

REACTION OF HYDROGEN ATOMS  
WITH PROPENE AT 77°K

by

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## INTRODUCTION

When a hydrogen atom reacts with an olefin, the corresponding alkyl radical is usually formed. A free radical thus formed usually reacts with another radical or atom to yield an alkane or an alkene or both. In reactions of alkyl radicals with hydrogen atoms, the reaction products vary with the method of atomization and chemical conditions involved.

Propene frozen at  $77^{\circ}\text{K}$  has been bombarded with hydrogen and tritium atoms emanating from a tungsten which was suspended in an atmosphere of  $\text{HT}$  and  $\text{H}_2$  at low pressure. Products of the reactions were separated by gas chromatography and counted with a proportional counter placed in the effluent stream.

Propane, propene and 2,3-dimethylbutane were major products. Ethane and methane were minor products at low filament temperature and thin films. At elevated filament temperatures and thicker films various four to six carbon compounds were observed.

It was evident that  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{iso-C}_3\text{H}_7$  and  $\text{n-C}_3\text{H}_7$  radicals were formed by hydrogen atom reactions with frozen propene, on the basis of the reaction products. From the effects of dilution with inert hydrocarbons, a predominance of surface reactions of free radicals is strongly indicated.

## LITERATURE REVIEW

The literature has been reviewed in three major areas; atom-

ization of hydrogen molecules, reactions of hydrocarbons with hydrogen atoms, and reactions of alkyl radicals.

### Atomization of Hydrogen

Experimental method of atomization. There have been several methods of producing hydrogen atoms, e.g., thermal, electrical discharge, microwave discharge, heated filaments, photochemical and neutron irradiation.

The thermal method (10) is usually applied to the studies of H atoms with very stable compounds such as methane, ammonia and water gas. The great disadvantage of this method results from the very low efficiency of production of atoms except at moderately high temperatures.

Table 1. Dissociation of Diatomic Molecules (30).

Substance	Heat of dissociation Kcal.	(pressure 1 mm) Temp. °K at which the degree of dissociation is		
		1%	0.01%	0.0001%
Iodine	35.2	680	510	410
Bromine	45.2	850	640	510
Chlorine	56.9	1040	800	640
Hydrogen	102.7	1910	1425	1140
Deuterium	104.6	1920	1440	1160

Table 2. Heats of Dissociation of Hydrogen Isotopes in Kcal. per Mole (30).

Temperature °K	H <sub>2</sub>	HD	D <sub>2</sub>
0	102.985	104.064	104.991
298.16	104.177	104.992	105.962

There are two types of electrical discharge methods: glow and electrodeless discharge, and arc and spark discharge. No doubt the main effects of these discharges are due to localized heating of the gas to 1550°C or higher.

Wood (37) showed that hydrogen atoms could be pumped out of a glow discharge in hydrogen and carried for considerable distance before they recombined. For the success of the experiments, it was essential that the wall of the tube be "poisoned" to slow down the recombination of phosphoric acid, fused solid phosphoric acid or potassium chloride.

Photochemical or photosensitized methods are very useful for the study of free radicals in the gas phase. When a molecule absorbs light in the continuum the primary process involves splitting into atoms or radicals, and if some other substance is present, the fragments produced may react with it.



The reactions are generally chain processes.

In order that a photochemical reaction may occur it is necessary that the magnitude of the quantum of the incident light be large enough and also that the light be absorbed. The hydrogen molecule has a dissociation energy corresponding to a wavelength of about 2750 Å. If we add to hydrogen a substance which will absorb somewhere below 2750 Å and can transfer this energy to hydrogen we can produce a photosensitized dissociation of hydrogen.

Methods Using Heated Filaments. Langmuir and Freeman (11,20,21)

showed that at high temperature hydrogen was dissociated into atoms on the filament and that the atomic hydrogen produced reached the walls of the bulbs at low pressures, where its reactivity was shown by the reduction of metallic oxides and other reactions.

