad \text{propane} = 0.29 \times \frac{1.0}{1.55 + 1.0} = 0.11$$

Table 2 : Products of reactions of solid propene with field generated tritium.
(yields are shown relative to propene)

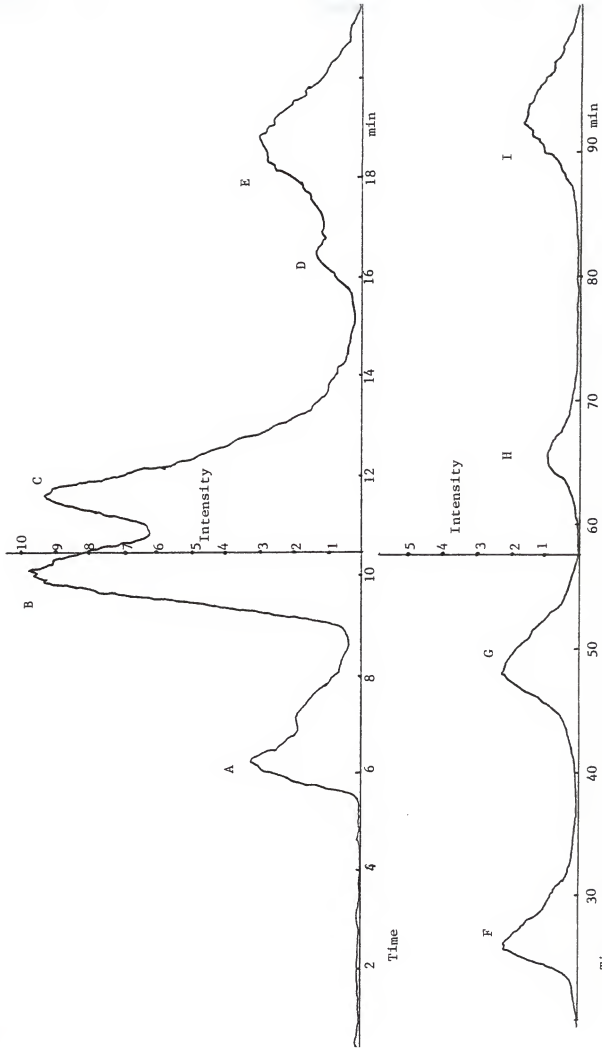


Figure 11: Chromatogram of products from the reaction of propane and field generated tritium.

peak reaction	A	B	C	D	E	F	G	H	I
1	1.00	3.20	3.10	0.45	1.75	2.37	1.56	0.55	1.41
2	1.00	3.10	3.91	0.53	1.73	2.37	2.17	0.60	2.43
3	1.00	3.33	3.87	0.53	1.87	2.67	2.52	0.58	2.58
4	1.00	2.82	3.86	0.68	1.84	2.86	2.93	1.11	4.32
5	1.00	3.11	3.61	0.43	1.79	2.38	2.07	1.03	3.62
AVERAGE	1.00	2.99	3.65	0.51	1.75	2.47	2.01	0.77	2.39

A :ethane,propane or hydrogen, B :ethene, C :propene

D, E, F :saturated C₆ hydrocarbons

G, H, I :unsaturated C₃ hydrocarbons or saturated C₇ hydrocarbons

Table 3 : Products of reactions of propane with field generated tritium.

(yields are shown relative to propane)

We are mainly interested in the primary reactions of field ionized hydrogen, like substitution of T for H, substitution of T for CH_3 and abstraction of H. These primary reactions give saturated hydrocarbon products which have equal or less number of carbon atoms than propane. The products from these primary reactions are shown in the first broad peak in Figure 11. These were analyzed in more detail to get a good separation among them and to get ratios of amount of these products to that of propane. The results appear in Figure 12. There are ethane and propane peaks, but no methane was detected as a product. The ratio of ethane to propane was 1.22:1.00.

