REACTIONS OF TRITIUM ATOMS
WITH FROZEN HYDROCARBONS

by

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INTRODUCTION

Several experimental techniques have yielded hydrogen atoms of different energies, and variations in their reactions have been observed. The present research was aimed at studying the reactions of hydrogen atoms possessing energies greater than the usual thermal range but less than those of recoil atoms from nuclear reactions. Experimentally hydrogen atoms of this energy range can best be produced by a thermal process such as the technique of atomization at a hot filament. The use of a hot filament imposes several experimental limitations: (1) only hydrogen must come in contact with the filament; (2) at pressures greater than a few microns hydrogen atoms may, before reacting, lose their excess energy through collisions; (3) if the pressure is reduced to prevent energy loss by collisions, the number of hydrogen atoms produced is extremely small.

Limitation 1 can be reduced by freezing the compounds to be reacted (hydrocarbons in the present study) with liquid nitrogen. At this temperature methane and possibly ethane are the only hydrocarbons with appreciable vapor pressure. Limitation 2 can be overcome if the pressure is reduced inside the reaction flask. Estimates, based on the kinetic molecular theory indicate the mean free path for hydrogen atoms is approximately 3 cm at 5μ pressure under our experimental conditions. By constructing a small reaction flask, a maximum filament-to-wall distance of 3 cm can be maintained. The small flask also reduces the surface area

of exposed frozen hydrocarbon for reaction. With a low hydrogen atom production and a small reaction surface, only a limited number of reactions occur. In order to follow a small number of reactions, tritium is mixed with the hydrogen. The resulting products are thus radioactive and can be observed by counting techniques.

LITERATURE REVIEW

The literature has been surveyed with emphasis directed in three major areas: hydrogen atom production, reactions of hydrogen atoms and radical-radical reactions.

Methods of Producing Hydrogen Atoms

Thermal Methods. In the case of hydrogen or deuterium molecules sufficient information exists to enable the equilibrium degrees of dissociation to be calculated fairly precisely at all temperatures (1). Table 1 gives the temperature corresponding to various amounts of dissociation when the pressure of the gas is 1 mm. With these diatomic molecules, very high temperatures

Table 1. Dissociation of hydrogen and deuterium

Substance	Heat of Dissociation kcal/mole	Temperature in $^{\circ}$K at Which the Degree of Dissociation Is		
		1%	0.01%	0.0001%
H_2	102.7	1910	1425	1140
D_2	104.6	1920	1440	1160

must be reached before the atom concentration becomes appreciable.

Thermal reactions of deuterium with methane, ammonia and

water appear to proceed through equilibrium concentrations of deuterium atoms (2). This method, however, is applicable only with exceptionally stable substances such as methane, ammonia and water since, with most substances the high temperature necessary to produce the hydrogen atoms would also result in decomposition and other complications.

Electrical Methods. The disruptive discharges, the arc and the spark, have the main effects of being thermal, and correspond to localized heating of the gas to 1500°C or higher. In general the results produced are so drastic that almost every possible atom or radical is produced by the discharge, and it is impossible to obtain much information about specific chemical reactions from work of this kind. Wood (3) has shown that hydrogen atoms could be pumped out of a glow discharge in hydrogen and carried for considerable distances before they recombined. Bonhoeffer (4) modified Wood's apparatus and made extensive investigations of the chemical properties of atomic hydrogen.

Heated Filaments. The classical experiments of Langmuir (5) were the first example of this method. Langmuir investigated the heat loss from metal filaments heated in the presence of hydrogen, oxygen or other gases. The apparatus was constructed similar to a standard filament light bulb. Langmuir showed that hydrogen was dissociated into atoms on a very hot filament. At low pressures the atomic hydrogen thus produced reached the walls of the bulb where the atomic hydrogen activity was shown by reduction of metallic oxides. The method has been widely used in the investigations of catalytic reactions.

Photochemical Methods. Hydrogen has a dissociation energy of

103 kcal/mole corresponding to a quantum of wavelength about 2750 Å but the continuum in its absorption spectrum does not begin till 849 Å (1). In this far ultraviolet region experimental difficulties become too great to make this a convenient method for studying hydrogen atom reactions. Darwent and Roberts (6) have used this method to produce hydrogen atoms.

Another method of approach, photosensitization, is to add to hydrogen a substance which will absorb at wavelengths less than 2750 Å and can transfer this energy to hydrogen. This method has been widely used with hydrogen.

Nuclear Reactions. Recoil tritium atoms can be produced in either the gas (7) or in the condensed phase by neutron irradiation (7). In the gas phase a small amount of helium-3 is mixed with the material being investigated and tritium is then produced under reactor neutron irradiation by the $He^3(n,p)T$ reaction. Tritium atoms are produced in the condensed phase by the $Li^6(n,\alpha)T$ reaction. As in most nuclear reactions, the energies resulting from such processes are high.

Reactions of Hydrogen Atoms

Reduction. Bonhoeffer (4) studied the reducing action of hydrogen atoms on such solids as metallic oxides, sulfides, halides and etc. Melville and Robb (8) used the reducing action of hydrogen atoms as a method for quantitative detection of hydrogen atoms. Molybdenum oxide, a light yellow powder, reacts readily with atomic hydrogen, turning blue in the process. It was thus possible to follow the rate of a reaction by colorimetrically comparing a

blank run with a run where another compound was competing for the
hydrogen atoms produced.

Recombination. The recombination of hydrogen atoms occurs by
the reaction:

$$2H \longrightarrow H_2 \tag{1}$$
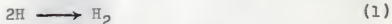
However, in the gas phase the recombination of two hydrogen atoms
to form a molecule results in such an excited state that dissoci-
ation occurs. Therefore, recombination requires a third body for
removal of the excess energy. Thus hydrogen atoms can be produced
in one part of the system and pumped into another part of the
system for reaction. Meta-phosphoric acid poisons hydrogen atom
recombination while glass and most other substances promote
recombination.

Gas Phase Reactions. Using the discharge tube method of Wood-
Bonhoeffer, Geib and Steacie (9) found that small amounts of
acetylene greatly accelerated the recombination of hydrogen atoms,
but no products other than hydrogen and acetylene were detected.
Similar results were obtained with atomic deuterium, but in this
case there was a rapid exchange of D for H.

LeRoy and Steacie (10) found atomic hydrogen, produced by
photosensitization, reacts with acetylene to produce ethane,
ethylene, butane and a polymer of the approximate composition
$(C_2H_4)_n$. Since the pressure of atomic hydrogen was several
orders of magnitude lower than that obtained by the discharge tube
method, they concluded that hydrogenated products could be produced
only in the presence of large H_2:H ratios.

The thermal dissociation of hydrogen on hot tungsten filaments
was used by Tollefson and LeRoy (11) in the investigation of the

reaction of atomic hydrogen with acetylene. The hydrogen was dissociated on a tungsten filament at $1650°C$ with hydrogen pressure varying from 1 to 14 mm pressure. The atoms produced were pumped 52 to 110 mm before they were mixed with acetylene. The number of hydrogen atoms present in the hydrogen stream was determined by measuring the temperature of a metal block heated by hydrogen atom recombination. Under these conditions all attempts to detect products other than hydrogen and acetylene were unsuccessful.

However, detectable products were found when the acetylene pressure was increased to a value sufficient to reduce the pressure of atomic hydrogen at the detector to zero. Although the analyses were subject to considerable experimental error, evidence was found for the presence of both an olefin and a paraffin. The paraffin appeared to be ethane.

