

REACTIONS OF SPECIES EMANATING FROM A LOW-PRESSURE  
HYDROGEN DISCHARGE WITH SOLID PROPENE

by *1264*

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## I. INTRODUCTION

Hot atom chemistry is a field of endeavor involving reactions of energetic atomic species with various molecules. The energetic atomic species possess a kinetic energy in excess of the activation energy of ordinary thermal reactions. Isotopes of hydrogen are most often used as the energetic atomic species. Only in recent years have methods been developed for producing hot species in the so called "chemical" energy range, which is from about one to twenty electron-volts. For example, reactions of hot hydrogen atoms from nuclear recoil or photo-decomposition have been studied extensively. A thermal reaction can be characterized by the threshold process which usually has a single reaction path and occurs at the lowest activation energy. Hot reactions, on the otherhand, are characterized by multiple reaction paths leading to many products at successively higher activation energies.<sup>1,2</sup>

Interest was focused in the present study on the investigation of energetic species emanating from an electrical discharge in hydrogen at very low pressure. Specifically this thesis deals with their chemical reactions with solid propene films at 77°K. The discharge system was designed so that the discharge could be initiated in hydrogen at a pressure as low as  $10^{-3}$  torr. Energetically active species produced in this range of pressure had a collision-free path before reaching the propene film. Tritium gas was utilized as a tracer so that the products could be analyzed

by the radio-gas chromatography technique. Solid propene at liquid nitrogen temperature was chosen as the reactant because of its well characterized chemistry with hydrogen atoms. Both hot and thermal hydrogen atom reactions with propene have been studied in this laboratory and elsewhere.<sup>3,4,5</sup> The magnitude of various product yields has been found to be dependent on the energy of the hydrogen atom. Therefore, by comparison of the yields in this study with previous results, it was thought possible to decipher the characteristics of the species produced by the gaseous discharge.

The primary reaction of a low energy hydrogen atom with the solid propene is addition to the double bond. The addition of the hydrogen atom to the less substituted carbon atom of the double bond requires the lowest activation energy. Thus, the addition reaction with propene results in the formation of an *i*-propyl radical. At the low temperature of the film, the radical so formed can undergo only reactions having a low activation energy. These reactions are considered as alkyl-alkyl radical disproportionation and combination, and hydrogen atom-alkyl radical abstraction and addition reactions. These thermal reactions thus result in the final products of propene, propane and 2,3-dimethylbutane. However, for a higher energy hydrogen atom, the limitation requiring the reactions to have a low activation energy is removed. Therefore, many other reactions of higher activation energy become possible which result in a variety of products. For kinetically energetic hydrogen atoms emanating from the

discharge, additional primary and secondary processes can be proposed. The most probable primary processes for energetic hydrogen atoms are the direct displacement reaction and the formation of other radical intermediates. The substituted parent molecule can be obtained from the direct displacement reaction which plays a major role in gaseous hot hydrogen reactions. The addition of the hydrogen atom to the more substituted carbon atom of the propene double bond results in the formation of a n-propyl radical, whereas the abstraction of a terminal hydrogen from propene results in the formation of an allyl radical. The radicals formed from the energetic hydrogen atom reactions might possess excess energy themselves and undergo various fates to become stable products.

## II. LITERATURE REVIEW

The literature review is focused on three areas : the formation of hydrogen atoms by electron impact in a discharge system, the general chemical effects of "hot" hydrogen atoms, and the reaction of hydrogen atoms with propene.

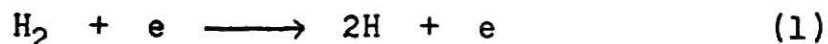
### A. Formation of Hydrogen Atoms by Electron Impact in a Discharge System

Continuous discharges result primarily from the acceleration and subsequent multiplication of electrons in gases. As an electron is accelerated to an energy exceeding the ionization potential of the gas, the process of an ionizing collision becomes increasingly probable. When separation of charge by ionization occurs, an additional free electron is created which may also be accelerated, and it in turn leads to more new ions.<sup>6</sup> While the steady state discharge is sustained through the processes of electron acceleration, multiplication, and collection, the electrons may also lose energy through other types of inelastic collisions such as excitation.<sup>7,8</sup>

The probability of observing a particular electron impact process depends in a critical manner on the electron energy. Under discharge conditions, however, very little is known regarding average impact energies. The purpose here is to show various primary and secondary processes which may ultimately lead to energetic hydrogen atoms. The electron impact processes which

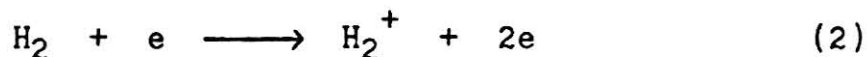
hydrogen molecules are known to undergo fall under four categories, 1) dissociation, 2) dissociative attachment, 3) ionization and 4) dissociative ionization. Processes under categories 2) and 4) occur with only very low comparative probability at all electron energies and further discussion of them is therefore deleted.<sup>9,10,11,12</sup>

The dissociation process (1) takes place principally by electronic excitation to the repulsive triplet state,  $1\ ^1\Sigma_g^+ \rightarrow 1\ ^3\Sigma_u^+$ . The onset electron energy for the dissociation process was experimentally found to be about 11.5 eV.<sup>7,13</sup>

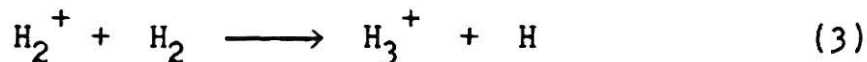


Because the transition is from an attractive to a repulsive state and because the Franck-Condon principle is obeyed, the resulting hydrogen atoms each possess a kinetic energy in the range of 2.2 - 5.2 eV with a most probable energy of 3.7 eV.<sup>14,15</sup> The cross section for the transition attains a maximum value of  $6\ \text{\AA}^2$  just above threshold and then slowly falls off.<sup>7,13,16,17,18</sup>

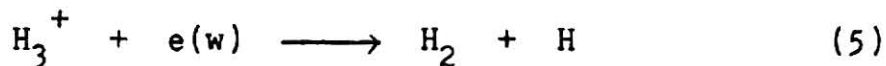
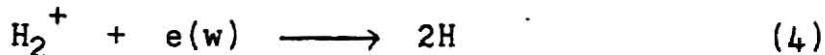
Another possible source of hydrogen atoms in this discharge could result indirectly from ionization. The reactions between atomic and molecular ions with the propene surface are thought to be negligible because of the geometry of the reaction cell which should confine the ions to the region of the discharge. The process (2) proceeds with a maximum cross section of  $1.1\ \text{\AA}^2$  at 70 eV.<sup>10</sup>



The molecular ion from (2) may in turn be lost through the probable ion molecule reaction (3).



The cross section for reaction (3) is  $27.4 \text{ \AA}^2$  at thermal reactant energies and it lessens somewhat as the collision partners increase in mutual kinetic energy.<sup>19</sup> Undoubtedly, however, the reactant ion in (3) does possess considerable kinetic energy (acquired from the electrical field of the discharge) and thus products in (3) may also be kinetically hot. Reaction (3) should therefore be considered a feasible source of active hydrogen atoms. In addition, the surface neutralization of kinetically hot molecular ions formed in processes (2) and (3) could also result in hot hydrogen atoms. These processes are shown in following equations (4), (5) and (5a).



There are no reports of surface neutralization processes in the literature, however.

## B. Chemical Effects of "hot" Hydrogen Atoms

Chemical effects of "hot" hydrogen atoms, especially of recoil tritium, have been investigated and reported in many recent reviews.<sup>1,2,20,21,22,23</sup> "Hot" atoms are characterized by their high translational energy and the reactions of hot atoms occur above the threshold or activation energy of the molecules. A hypothetical energy dependence of collision efficiencies is shown in Fig. 1. In "thermal" or "quasi-equilibrium" systems, only the threshold reaction path leading to HT would be significant. Conversely, a hot atom of given energy  $E'$  will react by all the indicated paths.<sup>1</sup>

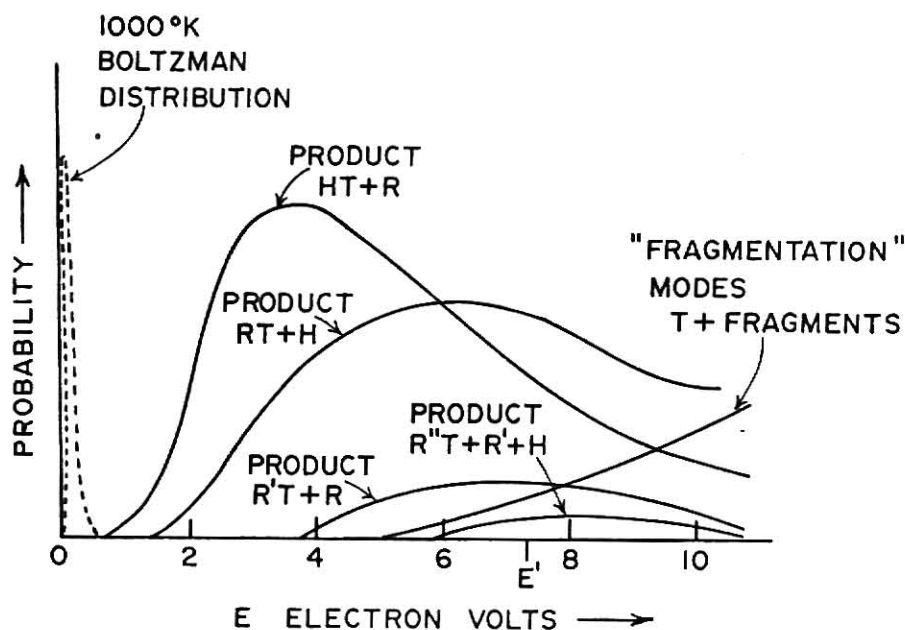


Fig. 1. Hypothetical collision yield dependence on kinetic energy for reaction of atomic hydrogen (T) with arbitrary compound RH. Excitation functions for reaction paths leading to various possible products are given. (a)

(a) From Ref. 1.

Hot hydrogen atoms can be produced by beam, photochemical, electrical discharge, and nuclear recoil techniques. The great majority of hot hydrogen atom studies have been made using recoiling tritium atoms from the  $\text{He}^3 (n,p) \text{T}^3$  process.<sup>24,25,26,27</sup>

The transformed nuclei are generally produced as positive ions of high energy up to  $10^5$  eV. These energetic ions, however, lose their energy in successive collisions with the medium and become neutralized long before they reach the "chemical" energy range ( $<100$  eV). In further collisions these hot species may react in the energy region for chemical bond formation (2-10 eV). Some may reach thermal energies and react as thermal atoms. A comparison of intrinsic properties of thermal and hot reactions is given in Table I.

Table 1. Comparison of Intrinsic Properties of Thermal vs. Hot Reactions.(a)

| Property                                | Thermal or Threshold    | Hot                    | Experimental Criterion                                     |
|-----------------------------------------|-------------------------|------------------------|------------------------------------------------------------|
| 1. Multiplicity of reaction paths       | generally only one path | usually multiple paths | nature of products                                         |
| 2. Collision efficiency                 | low                     | high                   | scavenger effects                                          |
| 3. Temperature dependence               | yes                     | very slight            | temperature dependence of competitive reactions in mixture |
| 4. Effect of chemically inert additions | no                      | yes                    | moderator effects                                          |

(a) From Ref. 1.