Butane

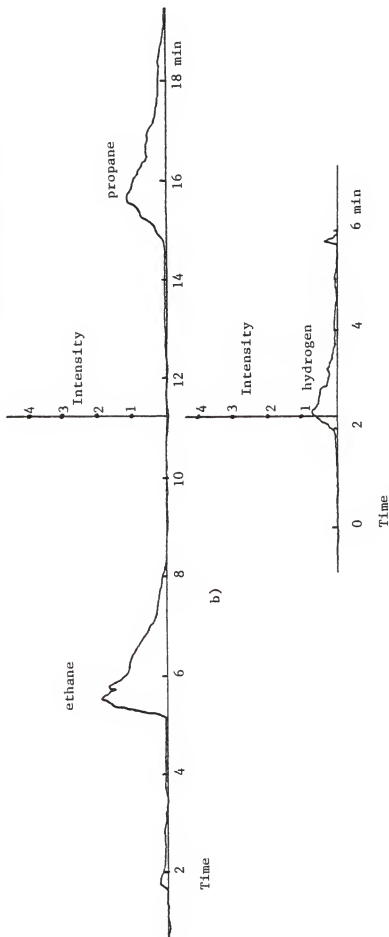
The results of reactions of propane with field ionized hydrogen were very much unexpected. To get a more generalized idea about the reactions of saturated hydrocarbons with field ionized hydrogen, butane was used as a sample.

The overall product distribution for the butane reaction with hydrogen is shown in Figure 13. As in the propane case, there are several products resulting from consecutive reactions.

The ratio of the amount of each peak to that of the first peak A was calculated and averaged in Table 4. In the propane case, the ratios are constant but in the butane case, the ratios of products varied as is shown in Table 4.

ethane:propane=1.22:1.00

a)



b)



Figure 12: Chromatogram of products ($\langle C_4 \rangle$) from the reaction of propane with field generated tritium.
 a) 12 foot-Poropak Q column at 101°C from liquid nitrogen trap.

b) 12 foot-Poropak Q column at 21.5°C from molecular sieve trap at 123°K .

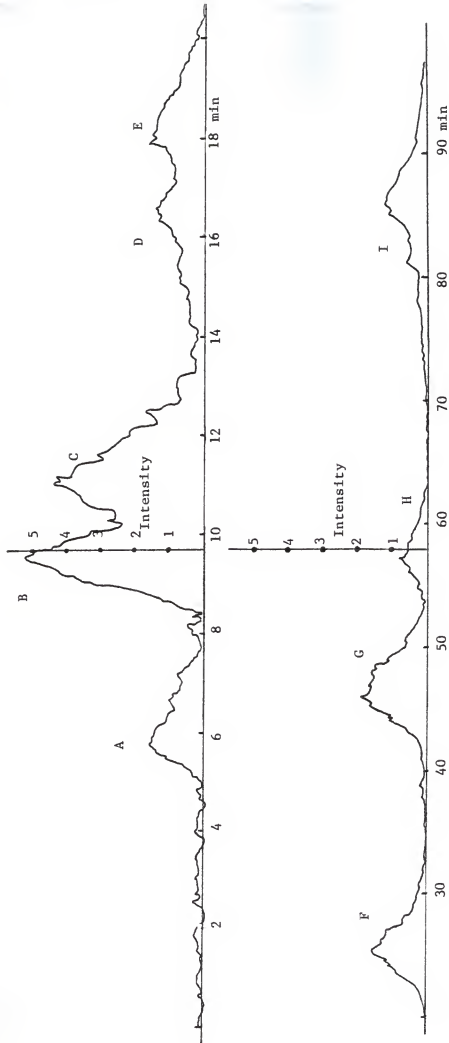


Figure 13 : Chromatogram of products from the reaction of butane and field generated tritium.