Schiff and Steacie (12) and others (13, 14) studied gas-phase reactions of thermal hydrogen and deuterium atoms with benzene, some cycloalkanes and the corresponding alkanes. Methane was the major product of each reaction. Of the cycloalkanes, cyclopropane and cyclobutane did not exchange with deuterium atoms, but benzene, cyclopentane and cyclohexane underwent considerable exchange. In the case of normal alkanes, the degree of exchange increased with increasing molecular weight. In the reaction of deuterium atoms with ethane, methane was the main product formed. This was also true for both the hot filament method of Berlie and LeRoy and the mercury photosensitization (15). It was concluded that hydrogen abstraction was the initial reaction:
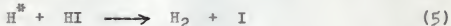
$$D + C_2H_6 \longrightarrow C_2H_5 + HD$$

or in a more general case

$$H + RH \longrightarrow R + H_2 \qquad (3)$$
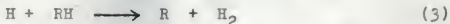
The role of hot hydrogen atoms in the photolysis of HI at 2537 Å has been described by Schwarz, Williams and Hamill (16). The reactions observed were:

$$HI \longrightarrow H^* + I \qquad (4)$$

$$H^* + HI \longrightarrow H_2 + I \qquad (5)$$

In this study products of hot atom reactions were chemically indistinguishable from the products of thermal atom reactions. They found, however, that the yield of hydrogen was significantly reduced by dilution with inert gases.

The technique of competing reactions was used by Carter, Hamill and Williams (17) to distinguish between hot atom reactions and thermal atom reactions. For this, they used DI instead of HI. The deuterium atoms formed were reacted with hydrogen, methane, ethane and neopentane, all of which contained hydrogen in the molecule. The hot deuterium atoms abstracted hydrogen forming HD while both hot and thermal deuterium atoms formed D_2. By varying the wavelength of radiation producing photolysis, the kinetic energy of the deuterium atoms was varied. Results show the greater the kinetic energy of the deuterium atoms, the greater the yield of HD. Others have shown similar results by photolysis of D_2S (18) and D_2CO (19).
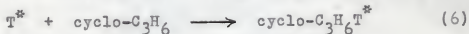
Tritium Recoil. Rowland (20, 7) Wolfgang (21) and others (22-24) have studied extensively high energy tritium atoms recoiling from the nuclear reaction $He^3(n,p)T$. The compound to be studied is mixed in a sealed tube with a small amount of helium-3. Tritium

atoms produced under reactor neutron irradiation recoil with several Kev of energy. This energy causes the tritium atom to move through the compound to be labeled producing ionization, collision and excitation until its energy is reduced to the range of chemical-bond energies. The kinetic energy retained at the end of the recoil track is largely expended in breaking one or more chemical bonds.

Combination of the recoil atom with the fragments produced makes a new radioactive molecule which may or may not be chemically similar to the initial organic molecule, except for substitution of the radioactive isotope. These recoil tritium atoms undergo reactions with essentially all organic molecules with introduction of 10 to 50% of the radioactivity into the otherwise unchanged parent molecule. Irradiations of gaseous mixtures of hydrocarbons and helium-3 have been reported for several alkanes (25) and alkenes (26). The mechanism for hot hydrogen atom displacement reactions with alkanes has also been postulated (21).

The reaction of tritium atoms with cyclopropane is of special interest. As indicated previously, Schiff and Steacie (12) did not get exchange reactions to occur with thermal hydrogen or deuterium atoms produced by the discharge method. Lee, Musgrave and Rowland (27, 28) found that recoil tritium atoms react with cyclopropane in the gas phase under a variety of experimental conditions. The reaction gives labeled cyclopropane as a product without isomerization or decomposition of the molecule.

The "hot" reactions are explained in terms of single-step interactions of energetic tritium atoms with cyclopropane molecules.

$$T^* + \text{cyclo-}C_3H_6 \longrightarrow \text{cyclo-}C_3H_6T^* \qquad (6)$$
$$\text{cyclo-}C_3H_6T^* \longrightarrow H + \text{cyclo-}C_3H_6T \qquad (7)$$

The recoil process provides more than sufficient energy for reaction.

Liquid Phase. The reactions of hydrogen atoms in non-aqueous solutions have received little attention. The principle reason appears to be the difficulty in generating hydrogen atoms in situ. Most methods applicable in the gas phase cannot be carried out in solution. One of the few feasible methods of hydrogen atom production is the photolysis of formaldehyde, but as this is restricted to temperatures above 100°C, technical problems encountered have limited the value of the method.

Several attemps have been made in which an electric discharge was passed through hydrogen gas just prior to bubbling it through solutions (29, 30). The results are quite scattered and the method is not considered promising for general application. However, others have found that hydrogen atoms, produced in the gas phase and introduced into aqueous solutions, are capable of oxidizing ferrous to ferric ions (31, 32) and iodide (33) to iodine. The reaction was shown to be pH dependent (32, 33) and a mechanism was proposed for the oxidation of ferrous to ferric ions (32).

Hardwick (34) devised a method in which hydrogen atoms are produced in situ by radiolysis of a saturated hydrocarbon solvent. The atoms produced are allowed to react competitively with a reactive solute and solvent. He measured the relative reactivity amoung several alkanes and naphthenes in the liquid phase and then made a comparison of the collision yields for the reactions of hydrogen atoms plus paraffin in solution and in the gas phase. In most cases the agreement was good.

Solid Phase. Langmuir (5), using the hot filament method, found a variation in the reactions of hydrogen atoms with phosphine. The phosphine was introduced into the bulb and frozen with liquid

air. At -185°C phosphine has a vapor pressure of 1.9μ , and consequently at a filament temperature of 1240°K the phosphine was decomposed as rapidly as it came in contact with the filament. The hydrogen accumulated while yellow phosphorus was deposited on the bulb.

When a filament at higher temperature, i.e. 2020°K, was heated in phosphine, the gas was still dissociated by coming in contact with the filament. The hydrogen formed was dissociated into hydrogen atoms with enough energy to recombine with the phosphorus to form phosphine. This prevented the accumulation of yellow phosphorus and hydrogen.

Klein and Scheer (35, 36) used a similar experimental technique to study hydrogen atoms with solid olefins such as propene (37, 38) at 77°K. This method, under their experimental conditions, gives the corresponding alkanes and alkyl radical dimer. So-called "cracking" products, resulting from C-C bond rupture of excited species, are never observed. Furthermore, they found some olefins show rapid hydrogen atom uptake while others react slowly or not at all. These rate differences are ascribed to small differences in activation energies which are readily observed at these low temperatures. The activation energy for hydrogen atom addition to propene was measured (39).

The reactions observed by Langmuir and Klein and Scheer depend upon interaction of hydrogen and production of hydrogen atoms at a hot tungsten filament. Studies by Roberts and Bryce (40) on the production of hydrogen atoms by a heated tungsten filament indicated that at a constant filament temperature, the rate of dissociation was proportional to the square root of the pressure. The hydrogen

atoms produced were effectively removed by reaction with molybdenum oxide. Under these conditions and at constant filament temperature hydrogen atom production was:

$$n = 7.1 \times 10^{24} \sqrt{P} \ e^{-\frac{49,200}{RT}}$$

where n is the number of hydrogen atoms produced per cm^2 of filament per second. The pressure P is in mm of mercury. Two alternate mechanisms for the hydrogen atom production were suggested (41): (1) evaporation of atoms from the adsorbed film, and (2) a gas molecule strikes a bare tungsten atom, one atom sticks and the other goes into the gas phase.

Brennan and Fletcher (42) investigated the dissociation of hydrogen at a tungsten filament in the temperature range 1200 to 1800°K and at pressures between 10^{-2} and 10^{-6} mm. At temperatures below 1400°K and at pressures exceeding 10^{-6} mm, they proposed that equilibrium was established between adsorbed and gaseous hydrogen. From a consideration of both atomization and recombination reactions, they demonstrated that the reaction W-H = W + H was applicable. The observation that molecular and atomic hydrogen leave the filament in their equilibrium ratio, as determined by the temperature of the filament and the pressure of hydrogen, was shown to be compatible only with this description of the reaction.