Klein and Scheer (16) reported that tungsten centrally located in a vessel was heated to  $1800^{\circ}\text{C}$  to produce hydrogen atoms. They reached the walls without recombining. The reaction with olefins was followed by the pressure decrease. Hydrogen initially at 30 microns reacted completely with propene in 8 seconds. At least 80 percent of propene, butene-1 and isobutene could be hydrogenated at liquid nitrogen temperature.

Microwave Discharge Method. Shaw (27) has studied dissociation of hydrogen in a microwave discharge and reported that the maximum yield of hydrogen atoms was obtained at a pressure of 0.5 mm Hg and was about 25 percent less at 0.25 mm and 1.0 mm. At 0.5 mm Hg about 90 percent of the hydrogen was dissociated. The main advantages of the microwave discharge are the same as those for the electrodeless discharge with the added feature that an efficient coupling of the microwave power to a discharge can be achieved readily.

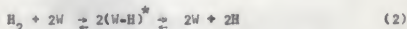
Kinetics of Hydrogen Atomization on Hot Tungsten Filaments.

Brennen and Fletcher (4) found that at temperatures below  $1400^{\circ}\text{K}$ , and at pressures exceeding  $10^{-6}$  mm, the rate of atomization of hydrogen is

$$V_a \text{ (atoms cm}^{-2}\text{sec}^{-1}\text{)} = 18 \cdot 10^{24} (P_{\text{H}_2})^{\frac{1}{2}} \exp -52600/RT. \quad (1)$$



Their proposed mechanism of atomization is



which was discussed in terms of the absolute reaction rate theory. At a temperature of  $1800^\circ\text{K}$ , the rate of reaction was found to be linearly dependent on  $P_{\text{H}_2}$  at pressures less than  $10^{-6}$  mm. The mechanism proposed involved free translatory motion of adsorbed atoms at the temperature of reaction, and an activation energy of one-half the bond energy was proposed as consistent with this mechanism.

T. W. Hickmott (14) proposed that when hydrogen chemisorbs on tungsten at  $77^\circ\text{K}$ , the sticking probability is 0.1. He found that the rate of evaporation of atomic hydrogen, for a filament temperature above  $1100^\circ\text{K}$ , was

$$V_a = (2.2 \cdot 10^{13}) n \exp -67000/RT \text{ molecules/cm}^2 \text{ sec.} \quad (3)$$

where  $n$  is the number of adsorbed hydrogen molecules/cm<sup>2</sup>.

From the study of hydrogen atom production by a hot filament and trapped by glass at liquid nitrogen temperature, Hickmott (14) proposed that the total rate of reaction,  $dn/dt$ , could be expressed as:

$$dn/dt = (dn/dt)_{\text{adsorp}} - k_A n - k_2 n^2, \quad (4)$$

where  $(dn/dt)_{\text{adsorp}}$  = rate of adsorption of atomic hydrogen by the filament and is neglected since it is assumed that all atomic hydrogen is trapped or recombined at the walls, and rate of atomization,

$k_A = \gamma_a \exp -\Delta H_a/RT$ . Rate of desorption,  $k_2 = \gamma_2 \exp -\Delta H_2/RT$ , may be



determined from desorption kinetics. He found

$$\Delta H_a = 67 \text{ Kcal/mole}$$

$$\Delta H_2 = 31 \text{ Kcal/mole}$$

which is in agreement with the value of the heat of dissociation of hydrogen,

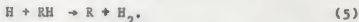
$$D(H-H) = 2\Delta H_a - \Delta H_2$$

$$2 \cdot 67 - 31 = 103 \text{ Kcal/mole.}$$

Also Hickmott (15) proposed that recombination of atomic hydrogen on glass surfaces at 77°K occurs at low surface coverage of adsorbed hydrogen atoms. In other words, the rate of recombination of hydrogen atoms bound to the glass is proportional to the number adsorbed and is much smaller than the rate of hydrogen atoms impinging on a glass surface from the vapor phase.

#### Reaction of Hydrocarbons with Hydrogen Atoms

Reactions in the Gas Phase. Schiff and Steacie (26) proposed the initial reaction of hydrogen atoms with alkanes is the abstraction reaction,



This is only responsible for the products formed in the reaction, and other primary processes may be responsible for the exchange of hydrogen. The rate of exchange increased with increasing molecular

weight.