peak reaction	A	B	C	D	E	F	G	H	I
1	1.00	3.17	2.77	0.38	1.41	2.24	1.71	0.81	1.66
2	1.00	1.66	1.52	0.25	0.46	0.70	0.43	0.37	
3	1.00	2.62	2.19	0.22	0.68	1.14	1.49	0.34	0.58
4	1.00	2.44	2.46	1.00*	1.46	1.78	2.44		
5	1.00	2.92	2.46	0.35	1.02	1.34	0.92	0.52	0.91
6	1.00	2.38	2.04	0.20	0.64	0.86	0.57	0.23	0.49
7	1.00	3.26	3.36	1.05*	2.04	4.05*	0.60	3.18*	2.51
8	1.00	3.00	3.04	0.28	1.08	1.90	2.08	1.42	3.20
AVERAGE	1.00	2.68	2.48	0.21	1.10	1.25	1.28	0.46	1.17

* ; too much to be counted for an average

A ; ethane, propane or butane, B : ethene, C : propane

D, E, F : saturated C₆ hydrocarbons

G, H, I : unsaturated C > 3 hydrocarbons or saturated C > 6 hydrocarbons

Table 4 : Products of reactions of solid butane with field generated tritium.

(yields are shown relative to the first peak)

To know in more detail about the first broad peak which represents the products from the primary reactions of field generated tritium as in the propane case, the products of the first peak were separated and analyzed again. The result appears in Figure 14. In Figure 14, there are ethane, propane and butane peaks but no methane was detected at all as a product. The ratios of ethane and propane to butane are 1.30:1 and 1.05:1, respectively.

Yield of tritium atoms in the products

The number of tritium atoms in the products was calculated from the measured activity. The measured activity of the signal from the vibrating reed electrometer was proportional to the disintegration rate by a factor of 1.68×10^{-3} μCi per recorder integration unit. An integration unit corresponds to the integration value obtained from the recorder integrator times the attenuation scale setting of the vibrating reed electrometer in volts.

From the current measured during the reaction, the number of hydrogen ion species produced by a tip in the field ionization for the reaction time was calculated.

A tip as an emitter was replaced by a thin wire for the further study of the relationship between the ion current and the yield of tritium atoms in the products. Product distributions for the reactions of propene, propane and butane with field ionized hydrogen by a thin wire are shown in Figure 15, 16, and 17, respectively. These distributions by a thin wire are a little different from those by a tip. From these results, the yields of tritium atoms in the reactions by a thin wire were also calculated as in the tip case. All calculation results are summarized in Table 5.

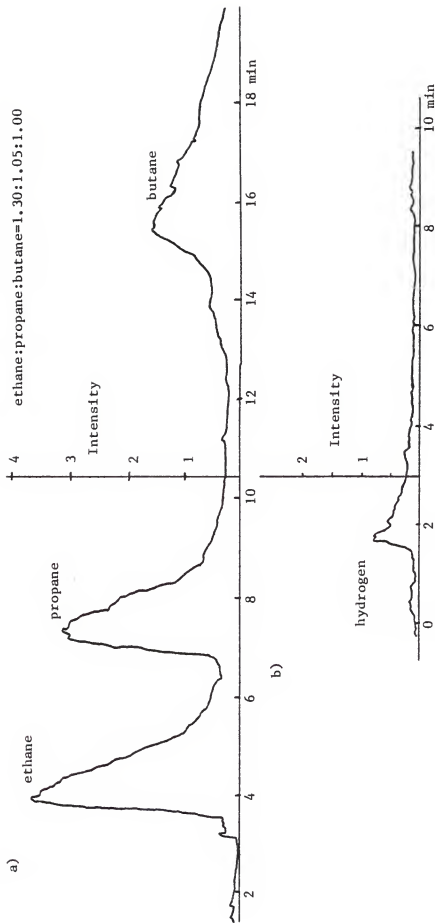


Figure 14 : Distribution of products ($\leq C_4$) from the reaction of butane with field generated tritium.
 a) 6 foot-Poropak Q column at 101°C from liquid nitrogen trap.
 b) 12 foot-Poropak Q column at 25°C from molecular sieve trap at 123°K.