At temperatures in the region of 1800°K, the rate of reaction ceased to be proportional to $\sqrt{P}$ at relatively high pressures and become linearly dependent on P at pressures less than 10^{-6} mm. They found the hydrogen atom production to be:

$$v_a = 18 \times 10^{23} \ P \ e^{-\frac{52,600}{RT}}$$

atoms/cm^2 sec. They believed that contamination of the tungsten filament by stopcock grease accounted for the lower activation energy values obtained by others.

Ehrlich (43) has considered the problem of atom production by a hot filament. From analysis of the kinetic processes at the surface, adsorption, diffusion and evaporation, he proposed for hydrogen pressures of 10^{-6} mm and filament temperatures of $1600°$K the rate of formation of atomic hydrogen is limited by impingment of molecular hydrogen on the surface. Furthermore, $\sqrt{P}$ dependence of the rate of production of hydrogen atoms should change to a rate directly proportional to pressure.

Hickmott (44) attacked the problem by determining the rate of formation of atomic hydrogen in a constant flow system under steady state conditions, rather than measuring rate of removal of hydrogen by atomization and trapping of the free atoms in a system containing a fixed amount of hydrogen. Under these conditions the rate of evaporation of atomic hydrogen, when the filament temperature was raised above $1100°$K was:

$$v_a = (2.2 \times 10^{13})\ n\ e^{-\frac{67,000}{RT}}$$

molecules/cm^2 sec, where n is the surface coverage in molecules/cm^2.

Tritium Recoil. In the tritium recoil labeling of organic compounds (7, 3), lithium salts are mixed with the organic compound to be labeled and the mixture is irradiated with a high flux of thermal neutrons. Tritium is produced in high yield by thermal Li^6 (n,α)T reactions with thermal neutrons. This reaction is quite similar to the He^3(n,p)T reaction except the former is for solid phase reactions.

Radical Reactions

Free radicals may be defined as molecular fragments having an unpaired electron. Because of the unpaired electron, free radicals are highly reactive and normally have a very short lifetime. Low temperature studies, however, give indications that free radicals can be stabilized. Under the proper preparatory conditions, free atoms and low molecular weight radicals can be trapped for relatively long periods of time in solidified gases at low temperature (45). This is known as the "matrix isolation method".

If the matrix isolation method is to be applied successfully, two conditions must be maintained: (1) diffusion to the vicinity of another atom must be prevented, (2) reaction with the solid must not occur.

Diffusion in a solid is strongly temperature dependent. For nitrogen or oxygen atoms trapped in a solid formed of the parent molecule, recombination occurs between 10 and 30°K (46). Fontana (47) considers that the temperature dependence of viscosity must be unusual if recombination occurs. It is significant that no workers appear to have been able to obtain concentrations of trapped radicals within a factor of ten of the theoretical value calculated by Jackson and Montroll (48) and Golden (49). This indicates that diffusion is an important factor in limiting the trapped radical concentration. Jackson (50) developed a model for calculating the concentration at which free radicals become unstable. By applying this model, theoretical results are closer to experimental results (51).

Bass and Broida (45) supplemented this idea. They proposed

that solids formed by rapid condensation at a temperature well
below half the melting point are probably extremely imperfect
crystals or amorphous. Free radicals formed in such a solid are
lost by diffusion resulting in reaction, if the temperature ever
reaches or exceeds about one-half the melting point. For single
atoms the value may be as low as 0.1 to 0.4 of the melting point,
since it is only reasonable to expect single atoms to diffuse much
more rapidly than polyatomic molecules.

Jen and co-workers (52) have trapped alkyl radicals formed in
the gas phase. They produced methyl radicals in a mild electrical
discharge through methane and stabilized the products at liquid
helium temperature. Larger alkyl radicals have been trapped only
by solid state photolysis, irradiation or hydrogen atom reactions
with olefins.

Klein and Scheer (35) believe that reactions of hydrogen atoms
with solid olefins provide a possible method for the preparation of
alkyl radicals stabilized in a matrix. Their mechanism implies
that hydrogen atoms diffuse readily through solid hydrocarbons,
reacting with the olefins to produce matrix stabilized alkyl free
radicals. These free radicals can build up in concentration in
accord with the limitations imposed by the values of the rate
constants of the hydrogen atoms addition to the olefin and to the
alkyl radical. Spin resonance measurements (54), through lack of
a detectable resonance signal, indicated that the steady state
concentration of radicals must be less than 10^{15} per cc, the
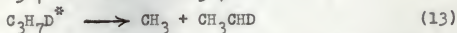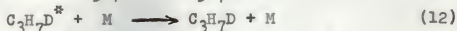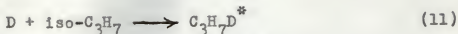detection limit of the instrument.

Moore and Taylor (55) found a convenient method of preparing a
free aliphatic radical in the gas phase. This is accomplished by

addition of a hydrogen atom to the corresponding olefin. If hydrogen atoms are produced by mercury photosensitization, their concentration will be low compared to the radical concentration, and subsequent reactions of the radicals with each other may be studied. Observations with ethylene, propylene and n-butylene show that dimerization is the main reaction with lesser amounts of the corresponding alkane. Moore and Wall (56) extended the investigation to isobutene and butene-2. From the analysis they concluded: (1) when a hydrogen atom adds to isobutene, the tertiary butyl radical is formed. Any isobutyl radicals decompose immediately into methyl and propene; (2) addition of a hydrogen atom to butene-2 produces mostly methyl plus propene and a little sec-butyl; (3) addition of a hydrogen atom to butene-1 produces considerable sec-butyl. Any n-butyl decompose into ethyl plus ethene; and (4) the isomeric constitution of the octanes suggests that radicals add to olefinic double bonds at the carbon atom with highest electron density.

Heller and Gordon (57) studied the reactions of isopropyl radicals in the gas phase by photolysis of diisopropyl ketone. They found these radicals can disproportionate, combine or abstract hydrogen from the parent ketone RH according to the following reactions:

$$iso\text{-}C_3H_7 \ + \ iso\text{-}C_3H_7 \ \longrightarrow \ C_3H_8 + C_3H_6 \quad (8)$$
$$iso\text{-}C_3H_7 \ + \ iso\text{-}C_3H_7 \ \longrightarrow \ C_6H_{14} \quad (9)$$
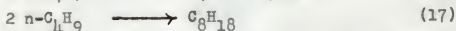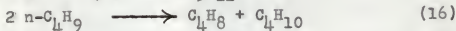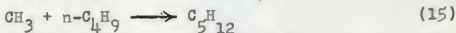$$iso\text{-}C_3H_7 \ + \ RH \ \longrightarrow \ C_3H_8 \ + \ R \quad (10)$$

They (53) also studied the reactions of deuterium atoms with isopropyl radicals. The products observed were explained by the reactions:
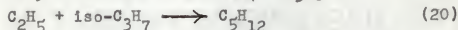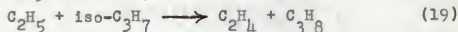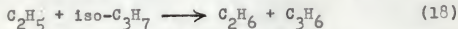
$$D + iso-C_3H_7 \longrightarrow C_3H_7D^* \tag{11}$$

$$C_3H_7D^* + M \longrightarrow C_3H_7D + M \tag{12}$$

$$C_3H_7D^* \longrightarrow CH_3 + CH_3CHD \tag{13}$$

The minimum half-life of the excited propane was calculated from the pressure variation to be 2×10^{-6} seconds.