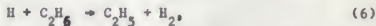
The activation energies listed in the Table 3 are derived from collision-yield data at room temperature, on the assumption that the steric factor is 0.1. Actually, the activation energies of the reactions of hydrogen atoms with the paraffins are lower than the value in Table 3.

Table 3. Activation Energies (31).

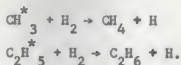
Compound RH	Activation energy of $H + RH \rightarrow R + H_2$ Kcal/mole
CH <sub>4</sub>	12.9
C <sub>2</sub> H <sub>6</sub>	9.0
propane	8.7
n-butane	9.3
s-butane	9.3
neo-pentane	9.2

because the steric factors are of the order of  $10^{-2}$  to  $10^{-5}$ . Berluc and LeRoy (1), using hydrogen atoms produced thermally by means of a hot filament, proposed that the consumption of hydrogen atoms along the reaction vessel in the Wood-Bonhoeffer method is a major source of error.

They obtained a value of the activation energy for the reaction,



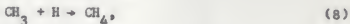
of 6.2 Kcal. with a steric factor of the order of  $10^{-3}$ . This probably indicates that all the above activation energies are too high, and that the frequency factors for all these reactions are correspondingly low. Also we can expect the following reverse reactions



The reactions of various hydrocarbons with hydrogen atoms were investigated by the discharge-tube method by Bonhoeffer and Hartek (2). Methane was found inert in the presence of atomic hydrogen at room temperature (no reaction occurred up to 1830°C). They therefore concluded that the reaction,

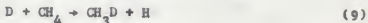


had an activation energy of at least 17 Kcal. (assuming a steric factor of 0.1). It might be suggested that the following reaction occurs readily,



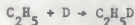
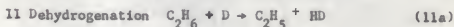
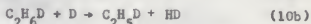
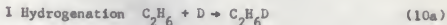
and proceeds more rapidly than other possible reactions of the methyl radical such as  $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$  so that methane is reformed as fast as it is consumed.

Geib and Steacie (12) studied this reaction using D atoms produced by the Wood-Bonhoeffer technique.

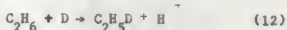


They found that at higher temperatures the D atom concentration fell off greatly. Thus it could be assumed that atoms are consumed by reaction (7) at higher temperature.

Stacie and Phillips (32) investigated the reaction of D atoms with ethane, using the Wood-Bonhoeffer method and found an activation energy of 6.3 Kcal. assuming a steric factor of 0.1 for the exchange reaction. They proposed three main possibilities for the mechanism of the reaction.



III Exchange by methathesis

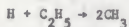
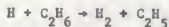


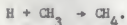
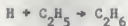
They (33) concluded that mechanism II is correct and that the measured activation energy (6.3 Kcal/mole) is that of reaction 11a. However, Trenner, Morikawa and Taylor (34) concluded that at room temperature the main reaction is



with activation energy of 7.2 Kcal. and that the exchange reaction is only appreciable at temperatures from 100°C up.

All reactions for ethane with hydrogen atoms are,





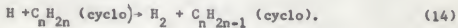
Obviously the initial reaction leads to exchange.

Schiff and Steacie (26) stated that of the cycloalkanes, cyclopropane is most inert and cyclopentane the most reactive with H atoms. Cyclopropane and cyclobutane do not exchange with thermal D atoms at room temperature but benzene, cyclopentane, and cyclohexane undergo considerable exchange.

Table 4. Reactions of Cyclohydrocarbons and D Atoms (26).

H atom collision yield $10^7$	Activation Energy, P 0.1	D. Atom	
		Coll. Yield $10^7$ for Decom.	$10^7$ for Exch.
cyclopropane	0.11	9.5	0.34
cyclobutane	1.1	8.2	0
cyclopentane	3.0	7.5	5.2
cyclohexane	1.4	8.0	3.3

Table 4 shows the same order of reactivity as that for hydrogen abstraction from the cycloparaffins by methyl radical and suggests that the bond dissociation energy  $D(\text{R-H})$  controls the reactivities. Collision yields for exchange follow the same order, thus suggesting that the primary process in each case is,



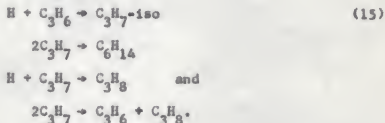
Moore and Taylor (23) investigated the mercury sensitized reaction of hydrogen-propene mixtures. The experiments were carried out

with 40 mm of propene and sixfold excess of hydrogen.