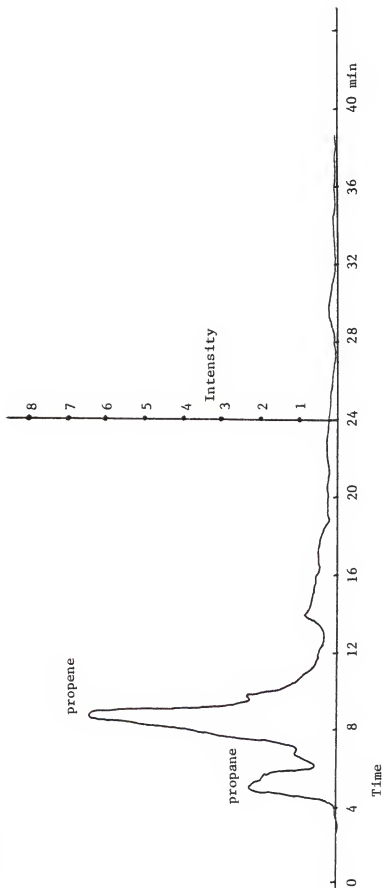


Figure 15 : Chromatogram of products from the reaction of propene with field generated tritium by a wire as an emitter.

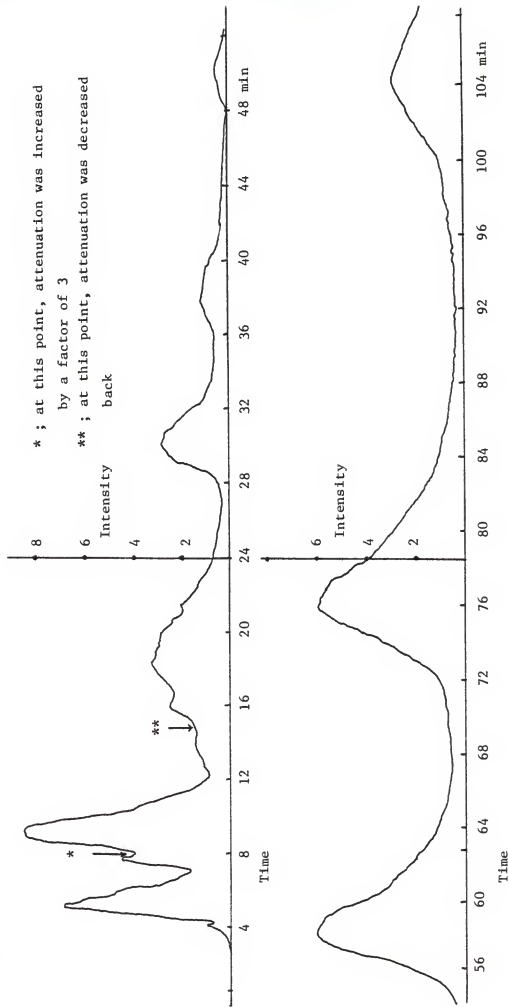


Figure 16 : Chromatogram of products from the reactions of propane with field generated tritium by a wire as an emitter.