Thynne (58) observed both dimerization and disproportionation of butyl radicals from butyl formate sensitized by methyl radicals. The methyl radicals were produced by photolysis of acetone. The products were explained by the following reactions:

$$CH_3 + n-C_4H_9 \longrightarrow CH_4 + C_4H_8 \tag{14}$$

$$CH_3 + n-C_4H_9 \longrightarrow C_5H_{12} \tag{15}$$

$$2\ n-C_4H_9 \longrightarrow C_4H_8 + C_4H_{10} \tag{16}$$

$$2\ n-C_4H_9 \longrightarrow C_8H_{18} \tag{17}$$

The ratio of disproportionation to combination was measured. The ratio of the yield from reaction 14 to that from reaction 15 was 0.15; the ratio of reaction 16 to 17 was 0.94.

Thynne (59) also studied the reaction of ethyl and isopropyl radicals. This was achieved by decomposition of isopropyl formate sensitized by ethyl radicals. Three reactions were proposed:

$$C_2H_5 + iso-C_3H_7 \longrightarrow C_2H_6 + C_3H_6 \tag{18}$$

$$C_2H_5 + iso-C_3H_7 \longrightarrow C_2H_4 + C_3H_8 \tag{19}$$

$$C_2H_5 + iso-C_3H_7 \longrightarrow C_5H_{12} \tag{20}$$

Reactions 18 and 20 occurred to the greatest extent. The ratio of the yield from reaction 18 to that from reaction 20 was 0.43. This compares with 0.63 for isopropyl-isopropyl radical reactions (53).

EXPERIMENTAL METHODS

Compounds Reacted

Since the reactions which hydrogen atoms undergo with hydro-
carbons are energy dependent, in the early work it was desired to
see what compounds would react with tritium atoms produced under
our experimental conditions. Liquid hydrocarbons were chosen
because of their ease of handling. They consisted of aliphatic
hydrocarbons (both paraffins and olefins) and an aromatic hydro-
carbon. Those reacted were n-pentane, 1-hexene, cyclohexane,
cyclohexene and benzene. Upon finding that reactions occurred
readily with all of the above compounds, it was of interest to see
what reactions would occur with the most inert of the paraffins,
cyclopropane and the related light hydrocarbons ethane, propane
and n-butane.

With the liquid hydrocarbons, high purity reagents were used;
the gaseous hydrocarbons were obtained from Matheson with reported
purities of at least 99.5%. In all cases the hydrocarbons were
analyzed by gas chromatography to ensure purity.

Preparation of Tritium

Molecular hydrogen containing tritium was prepared in this
laboratory. In the early experiments hydrogen, with a tritium
content of approximately 0.9 mc/mmole, was prepared by reacting
approximately 5μl of tritiated water with 1.5 g of metallic zinc
in an evacuated Pyrex (# 1720) fusion tube at 640 to 670°C for one
hour. The hydrogen containing tritium used in the later experiments
was prepared similarly except that the tritiated water had a

specific activity of 18 mc/mmole.

Introduction of Tritium

The fusion tube was placed in the vacuum system before being broken. The tritium was stored in either of two ways. (1) It was absorbed on titanium metal flags which were spot welded 1.5 cm apart on a 16 cm tungsten filament. By controlling the current flowing through the tungsten filament with a variable transformer, the temperature of the flags and hence the hydrogen release, could be controlled. (2) The hydrogen was stored in chamber A (see Plate 1) and was released into the system through a high vacuum needle valve B.

Pressure Measurement

In the calibration of the Pirani guage (Consolidated Electrodynamics model GP-110) against the McLeod guage, a liquid nitrogen trap was placed between the McLeod guage and the system to protect the system from introduction of mercury vapor. The stopcock to the McLeod guage was opened, connecting it with the remainder of the system. An oil diffusion pump was used to evacuate to a pressure of less than 0.05μ Hg. The system was then isolated from the vacuum pumps, hydrogen was introduced into the system and the two guage readings compared. The McLeod guage was then isolated from the remainder of the system while the Pirani guage was used for following the pressure changes.

Temperature Measurement

With hydrogen at the desired pressure, the temperature of the

EXPLAINATION OF PLATE I

Apparatus for studying Hydrogen Atom Reactions

Molecular hydrogen containing tritium was stored in chamber A and released into the system through a high vacuum needle valve B. Reaction chamber C was made of thin-walled Pyrex glass and was immersed in liquid nitrogen. The Pirani guage, used for pressure measurements during the reaction, was calibrated with the McLeod guage before the reaction. The sampler D was used for introduction of the reaction sample. After the reaction, the loop was immersed in liquid nitrogen for removal of the sample.

PLATE I
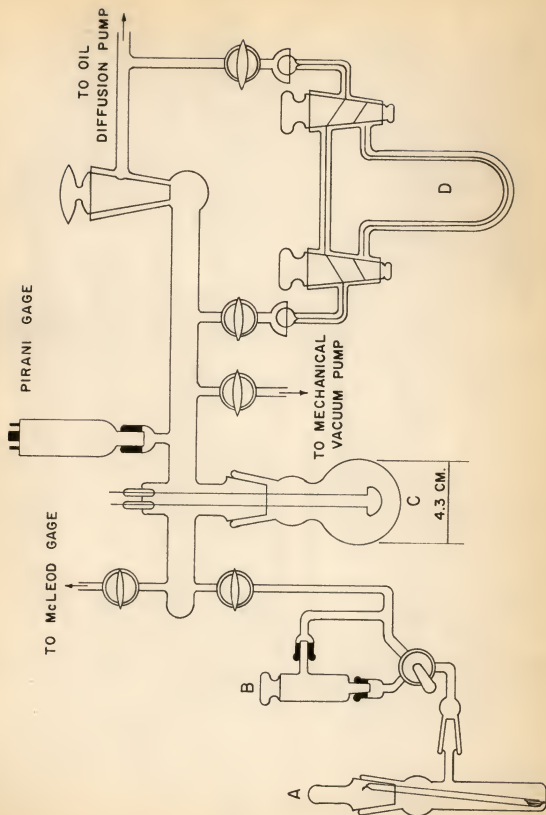
filament was determined. The filament was a 3.1 cm x 3 mil tungsten
wire or an 8 cm x 3 mil coiled tungsten wire suspended at the
center of the reaction flask by two molybdenum leads. A variable
transformer was used to control the filament temperature. An
optical pyrometer (Pyrometer Instrument Co. Model 95) was used to
measure the temperature of the filament at its center. Approx-
imately two thirds of the 3.1 cm filament was at the reported
temperature with the remainder at a lower temperature.

Reaction Vessel

Several different reaction vessels were used. In early ex-
periments a 250 cc volume flask was used. This was modified by
surrounding the filament with an open-structured grid in order to
eliminate thermionic emission. The negative pole of a 67.5 volt
battery was connected to the grid and the positive pole to one end
of the filament. The reactions were not noticeably affected by
the grid. With this in mind the reaction chamber C shown in
Figure 1 was constructed. It was a 50 ml flask made of thin-walled
Pyrex glass with a maximum filament-to-wall distance of 3 cm
(about the estimated mean free path of hydrogen atoms at 5μ).

Sample Introduction

The method of sample introduction depended upon whether the
sample was liquid or gaseous at room temperature. With liquid
samples, 0.1 to 0.25 ml of hydrocarbon was placed in an open portion
of the vacuum system with a hypodermic syringe or pipet, and then
the system was closed. With the hydrocarbon frozen, the system was
evacuated. The stopcock to the vacuum pump was shut off and the

hydrocarbon was allowed to transfer to a coldfinger extending into the reaction flask. While the hydrocarbon was condensed on the coldfinger, the reaction vessel was immersed in liquid air. As the coldfinger warmed up, a thin layer of hydrocarbon was uniformly deposited on the inner surface of the reaction vessel.