The main products were:

Methane	2 percent	n-Butane	5 percent
Ethane	1 percent	Isopentane	2 percent
Propane	26 percent	2,3-Dimethylbutane	64 percent

This indicates that the main reactions are:



The first reaction (15) has a low activation energy.

Further work by Moore (24) gave, in an 8:1 hydrogen-propene mixture, only one important  $\text{C}_6$  compound in the products, 2,3 dimethylbutane, so that reaction (15) is reasonable. He suggested that the difference between activation energies for the formation of  $n\text{C}_3\text{H}_7$  and  $\text{iso-C}_3\text{H}_7$  is 2.4 Kcal.

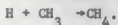
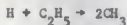
Table 5. Reaction of Hydrogen Atoms with Propene (25).

Temperature $^{\circ}\text{C}$	% Reaction	Collision yield $10^6$	Act. energy assuming $P=0.1$
30	44.9	0.918	7.0
100	42.3	1.63	8.3
170	39.0	1.95	9.6
250	38.8	2.92	10.8

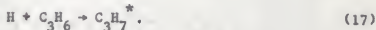
Rabinowitch, Davis and Winkler (25), using the discharge-tube method

suggested that the primary step is:  $H + C_3H_6 \rightarrow C_3H_7^*$ , (a)

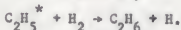
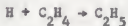
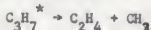
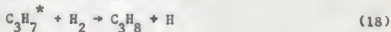
with secondary reactions:



Reaction (a) is about 40 Kcal. exothermic resulting in the formation of excited propyl radicals.



Therefore even at room temperature, the resulting propyl radicals undergo the following reactions which would normally be expected only at high temperatures:



The ethyl radical can be assumed to be "hot" for similar reasons. On this basis it is possible to account for their experimental results, including the independence of the products.

Reactions with Frozen Hydrocarbons. Klein and Scheer (16) reported that hydrogen and deuterium atoms produced at a hot tungsten ribbon reacted readily with some solid olefins at 77°K. They also reported that

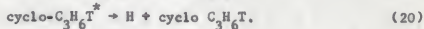
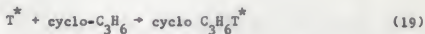


H and D atoms do not undergo exchange reaction with solid propane on the same condition (17). However, Shores and Moser (28) showed that the exchange of tritium for hydrogen occurred at 77°K when tritium atoms were generated by a hot filament and reacted with the presence of five hydrocarbons.

Table 6. Tritium Analysis of Chromatographic Fractions (28).

Compound	Compound Reacted	Distribution of Tritium %		Carrier
		Light Fraction	Heavy Fraction	
Benzene	21	1	4	cyclohexane-35
Cyclohexane	81	6	13	cyclohexane-39
Cyclohexene	22	4	5	cyclohexane-69
Hexene-1	27	1	3	n-hexane-69
n-Hexane	83	5	12	
n-Pentane	83	13	4	

Lee, Musgrave and Rowland (22) studied the reaction of cyclopropane with recoil tritium atoms in the gas phase and suggested the mechanism for exchange was



"Hot" reactions were proposed that involved single-step interactions of energetic tritium atoms with cyclopropane.

Shores (24) also has studied reaction of frozen cyclopropane with tritium atoms produced by hot tungsten ribbon. Table 7 shows that the main reaction is exchange.

Table 7. Reaction of Tritium and Cyclopropane at 77°K (29).