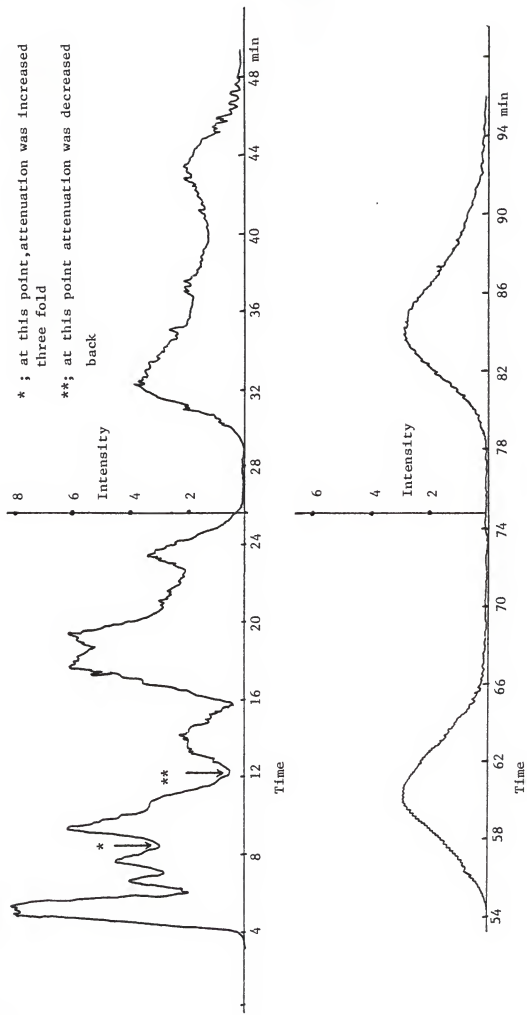


Figure 17 : Chromatogram of products from the reaction of butane with field-generated tritium by a wire as an emitter.

		number of tritium atoms in the products	number of tritium ions produced by FI
propene	tip	5.60×10^{12}	2.81×10^{12}
	wire	8.68×10^{12}	1.39×10^9
propane	tip	1.57×10^{13}	2.81×10^{12}
	wire	9.35×10^{13}	1.31×10^9
butane	tip	9.35×10^{12}	1.69×10^{12}
	wire	1.70×10^{13}	1.31×10^9

Table 5 : Comparison of yields of tritium atoms in the products to the number of hydrogen ion species produced by a tip and by a wire as field ion emitters.

In all three hydrocarbons, the number of tritium atoms in the products was larger than the number of tritium ion species produced by a tip or by a wire as field ion emitters. The number of tritium atoms in the products from the wire was larger than that from a tip, and the number of hydrogen ion species produced by a wire was smaller than the number from the tip.

DISCUSSION

Comparisons of results

I will discuss the results of my research by comparing them with the published results and mechanisms of recoil tritium and tritium beam studies. The mechanisms which I propose are conclusions based upon the product distributions which I observed. I did not perform any experiments in which attempts were made to trap intermediates such as free radicals and ions.

Propene reactions

The results obtained for the reactions of propene with field generated tritium are comparable with those from the recoil tritium method (see Table 5). There are no published results for the reaction of propene with hot hydrogen by the beam method.

method product	recoil tritium method			FI**
	(29)	(30)	(44)	
HT	0.76	0.70	0.82	*
CH ₃ T	0.03		0.04	0
C=C	0.33	0.32	0.33	0.79
C≡C	0.01	0.03	0.04	*
C-C	0	*	*	0.18
C-C-C	0.11	0.10	0.02	0.11
C-C=C	1.00	1.00	1.00	1.00
branched C ₆ H ₁₄	0.15	0.20	*	0.84
n-C ₆ H ₁₄	0.06	0.13	*	0.30

*; not determined

**; results obtained with the use of a tungsten tip.

Table 6 : Product distributions for the reaction of propene with field generated tritium and with recoil tritium.

As shown in Table 6, the product distribution observed from propene reactions with field generated tritium was similar to those observed for propene reactions with recoil tritium atoms. Substitution of T for H which gave labelled parent product, C_3H_5T , was found to be the most important reaction. Next in importance was the substitution of T for CH_3 which produced CH_2CHT .

Differently from recoil tritium reaction results, fairly large amounts of branched C_6H_{14} (~ 0.84) and $n-C_6H_{14}$ (~ 0.30) were produced for the reaction of propene with field generated hydrogen. These products, branched C_6H_{14} and $n-C_6H_{14}$, could be products of reactions of intermediates from the primary reactions.

Propane and butane reactions

Table 7 gives a comparison of the results of the reactions of propane with field generated hydrogen and those from recoil tritium. Table 8 gives a comparison of the results of the reactions of butane with field generated hydrogen with both those of recoil tritium and those of hydrogen beams.

With the saturated hydrocarbons propane and butane, there are large differences between product distributions from this study and those from recoil tritium or tritium beams.

As explained before, recoil tritium reacts principally by substitution of T for H and abstraction of H. The latter reaction could not be studied using the methods which were employed here in the system.