For the gaseous hydrocarbons, sampler D in Plate 1, containing a 1.325 ml loop for immersion into liquid nitrogen, was used to transfer both the gaseous hydrocarbons to the reaction chamber and the products from the reaction chamber to a gas chromatograph.

One end of the sampler was attached to a vacuum system and evacuated to less than $10\,\mu$. The system was closed and gaseous hydrocarbon was introduced to a desired pressure. The stopcock to the sampler was closed and the sampler was placed in the position as shown in Plate 1. The air was pumped out with the mechanical vacuum pump and the stopcocks to both the mechanical vacuum pump and the oil diffusion pump were closed before the sample was allowed to expand into the system and freeze out in the reaction vessel immersed in liquid nitrogen.

Sample Reaction

Samples were reacted differently depending upon the kind of hydrocarbon and the design of the vacuum system. In all cases the Pirani guage and the filament temperature were calibrated as previously described. A compound to be reacted was introduced into the vacuum system and frozen out with either liquid air or liquid nitrogen. Tritium was introduced into the system before the filament was switched on. With the 250 cc flask and the 0.9 mc/mmole tritium, from 0.1 to $0.2\,\mu$c was released into the system

(reaction flask and pressure guage) at a time. In the case of unsaturated hydrocarbons the pressure dropped from 10 to less than 1 μ within a few seconds during the reaction; reactions with paraffins showed little pressure change. Several times during a reaction with the paraffins, the system was evacuated and fresh hydrogen was released into the system. The total time for the saturated compounds was usually less than thirty minutes.

With the system shown in Plate 1, the same preliminary preparations were made. As soom as the sample was frozen, the system was evacuated to less than 0.05 μ . Hydrogen was then introduced through the high vacuum needle valve B. The isotopic composition of the gas phase was kept constant by continuously pumping out hydrogen being leaked into the system through the valve. The pumping rate was adjusted to give a turnover time of approximately one minute. The tritium content of the gas phase was thus maintained at 0.6 μc at a pressure of 5 μ. The reaction was timed from the instant the filament was turned on until it was shut off. The reaction time was usually five minutes.

Analysis

Following reaction, residual hydrogen and products that were gaseous at -195°C (methane and possibly ethane) were either removed by evacuation or were transferred with a Toepler pump into a sampling container and analyzed for methane by gas chromatography using a silica gel column.

Upon removing gaseous products, the remainder of the reaction products were transferred to another portion of the vacuum system for sampling. The labeled products (liquid at room temperature or 0°C

in the case of n-pentane) were separated by gas chromatography using a 140 cm Ucon non-polar column. Samples, 3 to 5 μl in size, were injected with a 10 μl syringe.

For cyclopropane and the other gases, samples were transferred into sampler D by immersing the loop in liquid nitrogen. The volume of the sampler was determined by measuring the volume of water required to fill it. One end of the sampler was removed from the vacuum system and a portion of the 2.00 ml volume was removed for total activity analysis. This was accomplished by placing another sampler, which had a volume of 0.68 ml above the stopcock, on sampler D and drawing a vacuum through the top part of D and the other sampler. The two way stopcock was switched, allowing the sample in the loop to expand into the sampler. The stopcock of the sampler was shut off and the remainder of the sample refrozen in the loop. Sampler D was placed in the chromatography carrier gas stream and the air in the sampler arms was flushed out with helium. As soon as the chromatography column reached equilibrium, the helium was passed through the loop, flushing the sample onto the column. Mixing of the sample with helium was minimized by using capillary tubing. A 15 foot dimethyl sulfolane column, operated at room temperature, was used for the separations.

Radioassay

For the total product analysis, the above portion of the sample was placed on the vacuum system and allowed to expand into a 250 cc ionization chamber which was then filled with hydrogen to atmospheric pressure and counted with a vibrating reed electrometer (60).

The vibrating reed electrometer was calibrated with standardized tritiated 1-hexene. For standardization 2 μl aliquots were placed into a toluene-phosphor counting solution and counted in a Tri-Carb liquid scintillation spectrometer which had an experimentally determined efficiency of 16.4 %. Two μl portions of the same 1-hexene sample were allowed to expand into an evacuated ionization chamber. It was then filled to atmospheric pressure with hydrogen and the discharge rate measured. The sensitivity in mv/μc sec was thus measured, and by knowing the fraction of the sample taken; the total activity of the sample was obtained. This, of course, did not include the activity of the methane since it was usually pumped off with the hydrogen.

In attempting to determine the distribution of tritium in the samples, different compounds were separated by the correct column packing but in spite of the sensitivity of the thermal conductivity cell, most activity peaks had no corresponding mass peaks, indicating that these components had a high specific activity. Therefore, fractions from the effluent gas chromatography stream were trapped in toluene-phosphor solution at 0°C and counted in a Tri-Carb scintillation spectrometer. In some cases, certain products were anticipated and carriers were used. This radioassay method left much to be desired because only a small number of the products could be identified.

The next method tried was that of Riez and Wilzback (61). The gas stream from the chromatography column was passed through an ionization chamber. This was an improvement since each component was detected as it left the chromatography column. This method had two disadvantages: (1) the vibrating reed electrometer used to

measure the ionization current was extremely temperimental; (2) the chamber was easily contaminated by condensation of certain compounds.

The most successful method of radioassay was with the use of a gas flow proportional counter similar to that described by Rowland and Wolfgang (62).

A 14 ml counter was constructed of brass tubing with a two mil tantalum wire suspended inside the tubing. A teflon plug, attached to a spring, kept the tantalum wire tightly stretched and insulated from the brass case.

The chromatography gas stream (helium) was converted into a counting gas by a continuous injection of methane in a 1:1 ratio. This gas mixture was passed through the proportional counter. A gas flow proportional counter of this type may detect activity as low as 10^{-9} curies (62).

RESULTS

Liquid Hydrocarbons

Table 2 summarizes the results of tritium atom reactions with six frozen hydrocarbons at low hydrogen pressures (initially ca. 10μ). Each of these hydrocarbons was reacted at a filament temperature of 1750°C. Reaction time varied with the compound reacted. Labeled products, liquid at room temperature or 0°C in the case of n-pentane, were obtained and analyzed. The use of carriers was made in some instances; the carriers indicated were added prior to the gas chromatographic separations. Identification of the light and heavy fractions was not made in all cases.

Under the reaction conditions indicated above, olefins react rapidly with hydrogen atoms. About 70% of the products observed were from addition reactions, 20 to 30% resulted from exchange of T for H and the remainder was either lower molecular weight compounds from cracking or combination reactions producing higher molecular weight compounds. Carriers were used to confirm the presence of some products.

The reactions of hydrogen atoms with paraffins were quite different from their reactions with unsaturated hydrocarbons. The rate of reaction with cyclohexane, n-hexane and n-pentane (Table 2) was much slower since exchange of T for H was the major reaction. The hydrogen pressure remained fairly constant, with only the cracking products incorporating hydrogen.

The reaction time for the paraffins was usually less than 30 minutes. Several times during the reaction, the gaseous products were pumped out and replaced with a fresh supply of hydrogen containing tritium.