Amounts of $\Delta$ , mmoles		$4.3 \cdot 10^{-2}$	$5.7 \cdot 10^{-4}$	$5.7 \cdot 10^{-5}$
Total tritium $\mu$ c		0.26	0.29	0.20
ethane	percent	9	19	35
propene		37	27	26
isobutane		4	8	11
butane		4	7	11
cyclopropane		36	26	4
isopentane & methylcyclopropane		4	6	7
2,3 dimethylbutane		3	4	2
Filament temperature		1600 C		
Hydrogen pressure		5 $\mu$		

Klein and Scheer (16,17,18,19) have investigated the reactions of hydrogen atoms with solid olefins at 77°K, the products were corresponding alkanes, alkenes and alkyl dimers. They observed that even with a hundred fold dilution of propene with inert diluent such as butane, the alkane/dimer ratio remains unaffected.

Table 8. Reaction of H Atoms with Propene and Butene-1 at 77°K  
Products Analysis by Mass Spectrometer (19).

H + propene		H + butene-1	
propene	37 percent	n-butane	56 percent
propene	58	butene-2 (mostly)	40
2,3-dimethylbutane	5	3,4-dimethylhexane	4
Temperature of tungsten ribbon		1500°C	

Further work by Klein and Scheer showed that the temperature of tungsten ribbon only affected the rate of hydrogen dissociation at the filament and did not affect the product distribution. Also they em-

phasized that hydrogen atoms readily diffuse through the olefin films and react to form alkyl radicals, which then combine with hydrogen atoms to give saturated products.

Table 9. Relative Rate of Hydrogenation at 77°K (19).

propene	10.0
butene-1	8.0
3 mebutene-1	4.0
isobutene	1.0
pentene-1	0.1
hexene-1	0

Klein and Scheer (19) applied the thermal conductivity equation for hydrogenation and concluded that the large amounts of heat evolved during hydrogenation do not cause significant temperature gradients and even the heat from the hot-tungsten ribbon could not cause a temperature difference of more than 0.025°C. The dependence on temperature of the rates (19) for different olefins suggested the following activation energies for  $H + \text{Olefin} \rightarrow R$  ( $E_{\text{act}}$  for  $R + H \rightarrow \text{Sat.}$  being assumed to be zero).

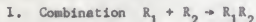
Table 10. Activation Energy for Olefins.

Olefin	Temperature	$E_{\text{act}}$ Kcal/mole
propene	77-86K	1.5
butene-1	91-113	1.0
isobutene	91-113	3.0
hexene-1	117-130	4.1

In the gas phase, they are all approximately 2.5 Kcal/mole (19).

### Reactions of Alkyl Radicals

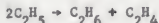
The presence of unpaired electrons in free radicals are very important in determining their chemical and physical properties. All radical reactions occur in such a way as to reduce the instability associated with the lone electrons. All the reactions of monoradicals belong to one of four groups (35).



II. Methathetical or transfer reaction



also disproportionation such as

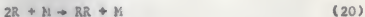


III. Addition of radical to an unsaturated compound



IV. Rearrangement or isomerization of radicals

The most of common bimolecular reactions are those which occur when two radicals disappear from a system with the formation of stable products. They are recombination and disproportionation of radicals. However, the combination of atoms or radicals in the gas phase is not a simple bimolecular reaction. When two atoms come together, the resultant complex contains sufficient energy to decompose. Decomposition will ensue unless this energy is removed by collision with another molecule. In this case the life of the activated complex is very short.

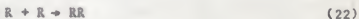
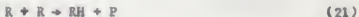


These reactions are therefore third order and may be considered termolecular where M is an energy transfer agent. Combination of radicals has zero activation energy. This is reasonable as one would not expect there to be any barrier for the combination of two radicals.

Table 11. The Combination of Small Radicals (35).

Reaction	Activation Energy Kcal/mole
$CH_3 + CH_3$	0
$C_2H_5 + C_2H_5$	2.0
$CF_3 + CF_3$	0
$NO_2 + NO_2$	0

Three significant products are formed in any system in which two alkyl radicals disproportionate;



where P is corresponding alkene. For propene + H at 20°C and 20 mm Hg,  $k_{\text{disp}}/k_{\text{comb}}$  is 1.05 (3). The activation energies for disproportionations are slightly larger than for combination. This difference is 0.8, 0.9 and 0.5 Kcal. respectively, for ethyl, isopropyl and isobutyl (3).