The most interesting hot atom reactions are those of hydrogen with hydrocarbons. The following mechanistic classifications have been suggested for hot tritium atoms with hydrocarbons :

- I. Hydrogen atom abstraction.
- II. Hydrogen atom displacement to form the labeled parent molecule.
- III. Hydrogen atom displacement of an alkyl group to form degraded alkane or alkene.
- IV. Radical formation.

In order to understand these reaction mechanisms further, two idealized and hence extreme models of momentum and energy transfer in hot atom collisions have been proposed. The first is the quasi-elastic atom-atom or "billiard-ball" collision model for high energies ( $> 10$ - $20$  eV). The other is the inelastic atom-molecule or "epithermal" collision model for lower energies ( $< 10$  eV). For the lowest energy mode (usually abstraction in the range of 1-2 eV) a "stripping" process has been proposed also.<sup>1,2</sup> A model also has been developed applying the kinetic theory in the explanation of the energetic aspects of hot hydrogen atoms.<sup>1,2,27</sup>

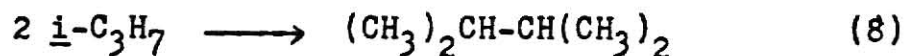
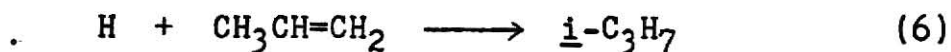
### C. Reactions of Hydrogen with Propene

Hydrogen atom reactions with propene both in the gas and condensed phases have been investigated. Here a comparative review of thermal and hot reactions of hydrogen with propene is made. The mechanistic aspects of radical-radical and radical-

hydrogen atom reactions are considered also.

### Radical-Radical Reactions

For a thermal hydrogen atom, the most probable primary reaction with propene has been thought to be addition to a terminal carbon of the propene double bond to form an i-propyl radical. This process, shown in reaction (6), requires the lowest energy and is favored by the steric effect. The heat of addition of hydrogen to propene is exothermic by about 43.5 Kcal/mole. The radical so formed with this energy further reacts via radical-radical reactions such as disproportionation and combination processes. These processes are shown in reactions (7) and (8), respectively.



Temperature, pressure and presence of moderator all affect the efficiency of these secondary processes. The activation energy difference between the recombination and disproportionation reactions is considered to be almost zero in the gas phase, but may be significant in the solid phase. The ratio of the rate constants for the two processes,  $k_d/k_c$ , for i-propyl radicals can

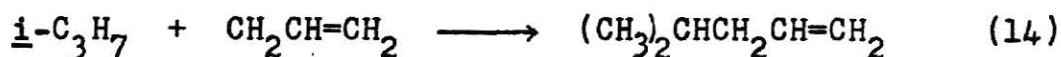
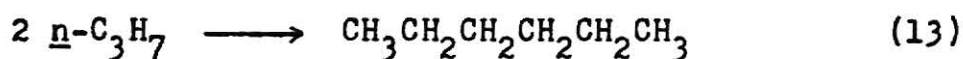
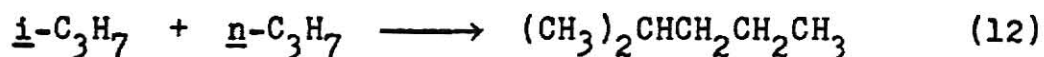
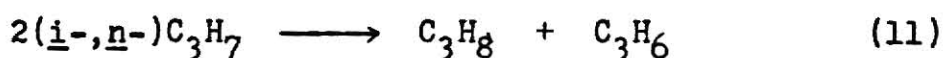
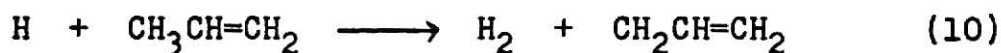
be expressed also as the  $C_3/C_6$  (2,3-dimethylbutane) ratio. Some  $C_3/C_6$  ratios for i-propyl radicals are compared in Table II.

Table II. Ratios of  $k_d/k_c$  ( $C_3/C_6$ ) for i-propyl radicals.

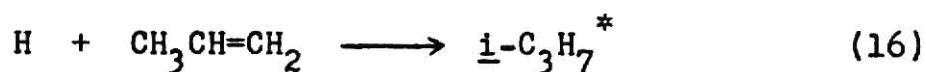
| <u>Gas Phase</u>       |           | <u>Condensed Phase</u> |                                                       |           |
|------------------------|-----------|------------------------|-------------------------------------------------------|-----------|
| $C_3$ (Propane)/ $C_6$ | Reference | $C_3/C_6$              | $\underline{E_c}^\ddagger - \underline{E_d}^\ddagger$ | Reference |
| 0.41 at 298°K          | 28        | 5.5 at 77°K            | 450 cal/mole                                          | 32        |
| 0.63 at 298°K          | 29        |                        |                                                       |           |
| 0.64 at 373°K          | 30        | 9.0 at 77°K            | 260                                                   | 33,34     |
| 1.5 at 383°K           | 31        |                        |                                                       |           |

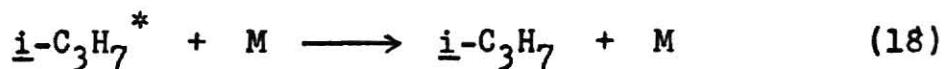
As the energy of the hydrogen atoms is increased, other primary and secondary processes are possible. Bradley, Melville and Robb reported evidence for the presence of i- and n-propyl radicals in 2-body gas phase interactions of mercury-photosensitized  $H_2$  with propene.<sup>35</sup> The possibility of allyl radical formation was also suggested. Reactions (9) and (10) show the formation of n-propyl and allyl radicals, respectively. The small yield (7.5%) of n-propyl radicals was explained by the activation energy difference of 1.5 Kcal between the formation of the i- and n-propyl radicals. Moore, who did not observe the n-propyl radical, gave a value of 2.4 Kcal/mole at 100°C for the activation energy difference.<sup>31</sup> The formation of n-propyl and allyl radicals

would introduce additional products, which are shown in reactions (11) - (15).

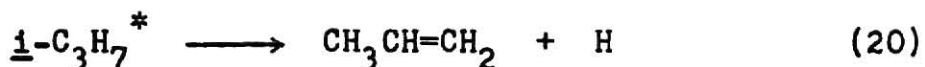
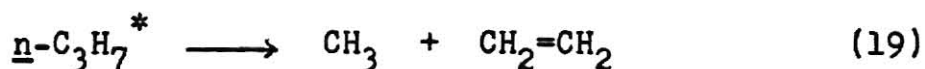


In a similar manner, Boddy and Robb inferred the presence of allyl, ethyl and methyl radicals in addition to the i-propyl radical.<sup>36</sup> The i-propyl radical was considered to be "hot" rather than in thermal equilibrium and to generate methyl radicals directly and ethyl radicals indirectly. The basic scheme of this behavior is shown in reactions (16) - (18). The hot or vibrationally excited states are noted with an asterisk.





From a further study on the vibrationally excited n- and i-propyl radicals at 25°C, Falconer, Rabinovitch and Cvetanovic proposed the unimolecular decomposition of these radicals as shown in reactions (19) and (20).<sup>37</sup>



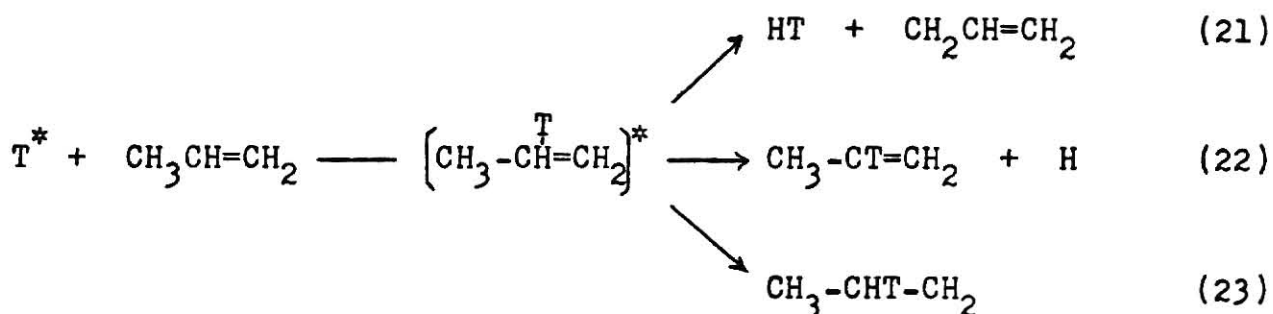
The decomposition of n-propyl radical was mainly by C-C rupture, whereas C-H rupture was the predominant path for i-propyl radical decomposition. Since reaction (17) requires the migration of a hydrogen atom, the preference of reaction (20) can be explained. "If the activation energy for the rearrangement of i-propyl radical and subsequent (or simultaneous) C-C bond split is as much as 3.5 Kcal/mole greater than that required for C-C split in n-propyl radicals, then the energy barrier for C-C rupture will be similar to that for C-H rupture. Lower entropy requirements, moreover, favor C-H splitting."<sup>37</sup> These decomposition processes are well known in recoil tritium atom reactions in both gas and condensed phases.<sup>38,39</sup>

The reactions of thermal hydrogen atoms with propene in the

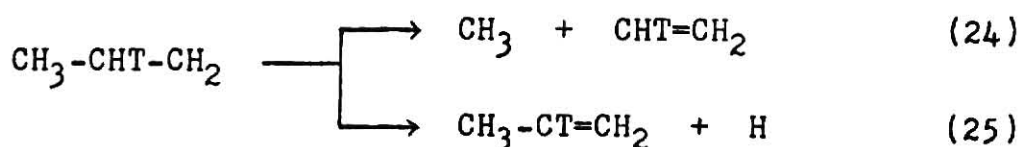
gas phase have rate constants for hydrogen addition to propene in order of magnitudes  $10^{11} - 10^{12}$  cc/mole/sec, whereas in the condensed phase the rate constants are the order of  $10^7$  cc/mole/sec.<sup>35-42</sup> Diffusion processes were thought to be the rate controlling factor for the latter case.<sup>33,34,42</sup> Klein and scheer obtained a value of 9 for  $C_3H_8/C_6$  ratio which is compared with other values in Table II.<sup>33</sup> The value was constant for a wide range of hydrogen and propene concentrations. This high ratio was explained by "the existence of excess energy in the radical since the addition of a hydrogen atom to propene was exothermic to the extent 43.5 Kcal/mole and as an indication that disproportionation was favored over dimerization for "hot" radicals at low pressure."<sup>33</sup> Additional evidence of energetic atom reactions in the solid phase was indicated by Yun and Moser.<sup>32,43</sup> The reactions of tritium atoms produced at a hot tungsten filament with solid propene film at 77°K were characterized by the formation of i- and n-propyl and allyl radicals. In addition to the disproportionation and combination reactions of all these radicals, "cracking" reactions of excited propane were thought possible. When helium was added, energetic reactions were significantly reduced and the only reactions were those of i-propyl radicals. Watkins and Moser also found this behavior for moderated T reactions with solid propene-d<sub>6</sub> at 63°K. For this thermal condition, the  $k_d/k_c$  ratio of 5.5 in Table II was obtained.<sup>44</sup>