With n-pentane, the gases at liquid air temperature were transferred with a Toepler pump into a sampling vessel and analyzed for methane which was found to be present in small quantities.[1]

Table 2 shows the results of a reaction of tritium atoms with benzene. In this particular reaction, cyclohexene and cyclohexadiene were not separated. By using 1-naphthylamine as a column packing, these two products were completely separated. Plate II is a chromatogram showing the distribution of labeled products

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[1]Storch (63) found ethane was the initial product of the decomposition of methane at low pressures on a hot carbon filament in a lamp bulb which was cooled in liquid nitrogen.
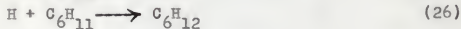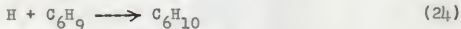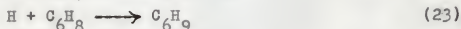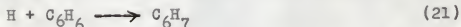
Table 2. Tritium analysis of chromatographic fractions

Compound	Compound reacted	Light* fraction	Heavy* fraction	Carrier fraction
Benzene	21	1	4	cyclohexane 35, cyclohexene 39
Cyclohexane	81	6	13	----
Cyclohexene	22	4	5	cyclohexane 69
1-hexene	27	1	3	n-hexane 69
n-hexane	83	5	12	----
n-pentane	83	13	4	----

*Light and heavy fractions were those collected before and after the emergence of the compound reacted, respectively, but did not include the activity in a carrier when one was present.

from one of the reactions with benzene carried out at a filament temperature of $1750^{\circ}C$ and 5μ pressure. The longer reactions contained a greater fraction of activity in the cyclohexane formed. This indicates that the following consecutive reactions occurred:

$$H + C_6H_6 \longrightarrow C_6H_7 \tag{21}$$

$$H + C_6H_7 \longrightarrow C_6H_8 \tag{22}$$

$$H + C_6H_8 \longrightarrow C_6H_9 \tag{23}$$

$$H + C_6H_9 \longrightarrow C_6H_{10} \tag{24}$$

$$H + C_6H_{10} \longrightarrow C_6H_{11} \tag{25}$$

$$H + C_6H_{11} \longrightarrow C_6H_{12} \tag{26}$$

Gaseous Hydrocarbons

Hydrogen atoms were reacted with cyclopropane under various

experimental conditions. Table 3[1] shows results of reaction of
cyclopropane at four different filament temperatures and three
different pressures. Plate 3 is a chromatogram showing the
distribution of labeled products that was obtained from one of the
reactions carried out at 1600°C and 5 μ pressure. As indicated
from this chromatogram and Table 3, cyclopropane-T and propane-T
were the most abundant products in all cyclopropane reactions.
Other products, excepting methane, methylcyclopropane and C_6 hydro-
carbons are designated. Analysis for methane requires special
procedures as indicated on page 23. Methylcyclopropane appeared in
detectable quantities only at the higher filament temperatures.
The C_6 hydrocarbons were present on the original chromatogram but
their retention volumes were too great to conveniently show.

Table 4 gives results of reactions with different amounts of
cyclopropane. Film thicknesses of frozen cyclopropane for these
reactions were approximately 4 x 10^{-5}cm, 6 x 10^{-7}cm and 6 x 10^{-8}cm.

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[1]It was found that there were traces of propene in the cyclo-
propane. Table 3A shows the results of similar reactions where
the cyclopropane was purified by gas chromatography before the
reaction with hydrogen atoms. The propene impurity increased the
amount of propane formed during the reaction.

EXPLAINATION OF PLATE II

Chromatogram of Benzene Reacted with Tritium Atoms

The chromatogram shows products from a 30 second reaction
of hydrogen atoms with benzene. The hydrogen atoms were produced
at 5 μ pressure at a filament temperature of 1750°C. The
reaction products were separated with a 3 foot 1-naphthylamine
column.

PLATE II
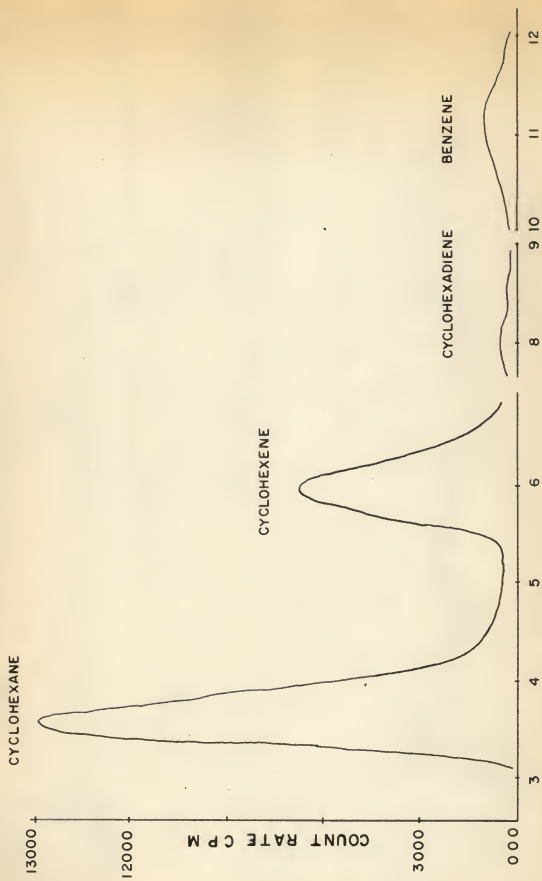
Table 3. Products of tritium atom reactions with cyclopropane

Filament Temperature	1100°C			1400°C			1600°C			1800°C	
Hydrogen Pressure, microns	3	5	7	3	5	7	3	5	7	3	5
Total Tritium, μc*	0.02	0.03	0.04	0.07	0.10	0.13	0.18	0.26	0.30	0.56	0.77
Distribution of tritium – percent											
Ethane	6	18	6	11	10	22	9	9	14	8	7
Propane	62	58	64	56	53	43	36	37	41	31	27
Isobutane	15	13	14	3	3	3	3	4	4	3	4
Butane	--	--	--	2	3	2	2	4	2	3	4
Cyclopropane	--	--	--	17	18	14	42	36	32	47	49
Isopentane + Methylcyclopropane	--	--	--	5	3	3	2	4	2	4	3
Pentane	--	--	--	1	4	2	2	2	2	2	2
Hexanes	17	11	16	6	6	11	3	3	3	2	4

*Does not include methane.

Table 3A. Products of tritium atom reactions with cyclopropane

Filament Temperature	1100°C	1400°C	1600°C
Hydrogen Pressure, microns	5	5	5
Distribution of tritium - percent			
Ethane	81	37	12
Propane	19	15	23
Isobutane	--	8	7
Butane	--	7	5
Cyclopropane	--	14	37
Isopentane	--	7	6
n-Pentane	--	5	4
Hexanes	--	7	6

EXPLAINATION OF PLATE III

Chromatogram of Cyclopropane Reacted with Tritium Atoms

The reaction products were separated with a 15 foot dimethyl
sulfolane column. Their activities were detected with a gas
flow proportional counter.

PLATE III
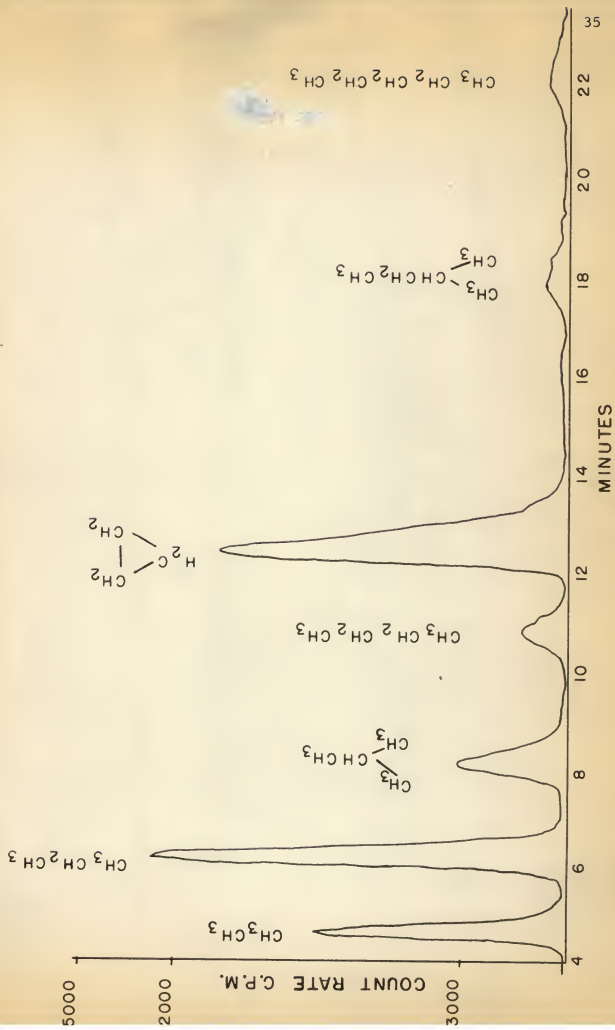
DISCUSSION

Reaction Mechanism

Mechanisms for reaction of hydrogen atoms vary with the method of atom production and the reaction conditions. In each case mechanisms involving free radicals have been proposed.