It appears that secondary radicals are more likely to disproportionate

ate than are primary radicals. This may be because the combination of secondary radicals is retarded by steric effects or simply that on a primary radical there are fewer hydrogen atoms suitably placed for removal on disproportionation.

The differences in free energy changes for combination and disproportionation have been compared with the ratios of the rate constants for three reactions.

(27)	$2\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_5 + \text{C}_3\text{H}_7$	$2\text{C}_3\text{H}_7$
Free energy difference	-3.1	-1.1	-0.1
$k_d/k_c$	0.46	0.61	1.05

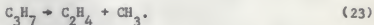
This indicates that the transition states for the two reactions must be very different.

For the decomposition of radicals, Bywater and Steacie (5,6, and 7) have obtained the following activation energies, using high temperature mercury-photosensitized reaction of ethane, propane, n-butane and isobutane.

$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	$E_a = 39.5 \text{ Kcal.}$
$\text{isoC}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$	20.0
$\rightarrow \text{C}_3\text{H}_6 + \text{H}$	38.0
$\text{isoC}_4\text{H}_7 \rightarrow \text{C}_4\text{H}_8 + \text{H}$	40.0
$\text{n-C}_4\text{H}_9 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$	23.0
$\text{n-C}_4\text{H}_9 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3$	23.0.

By trapping free radicals with radioactive iodine, Durham, Martin

and Sutton obtained a value of 19 Kcal. as the activation energy for



The photolysis of azoisopropane by 3660 Å wavelength has been studied by Durham and Steacie (9), the main products were  $\text{N}_2$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , 2,3 dimethylbutane and heavy products.

Table 12. Variation of  $k_{\text{propene}}/k_{\text{C}_6}$  with Temperature from Photolysis of Azoisopropane.

Temperature °C	Ratio
30	0.54
62	0.48
81	0.43
121	0.36

The required activation energy for a reaction, e.g., decomposition, disproportionation and so on, could come from the source of energy that is utilized for production of atoms or radicals.

Klein and Scheer (25,26) have concluded through their works that hydrogen atoms and iso- $\text{C}_3\text{H}_7$  radicals readily diffuse at 77°K. They have failed to detect radicals by means of E. S. R. at this temperature.

#### EXPERIMENTAL METHODS

##### Tritium and Reactant Compounds

The gaseous hydrocarbons which have been used as reactants are propane and butene-1. These hydrocarbons were obtained from Matheson



Company with a minimum purity of 99.5 percent.

Molecular hydrogen containing tritium was prepared. Tritiated water (specific activity 18 mc/m mole) was reduced by metallic zinc in an evacuated pyrex (#1720) fusion tube at 650°C. The fusion tube was placed in the vacuum system (See Fig. 1). The hydrogen was stored in chamber A and was released into system through a high vacuum needle valve B.

#### Measurement of Pressure and Temperature

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

With hydrogen at the fixed pressure, the temperature of filament was determined. The filament was a 3.1-cm 0.003" 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 Company Model 95) was used to measure the temperature of the filament at its center.

### Procedure for Reaction

The reaction chambers (round flask which had a tungsten filament at center, shown in Plate 1) were a 4.3 cm and an 8 cm diameter flask made of thin-walled, pyrex glass with a maximum filament to wall distance of 3-5 cm. (about the estimated mean free path of hydrogen atoms at  $5 \mu$ ).

For introducing the gaseous propene, sampler D in Plate 1, containing a 1.4 ml loop for immersion, was used to transfer both the hydrocarbons to the reaction chamber and the products from the reaction chamber to a gas chromatograph. The sampler was evacuated to less than  $10 \mu$ , and gaseous hydrocarbon was introduced into the sampler to a desired pressure. The stopcock to the sampler was placed in the position as shown in Plate I. The sample was allowed to expand into the system and freeze out in the reaction flask immersed in liquid nitrogen.

In the case of dilution of propene with propane, a second sampler E in Plate I (containing a 1.325 ml loop) was used. The desired amount of propane in sampler E was introduced with propene from sampler C before the reaction flask was immersed in liquid nitrogen.

As soon as the sample was frozen, the system was evacuated to less than  $0.05 \mu$  hydrogen was then introduced through high vacuum needle valve B.