Above all other methods, the recoil tritium reactions with propene have shown the most significant aspect of "hot" atom

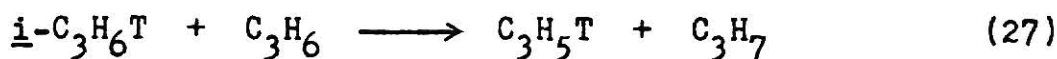
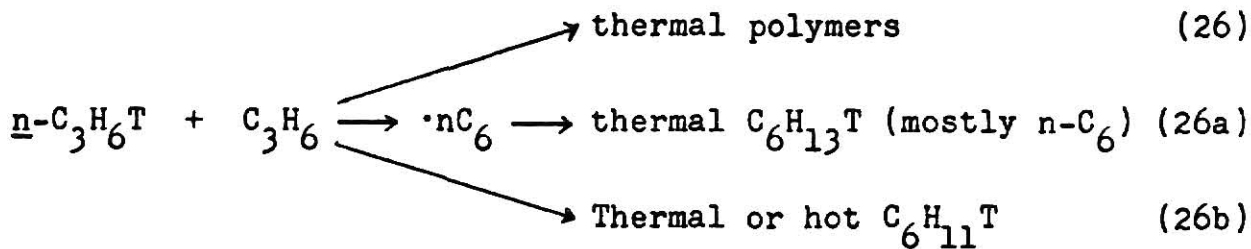
reactions. Lee, Musgrave and Rowland observed tritiated propene and HT as major products and also noteworthy amounts of ethylene, propane and some saturated dimers in the reactions with gaseous propene.<sup>45</sup> These products were explained by abstraction, direct displacement and "hot-radical" formation primary processes.



Chemically stable radioactive products (HT and  $\text{CH}_3\text{CT}=\text{CH}_2$ ) were formed in "hot" reactions of (21) and (22) by abstraction of hydrogen and direct displacement processes, respectively. Relatively high yields of tritiated free radicals were shown as "hot" products in reaction (23). Since the "hot" tritium atoms attacked the two carbon positions of the propene double bond indiscriminately, approximately equal amounts of both possible "hot" radicals (i- and n-propyl) were formed. These radicals, "excited both by the kinetic energy of the tritium atom and by the exothermicity of the addition reaction", were thought to equilibrate this energy and to decompose to a stable molecule and a radical as in<sup>38,45</sup> reactions (24) and (25).



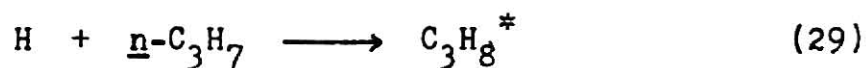
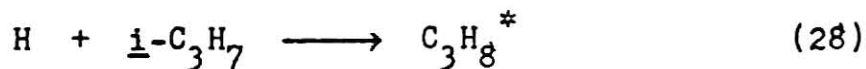
Other reaction pathways for these "hot radicals" from the recoil tritium reactions with liquid propene were also proposed by Mahan and Garland.<sup>39</sup> Proposed were reactions (26), (26a) and (26b) for n-propyl radicals and reaction (27) for i-propyl radicals.



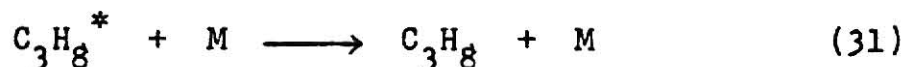
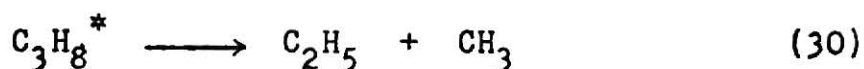
The radical-molecule disproportionation was considered to be more important for the i-propyl radicals while the radical-molecule combination was more important for the n-propyl radicals. It was proposed that "hydrogen detachment is the dominant hot radical-molecule reaction for the i-propyl radical while the hot addition, particularly to the end carbon atom of propene, predominates for the n-propyl radical."<sup>39</sup>

#### Propyl Radical-Hydrogen Atom Reactions

The reactions of hydrogen atoms with propyl radicals occur extensively in the gas phase. Reactions (28) and (29) are exothermic by about 94 and 99 Kcal/mole, respectively. With this exothermicity of the bond formation and the energy of the



hydrogen atom, excited propane are produced. This excited gas phase propane is known to "crack" into methyl and ethyl radicals with a high probability unless it is collisionally deactivated.<sup>46,47</sup> These processes are shown in reactions (30) and (31).

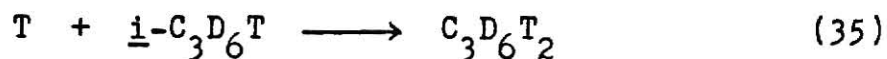
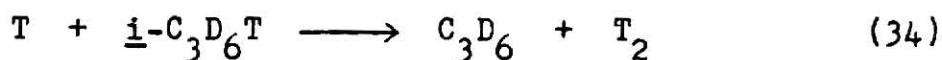
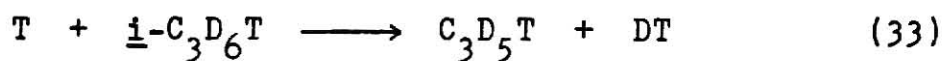
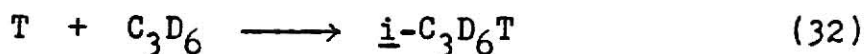


Heller and Gordon calculated a minimum for the half-life of this excited propane to be  $2 \times 10^{-6}$  sec.<sup>46</sup> This behavior of the propane was observed by Wijnen and Steacie at low and high pressure (50-100 Torr) region.<sup>47</sup>

For a condensed phase, the radical-hydrogen atom reaction was thought less significant. Klein and Scheer and Klein, Scheer and Kelley explained this condition from the point of the rate controlling diffusion process in the solid matrix.<sup>33,34</sup> The alkyl radicals, once formed on the surface, readily diffused a few molecular layers below the surface, and thus the possibility of those radicals to react with hydrogen atoms could be removed. However, for more active hydrogen, the greater possibility of hydrogen atom-propyl radical reactions was expected. The

formation of excited propane in the solid propene was proposed to account for the degraded alkane and alkene products observed by Yun and Moser.<sup>43</sup>

On the other hand, the reactions of moderated tritium atoms with propene-d<sub>6</sub> diluted with isopentane at 63°K showed evidence for a tritium atom-alkyl radical disproportionation reaction.<sup>44</sup> Watkins and Moser observed no i-propyl dimer (2,3-dimethylbutane) in the presence of isopentane.<sup>44</sup> Because of the small concentration of propene in the mixed film, it was concluded that i-propyl radicals were formed relatively far apart and were slow in diffusing. Under these conditions, the i-propyl radicals had a greater probability of encounter with T atoms than with other i-propyl radicals. The products were explained by reactions (32)-(35).



The observation of about equal amounts of DT and propene(T) was interpreted as evidence for the domination of the T atom-i-propyl radical disproportionation reaction as in (33). The hydrogen

atom-alkyl radical disproportionation and combination showed some similarities to alkyl-alkyl radical disproportionation and combination. Watkins and Moser determined disproportionation to combination ratios,  $k_d/k_c$ , for tritium atom reactions with  $\underline{i}\text{-C}_3\text{H}_6\text{T}$  and  $\underline{i}\text{-C}_3\text{D}_6\text{T}$  radicals at  $63^\circ\text{K}$  to be 3.55 and 3.05, respectively.<sup>44</sup> An activation energy difference of  $\underline{E_c} - \underline{E_d} = 0.43$  Kcal/mole was also estimated.

## EXPERIMENTAL METHODS

### Materials

The propene (C.P. Grade, Matheson Company) was purified by fractional, trap to trap distillation. Hydrogen flame gas chromatography showed a purity of 99.5%. Major hydrocarbon impurities were methane, ethane, ethylene and propane.

Tritium gas (New England Nuclear Corporation) was used as the discharge gas, and it also served as a tracer to determine products. Tritium was introduced to and stored in the vacuum system in a way which has been previously described.<sup>3,4,5</sup> The gas was introduced into the system by slow diffusion through a palladium thimble at  $\sim 200^{\circ}\text{C}$ . The "Carrier free tritium" was found to contain about 50% HT by gas chromatographic analysis.

Hydrogen gas (Airco, Research grade) was used to calibrate the Pirani gauge and also in some experiments to moderate the tritium atoms. It was released into the system by means of a high vacuum needle valve.

### Pressure Measurement

A Pirani vacuum gauge (TYPE GP-210, Consolidated Vacuum Co.) was used to measure the pressure of hydrogen and propene. This was calibrated daily against a McLeod gauge measurement of hydrogen pressure. In the calibration of the Pirani gauge, a liquid nitrogen trap was placed between the system and the McLeod gauge

before opening the stopcock to the system so that mercury vapor would not contaminate the system. The system was evacuated by a mercury diffusion pump to less than  $5 \times 10^{-5}$  Torr of pressure. Hydrogen gas was introduced into the evacuated, closed system, and the two readings on the gauges were compared and adjusted. The increase of tritium pressure when the thimble was heated was observed on the Pirani gauge, and the reading of pressure was checked and corrected by the McLeod gauge. The propene pressure was measured on only the Pirani gauge; absolute calibration was not made for this measurement.

### Discharge and Electrodes

A special interest in this investigation was to produce a stable glow discharge at low pressure ( $\sim 10^{-3}$  Torr). The final discharge system was constructed similar to that of a cold-cathode ionization manometer by Penning.<sup>6</sup> In this type of gauge, "electrons are ejected from a cold-cathode of tungsten and deflected by means of permanent magnetic field so that they travel in long, helical paths before reaching the tungsten anode. The total path length traversed by the electron from the cathode to the anode is much greater than the direct distance between the two electrodes. Consequently, the ionization produced per electron at any pressure is significantly greater in the magnetic field than in its absence".<sup>6</sup>

A Philips gauge (TYPE PHG-09) power supply was used as a

source to supply a maximum of 3,000 VDC between the electrodes. In this manner, a glow discharge was obtained at less than  $10^{-3}$  Torr hydrogen pressure. The internal discharge was initiated by a Tesla coil. At this discharge pressure the mean free path of any non-ionic active hydrogen species exceeded the electrode-propene film distance.

The final electrode design was arrived at after experimentation in both shape and construction material. Steel, molybdenum and tungsten electrodes were tried in various designs. The final electrodes were made of tungsten and the anode was partially looped through the cathode as shown in Fig. 2. The electrodes were gold soldered to four molybdenum leads which in turn were connected to the appropriate terminals of the Philips gauge power supply.

Another attempt was also made to obtain a glow discharge at low pressure. The device was a radio-frequency oscillator with a 600 VDC power supply. Copper, 4-turn coils were used as the oscillator and the receiver. A voltmeter was used to measure the peak voltage across the coils. The voltmeter also served as maximizing detector to tune the R.F. coupling from the oscillator circuit. Several shapes of copper electrodes were designed until the maximum discharge could be obtained at the lowest pressure in a magnetic field at 60 MHz across the electrodes. The distance between the electrodes was set at 3 cm so that the breakdown frequency could be avoided. None of the designs attempted, however, would produce a discharge in the  $10^{-3}$  Torr region and this discharge method was therefore abandoned.