Klein and Scheer (35, 36) studied the reaction of frozen olefins with hydrogen atoms produced by a hot tungsten filament. They proposed a free radical mechanism that involved addition of a hydrogen atom to a double bond to produce a free radical. Free radicals produced in this manner could either combine with hydrogen atoms to produce corresponding alkanes or two free radicals could combine. Free radicals usually react by disproportionation, combination or hydrogen abstraction (56-58). In each reaction of deuterium atoms with propene, Klein and Scheer (37) found the rate of disproportionation to be 9 times greater than combination. They maintained that labeled propene was produced only through disproportionation and not by hydrogen abstraction from the radical. They observed no cracking products from their reactions.

Schiff and Steacie (12) found that hydrogen atoms, produced by the discharge method, react with cyclopropane and most other paraffins to produce methane as the major product. They proposed hydrogen abstraction as the initial reaction. The free radical thus formed could react with a hydrogen atom, splitting into two free radicals. Methane results from the combination of a hydrogen atom with a methyl radical.
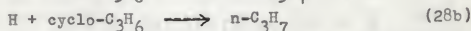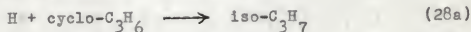
One of the principal mechanism used in explaining products of reactions with recoil tritons involves formation of an intermediate-

molecule-tritium complex possessing excess energy. This complex then undergoes subsequent reaction to form the reaction products. This mechanism was proposed because radical scavengers reduced the products from thermal reactions but did not affect the hot reactions.

Free radical reactions can account for all of the products we observed from reactions of hydrogen atoms with cyclopropane. For example, atom-radical and radical-radical combinations of hydrogen, methyl, ethyl, propyl, isopropyl and cyclopropyl free radicals can account for all of the products observed with cyclopropane. Cyclopropyl free radicals could result from hydrogen atom abstraction (Equation 27):

$$H + cyclo\text{-}C_3H_6 \longrightarrow H_2 + cyclo\text{-}C_3H_5 \qquad (27)$$
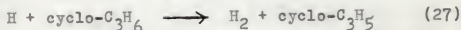
hydrogen atom addition to cyclopropane would yield isopropyl and propyl free radicals (Equations 28a and 28b):

$$H + cyclo\text{-}C_3H_6 \longrightarrow iso\text{-}C_3H_7 \qquad (28a)$$

$$H + cyclo\text{-}C_3H_6 \longrightarrow n\text{-}C_3H_7 \qquad (28b)$$

and methyl and ethyl free radicals could result from cracking of excited propane (53) following hydrogen addition to propyl free radicals (Equations 29a and 29b).

$$C_3H_7 + H \longrightarrow C_3H_8^* \qquad (29a)$$

$$C_3H_8^* \longrightarrow CH_3 + C_2H_5 \qquad (29b)$$
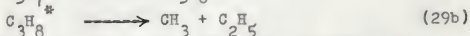
Exchange via formation of cyclopropyl free radicals instead of an intermediate cyclopropane-tritium-complex is preferred for two reasons: presence of methylcyclopropane as a product and a marked decrease of cyclopropane-T accompanying reduction of film thickness (Table 4). Formation of methylcyclopropane is accounted for by the combination of methyl and cyclopropyl free radicals (Equation 30).

$$\text{cyclo-}C_3H_5 + CH_3 \longrightarrow \text{cyclo-}C_3H_5CH_3 \qquad (30)$$
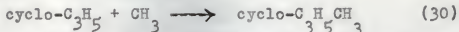
A decreased yield of cyclopropane-T would be expected as the concentration of cyclopropyl free radicals and hydrogen atoms is decreased in thinner films. Calculations using the atomization rate of Brennan and Fletcher (42), indicate that approximately 10^{17} atoms per second are formed at $1600^{\circ}C$ and 5μ hydrogen pressure. When the cyclopropane is 1000 molecular layers thick (4.3×10^{-2} mmoles), some cyclopropyl radicals that form probably become isolated in the matrix and react with hydrogen atoms diffusing through the matrix (Equation 31).

$$T + \text{cyclo-}C_3H_5 \longrightarrow \text{cyclo-}C_3H_5T \qquad (31)$$

By reducing the cyclopropane film to only 1 molecular layer (5.7×10^{-5} mmoles), there was very little matrix available for stabilization. The radicals probably reacted with energetic atoms or formed other cracking products.

The rate of formation of a molecule-tritium-complex should be independent of the film thickness. As long as the surface is covered, rate of formation of the molecule-tritium-complex possessing excess energy should be constant because the atoms would have to react on the surface to have excess energy. The molecular film thickness was found by knowing the number of molecules present, calculating the surface area of the flask and assuming a uniform coverage.

A study of product yield as a function of time should help establish the mechanism for exchange of T for H in saturated hydrocarbons. If the reaction involves formation of an intermediate molecule-tritium-complex possessing excess energy, the rate of exchange should be independent of time because the decomposition

of the intermediate is a fast process. If the exchange reaction occurs via a free radical intermediate, the free radical formed may diffuse into the matrix, becoming stabilized. The concentration of free radicals would build up until a steady state is reached. It would seem that only a few atoms would exchange at the beginning but as the steady-state concentration of radicals was reached, it would become a linear function. The rate of exchange involving a free radical intermediate would be expected to be time dependent.

A possible reaction mechanism could be that of induced tritium labeling of the organic compounds brought about by absorption of radiation. This technique, ofter called "gas exposure", was developed by Wilzbach (61,64). The activation energy necessary for labeling is provided by the disintegration of tritium. Absorption of energy is made large by using a high pressure (approximately 1 atm.) and a high isotopic concentration of tritium. Our reaction system conditions met neither of these requirements: therefore this mechanism could not possibly account for the tritium labeling shown in our results.

Reactions could possibly have been induced by thermionic emission from the heated filament. However, our results were not noticeably affected by elimination of thermionic emission with the use of a negatively charged grid. In a larger reaction vessel (250 cc volume) the filament was surrounded by a wire grid having an open structure. The negative pole of a 67.5 volt battery was connected to the grid and the positive pole to one end of the filament.

Effect of Experimental Conditions on Reaction Products

Hydrogen atoms react with hydrocarbons under a variety of

experimental conditions. With unsaturated compounds, both addition and substitution were observed; with saturated compounds, substitution was usually the principal reaction that occurred. Unlike previous results, hydrogen atoms reacted with n-pentane (36), 1-hexene (36) and cyclopropane (12). This is believed due to lower pressures and a shorter filament-to-wall distance, resulting in fewer hydrogen atom collisions before reaction. Reactions occurred because the hydrogen atoms were more energetic.