With field generated tritium, there occurred a large amount of substitution of T for CH_3 . In propane reactions, the ethane to propane ratio was 1.22:1 and in butane reactions, the propane to butane and ethane to butane ratios were 1.05:1 and 1.30:1, respectively.

method product	recoil tritium		** FI
	(29)	(28)	
HT	2.87	1.85	*
CH ₃ T	0.14	0.1	0
C-C	0.09	0.04	1.22
C=C	0.06	0.07	2.99
C-C-C	1.00	1.00	1.00
C-C=C	*	*	3.65
branched C ₆	*	*	3.16

* ; not determined

** ; results obtained with the use of a tungsten tip

Table 7 : Product distributions for the reaction of propane with field generated hydrogen and with recoil tritium.

method product	recoil tritium	tritium beam	** FI
	(28)	(22)	
HT	1.80	*	*
CH ₃ T	0.07	*	0
C-C	0.04	*	1.30
C=C	0.06	0.04	2.68
C-C-C	0.03	0.09	1.05
C-C-C-C	1.00	1.00	1.00
C-C=C	0.01	*	2.48
branched C ₆	*	*	3.63

* ; not determined

** ; results obtained with the use of a tungsten tip

Table 8 : Product distributions of butane reactions with field generated tritium, with recoil tritium and with tritium beams.

Also some attention should be paid to the fact that products which have a double bond, like ethene and propene are in larger yield than labelled parent compounds, and there are quite a lot of branched C_6 products and $n-C_6H_{14}$ products which result from reactions of the primary reaction products such as reactive free radicals.

Had we stopped the experiments with propene, a plausible mechanism involving mostly abstraction of H, substitution of T for H and substitution of T for CH_3 could have seemed in order. So we could have concluded that our system is similar to the recoil tritium or beam method and that the reaction mechanisms which have been developed for hot hydrogen and the discussion about the charge state of the hot hydrogen when it reacts with hydrocarbon could be applied to interpret our results.

But product distributions obtained from reactions of propane and butane with field generated tritium were remarkably different from those with recoil tritium or hydrogen beams. So several possible conditional differences between recoil tritium or beam method and our system will be discussed here.

Effects of the presence of ions: charge build-up on the hydrocarbon film and ion-molecule reactions.

Wolfgang and Menzinger (21) concluded that tritium ions striking the target of solid hydrocarbon built up a positive charge which first decelerated the beam and then repelled it entirely. To prevent this, Wolfgang and Menzinger (21) designed their system so that the target was continuously sprayed with low energy electrons from a flashlight filament 1.2 cm from the target.

My system was not constructed so that the target would be sprayed

simultaneously with ions and electrons. If charge build-up occurred in my system, then positive charges accumulated on the surface and caused a deceleration of the oncoming hydrogen ion species. However, the current measurement during the reaction was fairly constant, and a charge build-up was not indicated even though there was a lack of consistency between the current and the yield of the products. I cannot be definite on the extent to which charge build-up affected the results of my study.

In contrast with the recoil and beam methods, there may have occurred some ion-molecule reactions due to the presence of ions in the films.

Fraction of field ionized tritium ions involved in the reaction

A major difference between my work and either the tritium beam or the tritium recoil method appears to be the presence of field generated, reactive, neutral tritium species.

Table 5 shows that the number of tritium ions produced by field ionization at the tip or at the wire was much smaller than the number of tritium atoms involved in the reactions. This implies, surprisingly, that reactive species other than hydrogen ions are being produced by the applied electric field to a tip or a wire. These species are most likely hydrogen atoms. When there are a lot of hydrogen atoms produced besides hydrogen ions, the detectable current is very small but the product yield is very high.

With a thin wire, this atomization phenomenon by the applied electric field is very remarkable as is shown in Table 5. The number of tritium atoms in the products was 10^3 to 10^4 times the number of tritium

ions associated with the reaction. In Figure 15, the reaction of propene with tritium gave mainly propane and propene, but not 2, 3-dimethylbutane which is one of the characteristic products of the reaction of thermal tritium atoms with propene. The latter results from the combination of isopropyl radicals. The distribution of products gives indication that the species react for the most part before they become thermalized to the temperature of the target.