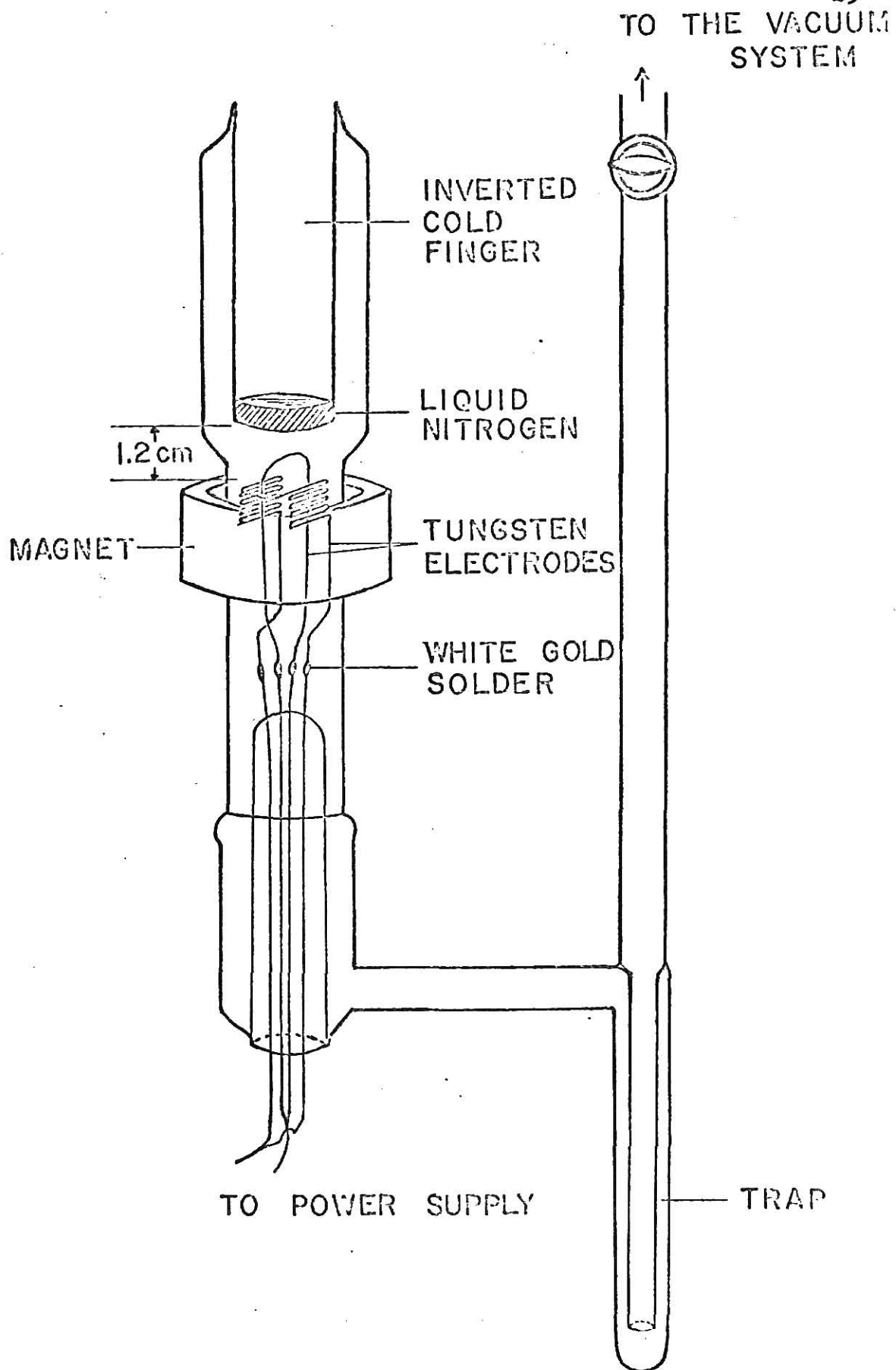


FIG. 2. DISCHARGE REACTION VESSEL

### Procedure for Reaction

Prior to the introduction of any materials into the system, both electrodes were heated to several hundred degrees and degassed. After cooling the leads were connected to the Philips gauge power supply and a preliminary discharge was initiated in  $10^{-3}$  Torr of hydrogen gas. A ring-shaped permanent magnet was positioned so that the discharge attained maximum intensity. After the magnet was properly positioned, the stopcock to the pump was opened and the gas was pumped out until the pressure read  $5 \times 10^{-5}$  Torr. The discharge was then terminated by switching the power supply to the off position. While the discharge could not be initiated below  $10^{-3}$  Torr, it was possible to sustain it to these much lower pressures after it was initiated.

Propene was introduced into the system by slowly warming a stored portion which had been immersed into liquid nitrogen. The stopcock separating the reaction vessel from the rest of the system was then closed so that a 150-cc volume of propene at  $5 \times 10^{-2}$  Torr could be retained. A small inverted cold finger at the upper side of the reaction vessel was half filled with liquid nitrogen in order to freeze propene on its inner surface. The system was then reevacuated to prepare for tritium introduction. Tritium was introduced slowly into the system by heating the palladium thimble. As soon as the Pirani gauge read the desired pressure, a stopcock to the tritium vessel was closed and the heating was discontinued. The tritium pressure was checked by a McLeod gauge. Again the reaction vessel was separated from the

rest of the system.

The power supply was switched on and the discharge was again externally initiated. A stopwatch was used for a measurement of the discharge time over the range 1-30 sec. The amount of liquid nitrogen in the inverted cold finger was maintained at the same small height in each run so that the surface area of 5 cm<sup>2</sup> and therefore the same propene thickness in a range of 500-600 Å was always achieved.

Frozen products were warmed up by heating the cold finger with a heat-gun and transferred into a sampler, whose two U-tubes were previously immersed in liquid nitrogen. In order to increase transfer efficiency, a small quantity of H<sub>2</sub> ( $\sim 10\mu$ ) was introduced in the vacuum system between the reaction vessel and sampler. The stopcocks to the reaction vessel and sampler were then opened and the non-condensable gases, HT, T<sub>2</sub> and methane, were trapped on the activated charcoal of the sampler at 77°K.

One of the U-tubes (I) of the sampler was used for collecting hydrocarbon products condensable at 77°K, and the other (II) containing charcoal was used to collect hydrogen isotopes and methane, also at liquid nitrogen temperatures. The charcoal was heated moderately by surrounding resistance wires beforehand to release any trapped substances.

### Analysis

After transferring the reaction products into the sampler

the liquid nitrogen was removed and charcoal in the U-tube (II) was heated. While it was heated, the stopcocks were opened to an effluent stream of the analyzing system. Helium gas (Air Products.) dried through an anhydrous  $\text{CaSO}_4$  (Hammond Drierite Co.) column was used as a carrier gas for the analysis. It carried the products in the U-tube (II) through a 6-foot, moderately activated alumina column in a liquid nitrogen containing Dewar flask to the gas chromatograph and the ion-chamber. The alumina column was used to separate HT and  $\text{T}_2$  at liquid nitrogen temperature and methane at room temperature. Methane was released from the column after the removal of the liquid nitrogen.

The remaining hydrocarbon products which had been collected in the U-tube (I) were separated by a 10-foot column of 40% silver nitrate in ethylene glycol on chromosorb P (mainly for  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_4$  compounds) in series with a 25-foot column of 15% isoquinoline on chromosorb P (for  $\text{C}_5$  and  $\text{C}_6$  compounds). The latter two tandem columns were placed in a chromatograph oven (Vapor Phase Analyzer, Central Scientific Co.). All analyses were carried out at room temperature, and the products were identified by the retention times of known compounds through the chromatograph.

After the separation of the products, the tritium activity of the radioactive products was measured by an ion-chamber (Cary 5010, Applied Physics Corp.) which was connected to the flow system of the chromatograph. The signals were rectified and amplified by a vibrating reed electrometer (Cary Model 31, Applied

Physics Corp.) and recorded on a graphic recorder (Model G-14, Varian Associates) with an integrator.

In order to prevent overlap of peaks, the volume of the ionization chamber was kept small ( $\sim 30$  cc), and nitrogen was added as a purging gas to the effluent stream at  $\sim 80$  cc/min. Calibration of the ion-chamber was possible by measuring the peak areas of standard samples. With this technique, as little as  $10^{12}$  product molecules could be detected, and the number of micro-curies (C) of each tritiated product was calculated as,

$$C = (5 \times 10^{-3} \mu C) \left( \frac{\text{electrometer range}}{\text{in volts}} \right) (\text{integrator counts}).$$

The whole analysis required 2 to 2.5 hours. The diagram of the reaction and analyzing system is shown in Fig. 3.