Our experiments show that different reactions occur under different experimental conditions. By controlling filament temperature and hydrogen pressures, the hydrogen atom production and the average energy of the atoms can be controlled. Brennan and Fletcher (42) have reported information on the mechanism of atomization of hydrogen on tungsten. They proposed that equilibrum is maintained between adsorbed and gaseous hydrogen and that atomic and molecular hydrogen desorb in their equilibrium ratio as determined by the temperature of the surface and the pressure of the undissociated gas. A Maxwell-Boltzmann distribution of hydrogen atom energies is reasonable on this basis. Using the results of Brennan and Fletcher, hydrogen atom production should increase twenty-fold as the filament temperature is increased from 1400 to 1800°C. The corresponding rate of tritium incorporation in cyclopropane varied with the reaction flask used, but never exceeded an eight fold increase. This indicates that pressure effects as well as atomization must be considered. Results from Table 3 show, at constant temperature and pressures below 7 μ, more tritium was incorporated at higher pressures. The product distribution was not affected very much by pressure changes below 7μ. A decrease in percent

exchange of T for H with cyclopropane was observed when $50\,\mu$ pressure of helium was added. The excess energy of the hydrogen atoms was removed through collisions with helium atoms, resulting in fewer reactions.

Temperature effects other than increased atomization, have also been observed. These effects are shown in Table 3. It can be seen that percent exchange increases with filament temperature in the energy range of 1400 to 1800°C. If the atoms leave the filament with a Maxwell-Boltzmann distribution of energies, the absence of detectable exchange at 1100° may be explained by activation energies. Schiff and Steacie (12) did not observe exchange of D for H in cyclopropane with deuterium atoms produced by the discharge method at higher pressures (several mm pressure). They suggested that the deuterium atoms were not energetic enough to overcome the high activation energy for the exchange process. Our results at low filament temperature are in agreement with Schiff and Steacie. Calculation of activation energies (Plate IV) from the present data gives unreasonably low values when the literature values of 44 to 67 kcal for the associated atomization process are considered. The activation energy should be greater than the activation energy for hydrogen atomization, yet our calculations yield activation energies for some reactions which are less than that required for atomization. This indicates that either the incorporation of tritium atoms is independent of the atomization process or some other processes may be occurring which cause the activation energy to appear lower than it actually is. One such process may be that of swamping the surface with hydrogen atoms. There are approximately 3×10^{16} surface

EXPLANATION OF PLATE IV

Plate IV is an Arrehnius plot to determine activation
energies for the two reactions indicated. The values 56
kcal/mole and 23 kcal/mole were calculated from the slopes.

PLATE IV
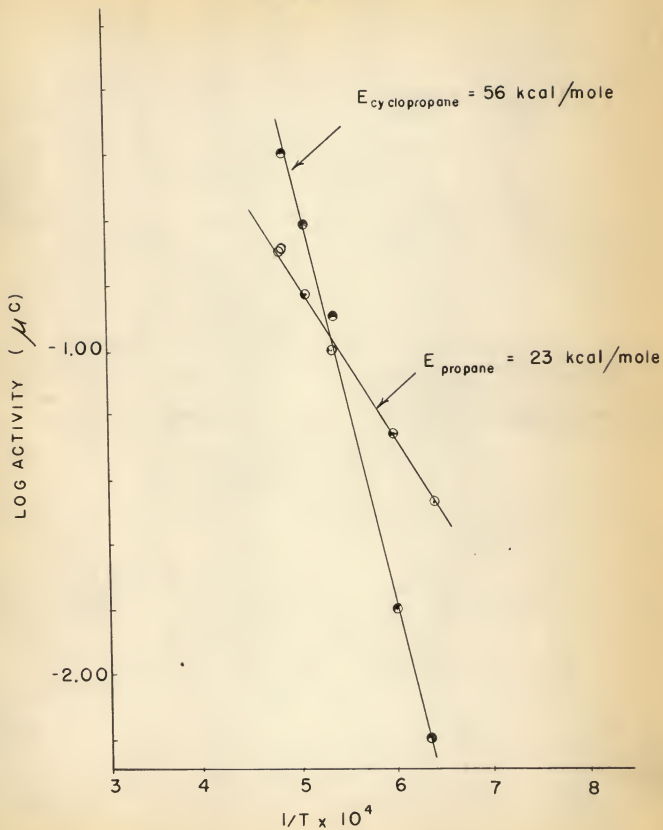
molecules while there are about 10^{17} hydrogen atoms produced per second at 1600°C and $5\,\mu$ hydrogen pressure. Another possible explaination may be that of contamination of the filament. Brennan and Fletcher (42) believe that contamination of the filament results in low activation energies. Nonuniform heating of the filament must also be considered. Approximately 2/3 of the filament was at the reported temperature with both ends at a lower temperature. This would result in fewer hydrogen atoms than calculated and this would have the effect of an increased activation energy.

Tritium Labeling

Tritium atom exposure could be a method of labeling organic compounds. For this method to be feasible, a high specific activity of the pure compounds must be produced at reasonable rates. We have found that 4.3×10^{-2} mmoles of cyclopropane will incorporate 0.77 μc of tritium in five minutes under our experimental conditions. Approximately 50% of the products from such a reaction is cyclopropane-T. If tritium gas were used under similar conditions, cyclopropane with a specific activity of 30 mc/mmole could be produced. Longer reaction times would increase the specific activity. We found that tritium atoms have reacted by exchange of T for H with all organic compounds tried. The compounds reacted include alkanes, alkenes, aromatics, alcohols (65), carbonyl compounds (65) and even complex molecules such as quercetin (66).

If good purification methods are available, tritiated organic compounds can readily be prepared at low costs. The products produced by this method are not specific in the positions labeled.

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REACTIONS OF TRITIUM ATOMS
WITH FROZEN HYDROCARBONS

by

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Reactions of tritium atoms with frozen hydrocarbons were studied. Tritium atoms were produced by the atomization of hydrogen containing tritium at a hot-tungsten filament. The average energy of the tritium atoms was dependent upon the filament temperature, which was kept constant throughout each reaction. Filament temperatures in the range of 1100 to 1800°C were used. Because collisions reduce the excess energy of the tritium atoms, hydrogen pressures were usually maintained below 10μ. A reaction vessel was constructed so that the maximum filament-to-wall distance was approximately one mean free path at 5μ pressure. Under these conditions a large fraction of the tritium atoms reacted with energies in excess of those corresponding to the temperature of the frozen hydrocarbon.

Thin films of frozen n-pentane, n-hexane, cyclohexane, cyclopropane, 1-hexene, cyclohexene and benzene were exposed to energetic tritium atoms for various times. The reaction products were separated by gas chromatography. Identification was determined by the retention volume of known hydrocarbons. Two methods of radioassay were used: the gas stream from the chromatography column was passed through an ionization chamber or proportional counter, or fractions from the effluent stream were trapped in a toluene-phosphor solution cooled to 0°C and counted in a Tri-Carb scintillation spectrometer.

Reaction products were dependent upon the compound reacted and the experimental conditions. With unsaturated compounds, addition and exchange were observed principally; with saturated compounds, substitution of T for H was usually the predominant reaction. With cyclopropane, a study of percent exchange vs. filament temperature showed that an increase in filament temperature resulted in an increase of cyclopropane-T. Absence of cyclopropane-T in products

at lower filament temperatures indicates that the activation energy
for exchange of T for H is larger than that for ring cleavage to
form propene-T. Pressure changes below 7μ affect the rate of
tritium incorporation but do not affect the product distribution
very much. The addition of helium as a moderator reduced the rate
of tritium incorporation and altered the product distribution.

A free radical mechanism was proposed for reactions with cyclo-
propane. Atom-radical and radical-radical combinations of hydrogen,
methyl, ethyl, propyl, isopropyl and cyclopropyl free radicals can
account for all of the products observed with cyclopropane. Reduct-
ion of film thickness resulted in reduction of cyclopropane-T.
This was believed due to a decrease in stabilization of the free
radicals as the cyclopropane matrix was reduced.