From this production of reactive but non-ionic hydrogen by the applied electric field, the inconsistency between the current and the product yields could be explained well enough even though it is not known yet how much hydrogen is atomized or is ionized.

The lack of an effect of charge build-up in my work could be a little bit explained by the reactions of species other than ions. Only a part of the reactive hydrogen existed as ions.

Summary

Reactive tritium was produced from HT and T₂ gas at tips and wires where there were large electric fields. The primary product for the reaction of propene with this field generated tritium was from the substitution of T for H. Next in importance was substitution of T for CH₃. But the principal types of reactions for propane and butane were substitution of T for CH₃ and substitution of T for C₂H₅ rather than substitution of T for H. The occurrence of secondary reactions was indicated by the presence of unsaturated compounds and compounds containing more carbon atoms than the reactant hydrocarbon.

The yield of tritium labelled products was much larger than the number of ions produced by electric field. Reactive neutral species

were generated in tritium gas by large electric field at tips and wires.

Positive ions in the films of hydrocarbons might be involved in ion-molecule reactions.

ACKNOWLEDGEMENTS

The author wishes her appreciation to Dr. H. C. Moser for his guidance, encouragement and helpful suggestions during the course of research.

The author thanks Kansas State University for the provision of funds which made the research possible.

LITERATURE CITED

1. H.D. Beckey, Z. Analyt. Chem., 197, 80 (1963)
2. M.G. Inghram and R. Gomer, Z. Naturforsch., 10a, 863 (1955)
3. F. Kirchner, Naturwissenschaften, 41, 136 (1954)
4. E.W. Muller and K. Bahadur, Phys. Rev., 102, 624 (1956)
5. M.G. Inghram and R. Gomer, J. Am. Chem. Soc., 22, 1279 (1954)
6. A.M. Falick, P.J. Derrick and A.L. Burlingame,
Int. J. Mass Spectrom. Ion. Phys., 12, 101 (1973)
7. B.W. Viney, Int. J. Mass Spectrom. Ion. Phys., 8, 417 (1973)
8. E.K.C. Lee and F.S. Rowland, J. Inorg. Nucl. Chem., 25, 133 (1963)
9. E.W. Muller, Z. Phys., 131, 136 (1951)
10. H.D. Beckey, H. Hey, K. Kevsen and G. Tenschert,
Int. J. Mass Spectrom. Ion. Phys., 2, 101 (1969)
11. E.M. Chait and F.G. Kitson, Org. Mass Spectrom., 3, 533 (1970)
12. E.W. Muller, J. Appl. Phys., 27, 474 (1956)
13. P.J. Derric, A.M. Falic and A.L. Burlingame,
Int. J. Mass Spectrom. Ion. Phys., 12, 101 (1973)
14. P.J. Derric, A.M. Falic and A.L. Burlingame,
J. Am. Chem. Soc., 94, 6794 (1972)
15. P.J. Derric, A.M. Falic and A.L. Burlingame,
J. Am. Chem. Soc., 95, 437 (1973)
16. H.D. Beckey, "Field Ionization in Mass Spectrometry", 1st. Ed.,
Pergamon Press, New York, 1971, p. 89.
17. E.W. Muller, "Advances in Electronics and Electron Physocs,"
vol. 13, Academic Press, New York, 1960, p. 83.
18. A.J.B. Robertson and B.W. Viney, J. Chem. Soc., A, 1843 (1966)