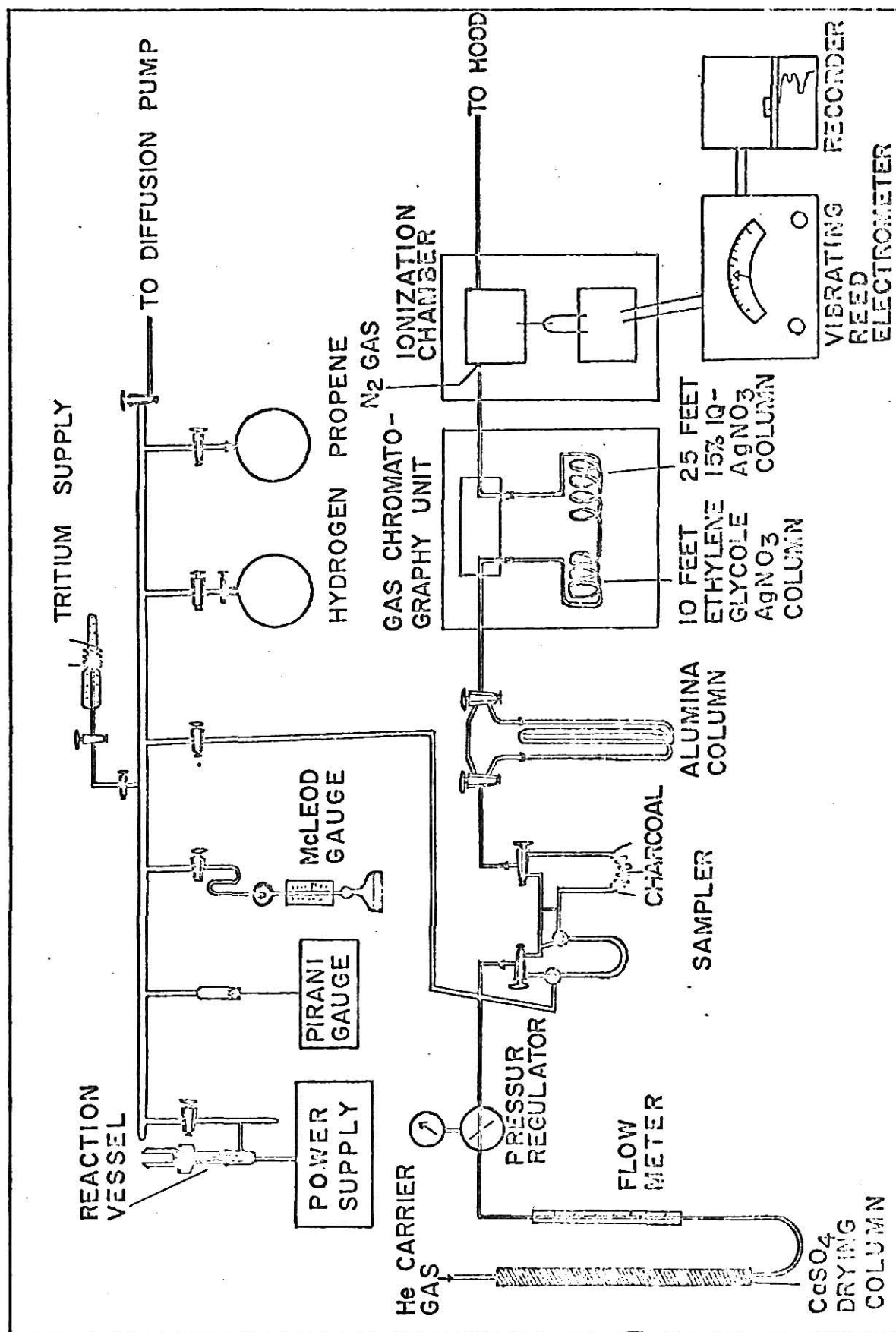


FIG. 3. REACTION AND ANALYZING SYSTEM

#### IV. EXPERIMENTAL RESULTS

The product distributions of gas-solid reactions of hydrogen with propene at 77°K are given in percentages as a function of discharge time in Tables III - VI. As storage time increased for the T<sub>2</sub> supply, the purity of the carrier free tritium gas appeared to be changed by the exchanging of T with most probably water to form HT. Thus 0.5-1 x 10<sup>-3</sup> Torr of tritium gas used for reactions of Tables III, IV and V was found to have HT/T<sub>2</sub> ratio of approximately 1, 1.5 and 2.0, respectively. Most values in these tables were obtained from the average of 2 or 3 runs. The distribution of products with addition of moderator H<sub>2</sub> is shown in Table VI and also partly in Table III.

For the blank runs, frozen propene was warmed up and evacuated from the reaction vessel before tritium was introduced. The blank runs showed that less than 0.5% of the yields for propene and propane were from the gas phase reactions of absorbed propene at the electrodes. On the other hand, 80-90% of the yields for methane, ethane, ethylene, i- and n-butane, and some C<sub>5</sub>'s were from gas phase electrode effects. Thus those compounds were excluded from the distribution of products of the gas-solid reaction scheme. HT was also not included because of the large initial amount compared to the final hydrocarbon yields.

By freezing propene in the trap located in the reaction vessel instead of above the discharge area, the effect of distance was tested. At this greater distance between the electrodes

and the frozen propene film, the tritiated propene and propane yields were only 20% of those observed at the ordinary distance. Also the only  $C_6$  compound in measurable amounts was 2,3-dimethylbutane. These yields are characteristic of thermal reactions.

In Tables VII - X, the ratios of certain products from reactions of Tables III - VI, respectively, are shown.

Table III. Product distributions of tritium atom reactions with propene at 77°K. <sup>(a), (b)</sup>

| (c), (d)<br>Tritiated<br>Reaction<br>Products | Discharge Time (sec.)    |      |      |      |      |      |      | (e)  |
|-----------------------------------------------|--------------------------|------|------|------|------|------|------|------|
|                                               | 3                        | 5    | 8    | 10   | 15   | 20   | 30   |      |
|                                               | Tritium Distribution (%) |      |      |      |      |      |      |      |
| C-C-C                                         | 26.6                     | 27.0 | 28.9 | 29.5 | 27.1 | 32.2 | 30.6 | 39.7 |
| C-C=C                                         | 54.2                     | 54.3 | 53.4 | 54.4 | 53.3 | 55.1 | 55.1 | 46.6 |
| C-C-C-C                                       | 2.2                      | 2.5  | 2.5  | 2.2  | 2.7  | 2.7  | 3.2  | 8.4  |
| C-C-C-C-C                                     | 3.1                      | 3.2  | 3.1  | 3.2  | 3.7  | 2.8  | 2.5  | 1.9  |
| C-C-C-C-C-C                                   | 1.6                      | 1.5  | 1.6  | 1.4  | 1.7  | 1.4  | 1.5  | 1.1  |
| C-C-C-C-C=C                                   | 8.5                      | 7.8  | 7.5  | 6.6  | 8.3  | 4.0  | 5.1  | 1.5  |
| C-C-C-C-C-C=C                                 | 3.7                      | 3.7  | 3.0  | 2.7  | 3.1  | 1.8  | 2.0  | 0.7  |

- (a) Tritium pressure was  $1 \times 10^{-3}$  Torr, HT/T<sub>2</sub> ratio of the gas was 1.  
 (b)  $50 \times 10^{-3}$  Torr of propene ( $4.0 \times 10^{-7}$  moles) was used (150 cc vessel).  
 (c) Products were separated on isoquinoline-AgNO<sub>3</sub> columns.  
 (d) HT, Methane, C<sub>2</sub>, C<sub>4</sub> and C<sub>5</sub> compounds are not included.  
 (e)  $50 \times 10^{-3}$  Torr of moderator H<sub>2</sub> was added.

Table IV. Product distributions of tritium atom reactions with propene at 77°K. (a), (b)

| (c), (d)<br>Tritiated<br>Reaction<br>Products | Discharge Time (sec.) |      |      |      |      | Tritium Distribution (%) |
|-----------------------------------------------|-----------------------|------|------|------|------|--------------------------|
|                                               | 3                     | 5    | 8    | 10   | 15   |                          |
| C-C-C                                         | 32.2                  | 30.3 | 31.3 | 32.5 | 31.8 | 33.9                     |
| C-C=C                                         | 58.7                  | 59.8 | 59.8 | 57.7 | 59.0 | 57.2                     |
| C-C-C-C                                       | 2.7                   | 2.9  | 2.9  | 3.3  | 2.7  | 3.1                      |
| C-C-C-C-C                                     | 1.5                   | 1.5  | 1.5  | 1.7  | 1.2  | 1.5                      |
| C-C-C-C-C-C                                   | 1.2                   | 1.3  | 0.9  | 1.4  | 1.9  | 1.5                      |
| C-C-C-C-C=C                                   | 2.8                   | 3.3  | 2.8  | 2.4  | 2.3  | 2.0                      |
| C-C-C-C-C-C=C                                 | 0.9                   | 0.9  | 0.8  | 1.0  | 1.1  | 0.8                      |

- (a) Tritium pressure was  $1 \times 10^{-3}$  Torr, HT/T<sub>2</sub> ratio of the gas was 1.5.  
 (b)  $50 \times 10^{-3}$  Torr of propene ( $4.0 \times 10^{-7}$  moles) was used (150 cc vessel).  
 (c) Products were separated on isoquinoline-AgNO<sub>3</sub> columns.  
 (d) HT, Methane, C<sub>2</sub>, C<sub>4</sub> and C<sub>5</sub> compounds are not included.

Table V. Product distributions of tritium atom reactions with propene at 77°K. (a), (b)

|                                                                                                            | <u>Tritium Pressure (x 10<sup>3</sup> Torr)</u> |      |      |      |
|------------------------------------------------------------------------------------------------------------|-------------------------------------------------|------|------|------|
|                                                                                                            | 1.1                                             | 1.2  | 1.2  |      |
|                                                                                                            | <u>Discharge Time (sec.)</u>                    |      |      |      |
| (c), (d)                                                                                                   | 3                                               | 5    | 8    | 10   |
|                                                                                                            | Tritium Distribution (%)                        |      |      |      |
| Tritiated                                                                                                  |                                                 |      |      |      |
| Reaction                                                                                                   |                                                 |      |      |      |
| Products                                                                                                   |                                                 |      |      |      |
| C-C-C                                                                                                      | 28.4                                            | 29.6 | 29.4 | 28.1 |
| C-C=C                                                                                                      | 60.7                                            | 57.7 | 57.1 | 55.9 |
| $\begin{array}{c} \text{C} \quad \text{C} \\   \quad   \\ \text{C}-\text{C}-\text{C}-\text{C} \end{array}$ | 4.0                                             | 4.4  | 4.3  | 5.2  |
| $\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \end{array}$               | 1.7                                             | 2.2  | 2.2  | 2.6  |
| C-C-C-C-C-C                                                                                                | 1.5                                             | 1.8  | 2.0  | 2.4  |
| $\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C}-\text{C}=\text{C} \end{array}$               | 2.4                                             | 3.0  | 3.7  | 4.0  |
| C-C-C-C-C-C=C                                                                                              | 1.2                                             | 1.2  | 1.3  | 1.7  |

(a) HT/T<sub>2</sub> ratio of the tritium gas was about 2.

(b) 50 x 10<sup>-3</sup> Torr of propene (3.5 x 10<sup>-7</sup> moles) was used (130 cc vessel).

(c) Products were separated on isoquinoline-AgNO<sub>3</sub> columns.

(d) HT, Methane, C<sub>2</sub>, C<sub>4</sub> and C<sub>5</sub> compounds are not included.

Table VI. Product distributions of tritium atom reactions with propene at 77°K. <sup>(a), (b)</sup>

| (c), (d)<br>Tritiated<br>Reaction<br>Products | H <sub>2</sub> Moderator Pressure (x 10 <sup>3</sup> Torr) |      |      |      |      |      |      |
|-----------------------------------------------|------------------------------------------------------------|------|------|------|------|------|------|
|                                               | 1.0                                                        | 1.1  | 1.0  | 1.0  | 1.0  | 1.1  | 1.0  |
|                                               | Discharge Time (sec.)                                      |      |      |      |      |      |      |
|                                               | 1.2                                                        | 3    | 5    | 8    | 10   | 15   | 20   |
|                                               | Tritium Distribution (%)                                   |      |      |      |      |      |      |
| C-C-C                                         | 31.3                                                       | 29.7 | 30.5 | 28.6 | 30.9 | 31.0 | 30.5 |
| C-C=C                                         | 56.6                                                       | 55.4 | 57.0 | 58.7 | 56.6 | 58.0 | 57.1 |
| C-C-C                                         | 4.7                                                        | 5.2  | 4.5  | 4.6  | 4.9  | 4.6  | 5.3  |
| C-C-C-C                                       | 2.7                                                        | 2.8  | 2.7  | 2.8  | 2.7  | 2.6  | 2.8  |
| C-C-C-C-C                                     | 0.9                                                        | 2.4  | 1.5  | 1.5  | 1.5  | 1.1  | 1.5  |
| C-C-C-C=C                                     | 3.1                                                        | 3.4  | 2.7  | 2.8  | 2.7  | 2.1  | 2.2  |
| C-C-C-C-C=C                                   | 0.7                                                        | 1.1  | 1.0  | 1.1  | 0.8  | 0.6  | 0.6  |

(a) Tritium pressure was  $0.5 \times 10^{-3}$  Torr. HT/T<sub>2</sub> ratio of the gas was about 2.

(b)  $60 \times 10^{-3}$  Torr of propene ( $4.2 \times 10^{-7}$  moles) was used (130 cc vessel).

(c) Products were separated on isoquinoline-AgNO<sub>3</sub> columns.

(d) HT, Methane, C<sub>2</sub>, C<sub>4</sub> and C<sub>5</sub> compounds are not included.

Table VII. Product ratios of tritium atom reactions with propene at 77°K.  
(The ratios were obtained from the data in Table III.)

| Tritium<br>Pressure<br>(x10 <sup>3</sup> Torr) | H <sub>2</sub><br>Moderator<br>Pressure<br>(x10 <sup>3</sup> Torr) | Discharge<br>Time<br>(sec.) | <u>Product Ratios</u> |                     |                     |                             |
|------------------------------------------------|--------------------------------------------------------------------|-----------------------------|-----------------------|---------------------|---------------------|-----------------------------|
|                                                |                                                                    |                             | $\frac{C_3}{C_6}$     | $\frac{C-C-C}{C_6}$ | $\frac{C-C=C}{C_6}$ | $\frac{C-C-C-C}{C-C-C-C=C}$ |
| 1                                              | 0                                                                  | 3                           | 4.2                   | 1.4                 | 2.8                 | 0.27                        |
| 1                                              | 0                                                                  | 5                           | 4.4                   | 1.5                 | 2.7                 | 0.33                        |
| 1                                              | 0                                                                  | 8                           | 4.6                   | 1.6                 | 3.0                 | 0.33                        |
| 1                                              | 0                                                                  | 10                          | 5.2                   | 1.8                 | 3.3                 | 0.33                        |
| 1                                              | 0                                                                  | 15                          | 4.0                   | 1.4                 | 2.8                 | 0.33                        |
| 1                                              | 0                                                                  | 20                          | 6.9                   | 2.5                 | 4.4                 | 0.68                        |
| 1                                              | 0                                                                  | 30                          | 8.1                   | 2.9                 | 5.2                 | 0.64                        |
| 1                                              | 50                                                                 | 10                          | 6.3                   | 2.9                 | 3.4                 | 5.5                         |

Table VIII. Product ratios of tritium atom reactions with propene at 77°K.  
(The ratios were obtained from the data in Table IV.)

| Discharge<br>Time<br>(sec.) | <u>Product Ratios</u>               |                                 |                                   |                                   |                                           |
|-----------------------------|-------------------------------------|---------------------------------|-----------------------------------|-----------------------------------|-------------------------------------------|
|                             | $\frac{\text{C-C-C}}{\text{C-C=C}}$ | $\frac{\text{C}_3}{\text{C}_6}$ | $\frac{\text{C-C-C}}{\text{C}_6}$ | $\frac{\text{C-C=C}}{\text{C}_6}$ | $\frac{\text{C-C-C-C}}{\text{C-C-C-C=C}}$ |
| 3                           | 0.55                                | 10.0                            | 3.5                               | 6.5                               | 0.96                                      |
| 5                           | 0.51                                | 9.1                             | 3.1                               | 6.0                               | 0.88                                      |
| 8                           | 0.52                                | 10.2                            | 3.5                               | 6.7                               | 1.04                                      |
| 10                          | 0.56                                | 9.2                             | 3.3                               | 5.9                               | 1.38                                      |
| 15                          | 0.54                                | 9.7                             | 3.4                               | 6.3                               | 1.18                                      |
| 20                          | 0.59                                | 10.2                            | 3.8                               | 6.4                               | 1.52                                      |

Table VIV. Product ratios of tritium atom reactions with propene at 77°K.  
(The ratios were obtained from the data in Table V.)

| Tritium<br>Pressure<br>(x10 <sup>3</sup> Torr) | Discharge<br>Time<br>(sec.) | <u>Product Ratios</u>               |                                 |                                   |                                   |                                           |
|------------------------------------------------|-----------------------------|-------------------------------------|---------------------------------|-----------------------------------|-----------------------------------|-------------------------------------------|
|                                                |                             | $\frac{\text{C-C-C}}{\text{C-C=C}}$ | $\frac{\text{C}_3}{\text{C}_6}$ | $\frac{\text{C-C-C}}{\text{C}_6}$ | $\frac{\text{C-C=C}}{\text{C}_6}$ | $\frac{\text{C-C-C-C}}{\text{C-C-C-C=C}}$ |
| 1.1                                            | 3                           | 0.47                                | 8.2                             | 2.6                               | 5.6                               | 1.7                                       |
| 1.2                                            | 5                           | 0.51                                | 6.9                             | 2.3                               | 4.5                               | 1.5                                       |
| 1.2                                            | 8                           | 0.52                                | 6.4                             | 2.2                               | 4.3                               | 1.2                                       |
| 1.2                                            | 10                          | 0.50                                | 5.3                             | 1.8                               | 3.5                               | 1.3                                       |

Table X. Product ratios of tritium atom reactions with propene at 77°K.  
(The ratios were obtained from the data in Table VI.)

| Tritium<br>Pressure<br>(x10 <sup>3</sup> Torr) | H <sub>2</sub><br>Moderator<br>Pressure<br>(x10 <sup>3</sup> Torr) | Discharge<br>Time<br>(sec.) | <u>Product Ratios</u> |                     |                     |                             |
|------------------------------------------------|--------------------------------------------------------------------|-----------------------------|-----------------------|---------------------|---------------------|-----------------------------|
|                                                |                                                                    |                             | $\frac{C_3}{C_6}$     | $\frac{C-C-C}{C_6}$ | $\frac{C-C=C}{C_6}$ | $\frac{C-C-C-C}{C-C-C-C=C}$ |
| 0.5                                            | 1.0                                                                | 1.2                         | 7.3                   | 2.5                 | 4.7                 | 1.5                         |
| 0.5                                            | 1.1                                                                | 3                           | 5.7                   | 2.0                 | 3.7                 | 1.5                         |
| 0.5                                            | 1.0                                                                | 5                           | 7.0                   | 2.4                 | 4.6                 | 1.7                         |
| 0.5                                            | 1.0                                                                | 8                           | 6.9                   | 2.2                 | 4.6                 | 1.6                         |
| 0.5                                            | 1.0                                                                | 10                          | 7.0                   | 2.5                 | 4.5                 | 1.8                         |
| 0.5                                            | 1.1                                                                | 15                          | 8.1                   | 2.8                 | 5.3                 | 2.2                         |
| 0.5                                            | 1.0                                                                | 20                          | 7.0                   | 2.4                 | 4.6                 | 2.4                         |

## V. DISCUSSION

### Evidence of Energetic Atoms Emanating from the Discharge

In a hydrogen discharge at low pressure, a variety of reactions were thought possible. Among all possible primary processes excitation and ionization by electron impact are known to occur with greatest probability.<sup>7,16</sup> The most probable excitation in turn is thought to be to the  $1^3\Sigma_u$  state which leads to dissociation of the hydrogen molecule into hydrogen atoms with 2.2-5.5 eV of kinetic energy. Ionization followed by ion-molecule reactions is another source of energetic hydrogen atoms. It was thought reasonable to assume that the ions were confined to the high electric field region between the electrodes of the discharge. Hydrogen atoms, however, probably were formed as products in ion-molecule reactions and surface neutralization processes.<sup>10,19</sup>

Evidence was found which suggests that under certain conditions the hydrogen atoms so formed lost some of their kinetic energy through collisions before they reached the film of propene. This behavior was shown in reactions with solid propene at different distances between the discharge area and the propene film. The reaction products of Table III-V were observed when the propene film was placed just above the discharge area at a distance of about 1.2 cm. The discharge was operated at very low tritium pressures ( $10^{-3}$  Torr), so that the tritium atoms had a mean free path in excess of the electrode-to-surface distance. Consequently the energetics of the reactions for these hydrogen atoms with the

propene film were characteristic of the initial energy distribution of the hydrogen atoms formed near the electrodes. The product distributions in Tables III-V suggest that initial reactions at the surface were of a hot chemical variety. Most tritium atoms striking the surface probably possessed from 2-10 eV of kinetic energy. However, evidence of these energetic species was not found when the electrode-to-surface distance became much greater than the mean free path. The kinetic energy possessed by reacting species was apparently lost in collisions with the media and became thermalized. This effect was tested when the propene was frozen in a trap instead of above the discharge area. At this greater electrode-to-surface distance, the only products observed were those of characteristics of thermal reactions (propane, propene and 2,3-dimethylbutane).

There was also another factor which affected the energetic species; the addition of moderator,  $H_2$  gas. The function of moderator was to thermalize the energetic species by collisions. Small amounts of the moderator had little effect as shown in Table VI. Addition of larger amounts of moderator ( $\sim 50 \times 10^{-3}$  Torr) showed a large moderator effect on the product distribution in Table III. Obviously, the energies of the species impinging on the film were greatly reduced since a large percentage had lost their energy in collisions with moderator molecules to become thermalized atoms before they reacted with propene molecules. Therefore, the extensive change was, as expected, that the products of the i-propyl radicals became dominant. This was indicated

by the decrease in propene yield and the increased yield of 2,3-dimethylbutane in spite of the decrease in the total C<sub>6</sub> compounds.

Since the energy of the electrons that collide with molecular T<sub>2</sub> is not known in the discharge, it is difficult to evaluate the average energy of tritium atoms emanating from the discharge and impinging onto the propene film. The distributions of products showed more "hot" atom characteristics than observed for atoms produced by thermal dissociation or electron bombardment.

#### Tritium Atom Reactions with Propene

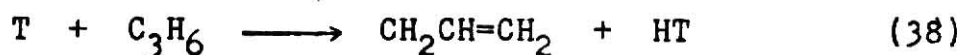
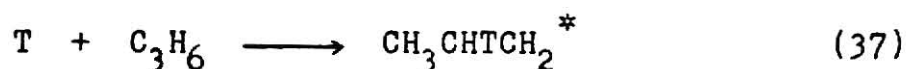
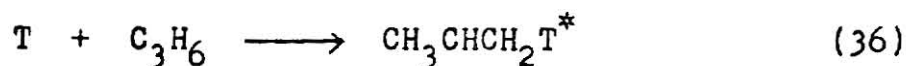
The major gas-solid products observed from reactions of tritium atoms with solid propene film at 77°K were propene, propane, and comparatively less, but significant amounts of C<sub>6</sub> compounds. All the degraded alkanes and alkenes mainly resulted from the gaseous electrode reactions. Therefore, these products were not treated as unique in the solid matrix. The main theme used in accounting for the other products, especially for all five of the C<sub>6</sub> compounds, was the formation of radical intermediates and formation of the labeled parent molecules from a direct displacement reaction.

There are three possible routes for the formation of radical intermediates each of which seems to have a different activation energy. Literature values for the activation energy for hydrogen atom addition to propene are reported in Table XI. Hydrogen atom

Table XI. Activation energy for the hydrogen atom addition reaction with propene.