19. H.D. Beckey, Z. Instrkde., 71, 51 (1963)
20. W.L. Fitz and S. Datz, Ann. Rev. Phys. Chem., 14, 61 (1963)
21. M. Menzinger and R. Wolfgang, J. Chem. Phys., 50, 2991 (1969)
22. A.J. Yencha, M. Menzinger and R. Wolfgang, J. Chem. Phys., 58, 1741 (1973)
23. G. Lagardea and J.M. Paulus, Radiochem. Radioanal. Letters, 19, 315 (1974)
24. H.A. Schwartz, R.R. Williams and W.H. Hamill, J. Am. Chem. Soc., 74, 6007 (1952)
25. J. Dubrin, J. Am. Chem. Soc., 47, 1867 (1967)
26. R. Wolfgang, "Progress in Reaction Kinetics," vol. 3, Pergamon Press, New York, 1965, p. 99.
27. D.C. Fee and S.S. Markowitz, Radiochim. Acta, 22, 91 (1975)
28. D. Urch and R. Wolfgang, J. Am. Chem. Soc., 83, 2982 (1961)
29. J.K. Lee, B. Musgrave and F.S. Rowland, J. Am. Chem. Soc., 82, 3545 (1960)
30. H.M. Chang and R. Wolfgang, J. Phys. Chem., 75, 3042 (1971)
31. M. Menzinger and R. Wolfgang, J. Phys. Chem., 72, 1789 (1968)
32. T.C. Clements and E.W. Muller, J. Chem. Phys., 37, 2684 (1962)
33. K.I. Mahan and J.K. Garland, J. Phys. Chem., 75, 1031 (1971)
34. Rosenberg and R. Wolfgang, J. Chem. Phys., 41, 2159 (1964)
35. M. Karplus, R.N. Porter and R.D. Sharma, J. Chem. Phys., 40, 2033 (1964)
36. R. Cipolloni and G. Stocklin, Radiochim. Acta, 9, 105 (1968)
37. D.S. Urch, Radiochim. Acta, 18, 176 (1972)
38. A.J. Johnson and D.S. Urch, Trans. Faraday Soc., 69, 1186 (1973)
39. Watkins, Ph.D. thesis, Kansas State University, Manhattan, KS., 1965

40. K. Nilblaeus, B.D. Roos and P.E.M. Siegbahn, Chem. Phys., 26, 59 (1977)
41. G. Izawa, E.K.C. Lee and F.S. Rowland, J. Phys. Chem., 77, 1210 (1973)
42. Y.Y. Su and Y.N. Tang, J. Phys. Chem., 78, 2531 (1974)
43. D.J. Malcome-Lawes, Radiochim. Acta, 19, 113 (1973)
44. D. Urch and R. Wolfgang, "Chemical Effects of Nuclear Transformations," vol. 2, IAEA, Vienna, 1961, p. 99

REACTIONS OF SOLID HYDROCARBONS WITH HOT HYDROGEN
PRODUCED BY ELECTRIC FIELDS

by

MYUNGSOOK RHEE

B.S., SOGANG UNIVERSITY, 1973

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the
requirement for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1978

ABSTRACT

Reactive hydrogen species were produced from gaseous HT and T₂ by applying a positive voltage (10-12 kV) to a tungsten tip of 5000 Å radius or a tungsten wire. The reactive hydrogen species were thought to be a mixture of ions (HT⁺, H⁺, T₂⁺ and T⁺) and hydrogen atoms (T and H). The field generated species were reacted with films of hydrocarbons of about 10⁻⁷ mol/cm² at 77 K. Tritium was used as a tracer for hydrogen, and reaction products were analyzed by radio-gas-chromatography. Because of the extreme sensitivity of this method, only a few minutes of reaction time was required to generate sufficient products for analysis. Reactions were normally carried out for five minutes at ion currents of 10⁻⁹ A to 10⁻¹¹ A.

The main tritium labelled products from reactions with propene were propene which results from the substitution of T for H and ethene which results from the substitution of T for CH₃. Besides these main products, a fairly large amount of C₆ products were detected. The presence of C₆ products implies the occurrence of consecutive reactions of intermediates from primary reactions. The product distribution for propene reaction was similar to that observed for propene reactions with hot recoil tritium.

For the reactions of the saturated hydrocarbons propane and butane, there occurred more substitution of T for CH₃ and for C₂H₅ than substitution of T for H. This result differs from those for the hot recoil tritium reactions. Besides the previously mentioned products, there were large amounts of propene and ethene and some C₆ products which also imply the occurrence of the consecutive reactions.