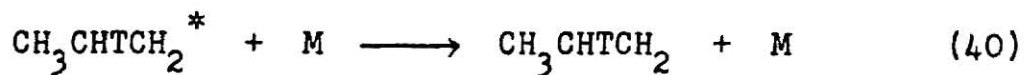
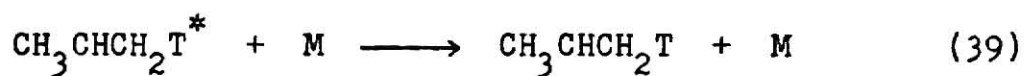
| Temperature °K | Activation Energy | Reference |
|----------------|-------------------|-----------|
| 77-90          | 1.1 Kcal/mole     | 4         |
| 77-90          | 1.5               | 48        |
| 304            | 1.8               | 49        |
| 304            | 2.6               | 50        |
| 298-388        | 5.0               | 51        |

addition to a non-terminal carbon atom of propene and hydrogen abstraction to form allyl radicals are known to have activation energies of a few kilocalories per mole.<sup>36,41</sup> Since the tritium atoms emanating from the discharge possessed considerable kinetic energy, the addition of tritium atoms to propene was not limited to the terminal carbon atom of the double bond. Thus it was possible to form all three kinds of radicals : i-propyl, n-propyl and allyl radicals. The formation of these radicals is shown by reactions (36)-(38).

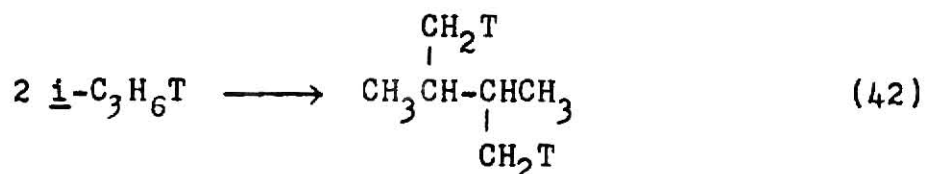


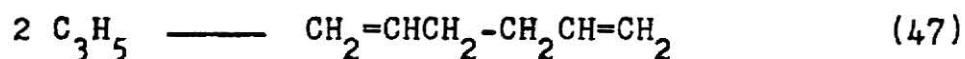
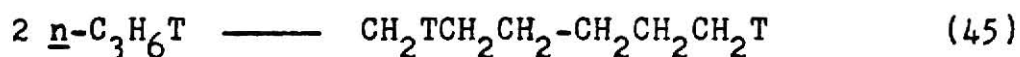
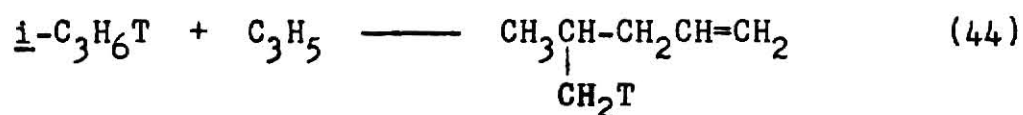
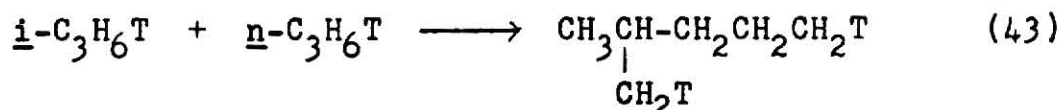
All three radicals have been reported in reactions of hydrogen atoms with propene in the gas phase and solid phase.<sup>5,35,43,45</sup>

The i- and n-propyl radicals formed in reactions (36) and (37), respectively, were "hot" radicals, because of the exothermicity of hydrogen addition to the double bond and also because of the initial kinetic energy possessed by the tritium atoms. These excited radicals, however, are easily deactivated either on the surface or in the bulk of the solid as in following reactions (39) and (40).



Most of the subsequent reactions are assumed to occur between thermalized radicals since they must diffuse to each other before reaction occurs. Time is thus available for deactivation by transfer of energy to the surrounding molecules. Such radicals are known to undergo further reactions by disproportionation or by combination to form stable products eventually. These reactions are shown in reactions (41)-(47).





The combination reaction (47) of allyl radicals could not be observed since the product molecule did not contain a labelling tritium atom.

In the field of free radical chemistry, disproportionation and combination of alkyl radicals are considered to be important reactions. All radical reactions occur in such a way as to stabilize the unpaired electron in the radical. Two radicals can combine to form a stable molecule or disproportionate by transferring one of the hydrogens from one radical to the other. Activation energies for disproportionation and combination reactions in the gas phase have been reported to be near zero, but to differ somewhat in the condensed phase. The values for the activation energy difference between the two processes are shown in Table II. This effect can be explained from the steric requirements in the solid state. The molecular motions such as rotation and translation are restricted in this state. In order for

radicals to combine, they must be aligned head to head, while disproportionation may not require such exact alignment. From this steric effect, the activation energy for combination reactions becomes higher than for disproportionation reactions.

Comparing the results of this study to others, the energetic aspects of the reactions can be discussed. In Table XII, the product distributions in percentages show the effect of varying energies possessed by the tritium atoms in the reactions with propene. For the reactions of hydrogen atoms thermalized to 77°K with solid propene, the only products observed were propane, propene and 2,3-dimethylbutane.<sup>32,44</sup> Those products were explained by the formation of i-propyl radicals and the subsequent radical reactions of disproportionation and combination. These thermalized hydrogen reactions were also observed when solid propene was bombarded by hydrogen atoms which were produced at a hot tungsten filament.<sup>33,42,44</sup> At the hydrogen pressure  $50 \times 10^{-3}$  Torr, the hydrogen atoms so formed were moderated, so that the products of i-propyl radical reactions were dominant.

The i-propyl radical is formed from the hydrogen atom addition to a terminal carbon atom of the propene double bond. The addition of a hydrogen atom to propene is known to be exothermic by about 43.5 Kcal/mole. Several different activation energies for this addition reaction are shown in Table XI. The preference of addition to a terminal carbon rather than non-terminal addition can be explained from the activation energy difference. Moore, who observed only i-propyl radical reactions, gave a value

Table XII. Effect of tritium atom energy on reaction products from propene.

| Products<br>(d)                   | Methods of Producing Tritium Atoms                                     |                                             |                                                     | Tritium Distribution (%) |      |  |
|-----------------------------------|------------------------------------------------------------------------|---------------------------------------------|-----------------------------------------------------|--------------------------|------|--|
|                                   | (a)<br>Thermal<br>Dissociation<br>Followed by<br>Moderation<br>to 77°K | (a)<br>Thermal<br>Dissociation<br>at 1350°C | (b)<br>Electron<br>Bombardment<br>30 eV<br>electron |                          |      |  |
| Methane                           |                                                                        |                                             | 1.2                                                 |                          | 1.8  |  |
| Ethane                            |                                                                        | 1                                           | 0.6                                                 |                          |      |  |
| Ethene                            |                                                                        |                                             | 1.5                                                 |                          | 19.5 |  |
| Ethyne                            |                                                                        |                                             |                                                     |                          | 1.8  |  |
| Propane                           | 47                                                                     | 45                                          | 39.1                                                | 27.0                     | 5.3  |  |
| Propene                           | 38                                                                     | 33                                          | 30.8                                                | 54.3                     | 59.2 |  |
| C <sub>4</sub> and C <sub>5</sub> |                                                                        | 3                                           | 0.3                                                 |                          | 3.0  |  |
| 2,3-Dimethylbutane                | 15                                                                     | 10                                          | 8.0                                                 | 2.5                      | 5.9  |  |
| 2-Methylpentane                   |                                                                        | 5                                           | 7.8                                                 | 3.2                      | (e)  |  |
| n-Hexane                          |                                                                        |                                             | 4.3                                                 | 1.5                      |      |  |
| 4-Methyl-1-pentene                |                                                                        | 2                                           | 5.2                                                 | 7.8                      | 3.6  |  |
| 1-Hexene                          |                                                                        |                                             | 1.2                                                 | 3.7                      |      |  |

(a) Ref. 4. (b) Ref. 5. (c) Ref. 45.

(d) HT formation was neglected as a product.

(e) 2-Methylpentane was included in 2,3-dimethylbutane.

of 2.4 Kcal/mole for the activation energy difference between n- and i-propyl radical formation.<sup>31</sup> Bradley, Melville and Robb, however, found only 7.5% n-propyl radicals which therefore gave an activation energy difference of 1.5 Kcal/mole.<sup>35</sup> Boddy and Robb argued that more i-propyl radicals resulted because the heat of formation of the i-propyl radical was 5 Kcal/mole less than that of the n-propyl radical.<sup>36</sup>

In contrast to the results of moderated hydrogen atoms, energetic hydrogen atoms showed products from the formation of n-propyl and allyl radicals. Yun and Moser, and Shores found that the n-propyl and allyl radicals increased with increasing filament temperature.<sup>5,43</sup> They proposed that at higher temperatures, hydrogen atoms obtained greater energy and consequently greater probability to produce the n-propyl or allyl radical. When the concentration of these radicals was great enough, the C<sub>6</sub> products of reaction (45) and (46) would be expected to result. From the Table XII these products were obtained by Shores and this work.

The ratios of rate constants of disproportionation to combination,  $k_d/k_c$ , of i-propyl radicals have been measured in both gas and the solid phases and are compared in Table II. On the other hand,  $k_d/k_c$  of n-propyl and allyl radicals, especially in the solid phase, are not known. Thus a quantitative evaluation of the yield of each radical is not possible. A qualitative comparison of the yield, however, could be obtained from the distribution of C<sub>6</sub> products. The relative amounts of radicals that reacted by combination from the tritium atom-propene reactions are

Table XIII. Distribution of radicals that reacted by combination to form C<sub>6</sub> compounds.

| Radicals | Methods of Producing Tritium Atoms                                                                         |                                |                                |                                |
|----------|------------------------------------------------------------------------------------------------------------|--------------------------------|--------------------------------|--------------------------------|
|          | (a)                                                                                                        |                                | (b)                            |                                |
|          | Electrical Discharge in T <sub>2</sub> (10 <sup>-3</sup> Torr) + H <sub>2</sub> (50x10 <sup>-3</sup> Torr) | Electron Bombardment at 2150°C | Thermal Dissociation at 1180°C | followed by moderation to 77°K |
| i-propyl | 40                                                                                                         | 69                             | 52                             | 80                             |
| n-propyl | 22                                                                                                         | 17                             | 28                             | 11                             |
| allyl    | 38                                                                                                         | 14                             | 20                             | 9                              |

(a) Ref. 5.  
(b) Ref. 4.

compared in Table XIII. The values were obtained by utilizing the specific activity which corresponded to the number of tritium atoms per C<sub>6</sub> compound of reactions (42)-(46). The specific activity of 4-methyl-1-pentene and 1-hexene was considered to be half that of the other C<sub>6</sub> products (2,3-dimethylbutane, 2-methylpentane and n-hexane).

The distributions of products in Tables III-VI and hence the product ratios in Tables VII-X as a function of discharge time were found to be fairly constant up to a discharge time of 20 sec. For time periods exceeding 20 seconds, however, the characteristics of thermalized reactions appeared to increase. For instance, the product distribution at 30 sec. discharge time (table III) indicated that the yield of products resulting from disproportionation reactions compared to those resulting from combination reactions seemed to increase, and that the yield of 2,3-dimethylbutane increased while that of 4-methyl-1-pentene decreased. This was probably so because the surface of the film was well covered with the products by this time, so that now the tritium atoms started to diffuse into the solid matrix, and the radicals formed needed to diffuse further. These atoms were probably thermalized during the diffusion process before they reacted with propene or radicals. Thus this hydrogen atom diffusion could also result in the formation of thermal products. It is known that the mobility of hydrogen atoms is greater than alkyl radicals, and they diffuse with a low activation energy (0.5-1.0 Kcal/mole) in a low temperature matrix.<sup>52</sup> However, this effect

was significant only when propene was highly diluted with inert molecules.

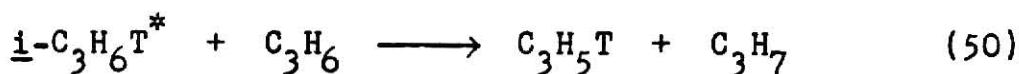
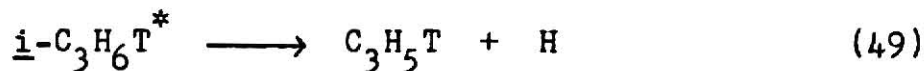
The product distributions differ notably from those observed in previous studies. The striking differences are : the high yield of the allyl radicals, the greater yield of propene over propane, and the larger amounts of 4-methyl-1-pentene and 2-methylpentane over 2,3-dimethylbutane. These features are more pronounced with recoil tritium atoms and reactions (41)-(47) can not be used to account for them completely.

First of all, to account for the high yield of the labeled parent molecule propene, the direct displacement reaction (48) can be proposed as the most probable process.

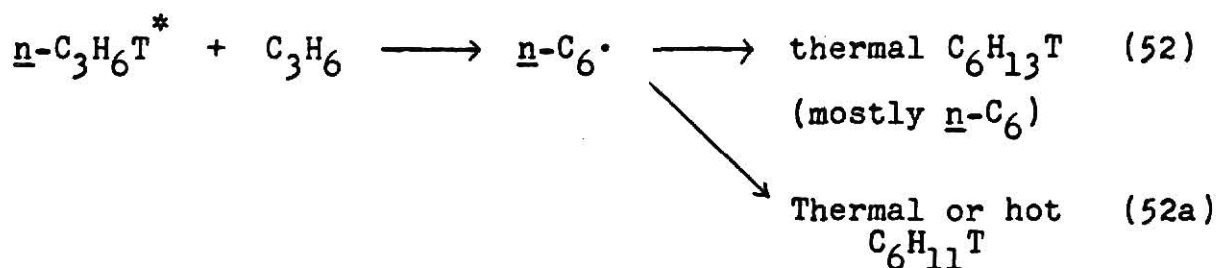


The substitution reaction takes place nearly independently of the particular bond strength, and is considered to be the most important process in the recoil "hot" tritium atom reactions with propene.<sup>45,55</sup> For the reactions of recoil tritium atoms with liquid propene at  $-98^\circ\text{C}$ , Mahan and Garland proposed that 33% of the labeled propene was formed by direct substitution while 67% of the propene was formed via radical intermediates.<sup>39</sup> Another possible route to obtain the labeled propene from radical formation was also proposed by Mahan and Garland.<sup>39</sup> Excited propyl radicals formed by the addition reactions could decompose or undergo radical-molecule disproportionation reactions to produce the labeled

propene as in reactions (49) and (50), respectively, unless they were deactivated previously by collision.



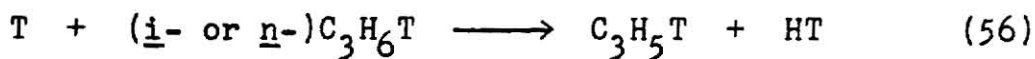
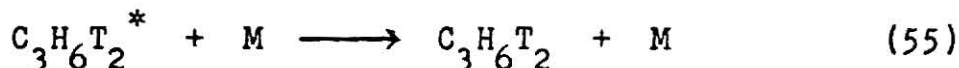
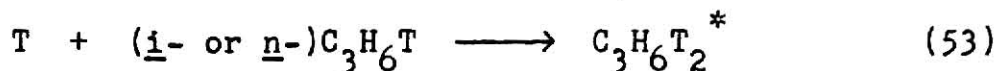
Cvetanović pointed out that the unimolecular decomposition by C-H rupture as in reaction (49) was dominant for the excited i-propyl radical, while C-C rupture as in reaction (51) was dominant for the excited n-propyl radical.<sup>37,56</sup> It is known that the excited n-propyl radicals formed from thermal H-atoms decompose by C-C bond breaking over 100 times faster than the i-propyl radicals by C-H bond breaking.<sup>56</sup> Breaking a C-H bond in propyl radicals has been suggested to have an activation energy of 35-38 Kcal/mole while that for breaking a C-C bond in a n-propyl radical has been suggested to be 25-30 Kcal/mole.<sup>39</sup> Since the rate of decomposition depends on the amount of excess energy, highly excited radicals can undergo decomposition by C-H bond rupture rapidly.<sup>57</sup> Similarly, the radical-molecule disproportionation reaction (50) was considered to be dominant for i-propyl radicals by hydrogen detachment. Whereas for n-propyl radicals, the hot addition to terminal carbon atom was thought to be the dominant path leading to C<sub>6</sub> compounds containing one T, which are shown in reactions (52) and (52a).



Under conditions where there was moderation of tritium atoms, the labeled propene yield was significantly reduced, as indicated by the C-C-C/C-C=C ratio change from 0.54 to 0.85. It seems that the amount of propene that was lost when the hydrogen atoms were moderated had resulted mainly from direct displacement reactions, rather than from the decomposition or molecule-radical disproportionation of "hot" radicals. Since the formation of degraded alkane and alkene from decomposition of hot n-propyl radicals as in reaction (51) or from "cracking" of "hot" propane in reaction (54) was already considered less significant in the solid matrix, the same analysis can also apply to the decomposition of "hot" i-propyl radicals. Moreover, the excited radicals are more likely to lose their energy during the diffusion process. Thus, the propene yields from reactions (49) and (50) now seem much less probable.

The radicals can also react with hydrogen atoms by combination and disproportionation reactions as in reactions (53) and (56), respectively. Doubly tritiated propane resulting from the reaction (53) is probably excited and decomposes as in reaction

(54) or is deactivated as in reaction (55).



These reactions, however, occur mainly at the surface of the solid. Even though the diffusion of hydrogen atoms is faster than that of radicals, the radicals formed on the propene surface react more readily with other radicals than with hydrogen atoms. At low pressures of hydrogen, the hydrogen diffusion and the surface reactions of hydrogen atoms and radicals are indeed negligible. Only under high hydrogen concentrations did surface reactions of hydrogen atoms with radicals become more notable. Yun and Moser suggested the possibility of the cracking reactions of the excited propane as in reaction (55) in the solid propene at 77°K.<sup>43</sup> It was also found that the tritium atom-i-propyl radical disproportionation reaction was the most probable process for the reaction of tritium atoms with propene highly diluted with isopentane at 63°K.<sup>44</sup> However, the addition of moderator H<sub>2</sub> gas ( $\sim 50 \times 10^{-3}$  Torr) did not change the amount of propane yield significantly in this study. This indicated that the effect of the tritium atom-radical reactions was slight under these conditions. The reactions

(53)-(56) were considered, thus, less important.

A large yield of 4-methyl-1-pentene and 2-methylpentane can be accounted for by the formation of allyl radicals from abstraction of a hydrogen atom in propene. This is also a characteristic "hot" atom reaction. The dilution of tritium by  $H_2$  gas changed the yields of these  $C_6$  compounds. Under these conditions energetic tritium atoms were thermalized so that thermal reactions of i-propyl radicals became significant. The yields of combination products were lessened because the activation energy for combination reactions is 0.3-0.4 Kcal/mole higher than that for disproportionation, and the yield of 2,3-dimethylbutane now became the dominant  $C_6$  compound. The ratio of 2,3-dimethylbutane/4-methyl-1-pentene changed from 0.32 to 5.5. In this system,  $k_d/k_c$  ratio could not be obtained since the product formation depended upon various processes. However, the results show a great indication of "hot" atom reactions. The atoms which emanated from the discharge were not so "hot" as recoil atoms, but were energetic enough to show some characteristics of "hot" atoms.

## VI. ACKNOWLEDGMENTS

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### VIII. VITA

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REACTIONS OF SPECIES EMANATING FROM A LOW-PRESSURE  
HYDROGEN DISCHARGE WITH SOLID PROPENE

by

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## ABSTRACT

The object of this study was to characterize the behavior of the chemically active species emanating from a very low pressure hydrogen discharge. The products from the reactions of the active hydrogen species with thin films of solid propene at 77°K were utilized to characterize the chemical behavior. Tritium was used as a tracer for hydrogen so that the products could be determined by radio-gas chromatography. The distribution of tritiated products showed that very hot hydrogen atom species were important.

The 3,000 volt DC discharge was similar to that in a cold-cathode ionization manometer. The discharge was initiated by placing an external radiofrequency coil near the tungsten electrodes. Discharges were obtained in pressures as low as  $10^{-3}$  Torr of tritium gas.

The gas-solid interaction of active tritium species with propene films resulted in HT, propane, propene, 2,3-dimethylbutane, 2-methylpentane, n-hexane, 4-methyl-1-pentene, 1-hexene and small amounts of methane, C<sub>2</sub>'s, C<sub>4</sub>'s and C<sub>5</sub>'s. Interest was concentrated on the C<sub>3</sub> and C<sub>6</sub> products. The product distribution indicated that the most probable primary interactions were addition, abstraction and substitution of hydrogen atoms. The former two processes resulted in the formation of three kinds of radicals : i- and n-propyl radicals from the addition of tritium atoms to the propene double bond and allyl radicals from abstractions of the terminal hydrogen atoms of propene. Radicals so

formed were thought to react further among themselves to form propane, propene and  $C_6$  compounds by disproportionation and combination reactions, and also with hydrogen atoms to form propane and propene by addition and abstraction of hydrogen atoms. However, the radical-hydrogen atom reactions on the surface appeared to be much less significant. A direct substitution of T for H is also proposed because of the unusually high yield of tritiated propene. Both n-propyl and allyl radicals have higher activation energies than i-propyl radical for formation by reactions of hydrogen atoms with propene. Thus the high yields of 4-methyl-1-pentene and 2-methylpentane relative to 2,3-dimethylbutane were substantive evidence supporting hot atom reactions.

Additional evidence supporting the existence of the hot interactions at low discharge pressure was also found when the tritium species were moderated by the addition of  $H_2$  gas. A significant reduction of the products previously attributed to the hot interactions was observed.

Hence, it is concluded that when additional moderating hydrogen is present, the reaction products are formed mainly by addition of thermal hydrogen to propene. The i-propyl radical was the important intermediate under these conditions. The product distributions obtained in this study at low tritium pressures indicated that the active hydrogen species were more kinetically hot than those produced by atomization at an incandescent filament, or by electron bombardment.