With the 250 ml flask and the 1.8 mc/m mole tritium, from 0.1 to  $0.5 \mu\text{c}$  was released into the system (reaction flask and pressure gauge) at a time. Usually the pressure dropped to less than  $1 \mu$  within

fifteen seconds except in the case of dilution.

For the measurement of rate of reaction, the pressure of the system during reaction was recorded continuously with a recording potentiometer connected to the vacuum gauge. The recorder response was calibrated with the McLeod gauge before reaction.

#### Analysis of Products

Following reaction, residual hydrogen and products that were gaseous at 77°K (methane) were removed by evacuation. After removing the gaseous products, the remainder of the reaction products were transferred to 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. 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, helium was passed through the loop, flushing the sample into the column. Mixing of the sample with helium was minimized by using capillary tubing.

Radioassay was made with the use of a gas flow proportional counter similar to that described by Rowland and Wolfgang (36). The gas stream (helium) was converted into a counting gas by continuous injection of methane (Matheson) 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 (36).

#### EXPLANATION OF PLATE I

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.

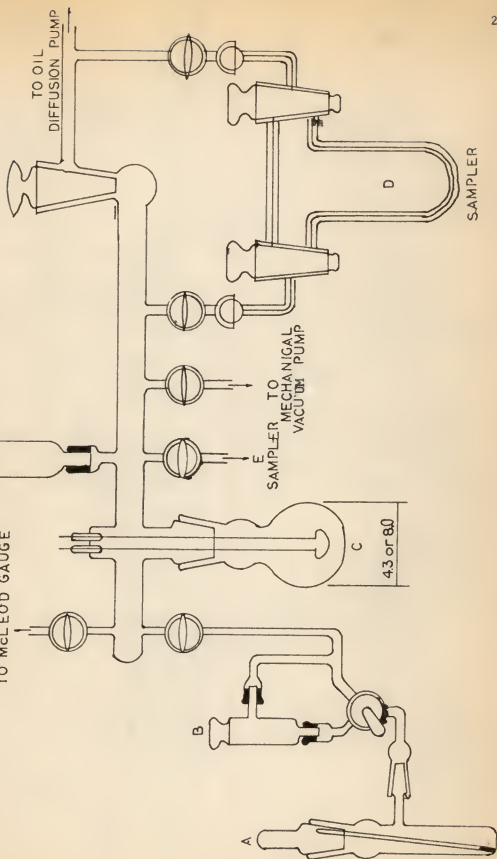
The Pirani gauge was used for pressure measurements during the reaction. The sampler D was used for introduction of the propene. Sampler E, similar to sampler D, was used for dilution.

After reaction, the loop D, was immersed in liquid nitrogen for removal of the sample.

PLATE 1

PIRANI GAUGE

TO McLEOD GAUGE



## EXPERIMENTAL RESULTS

## The Effects of Frozen Propene Concentration

Table 13 shows the results of reaction of  $2 \cdot 10^{-7}$  mole of hydrogen atoms with various amounts of propene. An 8 cm diameter reaction flask was used and the filament temperature was  $1500^{\circ}\text{C}$ . Each result listed represents the average of 3 or 4 reactions. Figure 1 is a chromatogram showing the distribution of products from one of the reactions.

Table 13. Products of Hydrogen Atom Reactions with Varying Amounts of Propene.<sup>1</sup>

Moles of Propene $\times 10^6$	ethane	Tritium Distribution, Percent		
		propane	propene	2,3-dimethyl butane
0.76	0.7	90	8.3	0
1.52	2.0	87	9.0	2.0
3.80	2.0	87	8.0	3.0
4.56	2.0	80	15.0	3.0
5.62	1.5	83	11.0	4.5
6.08	2.5	82	11.5	4.0
7.0	2.0	84	10.0	4.0
7.6	2.0	80	12.0	6.0

<sup>1</sup>Does not include methane.

FIG. 1. A CHROMATOGRAM OF THE DISTRIBUTION OF PRODUCTS FROM ONE OF THE THICK FILM REACTIONS AT 1500°C FILAMENT TEMPERATURE.

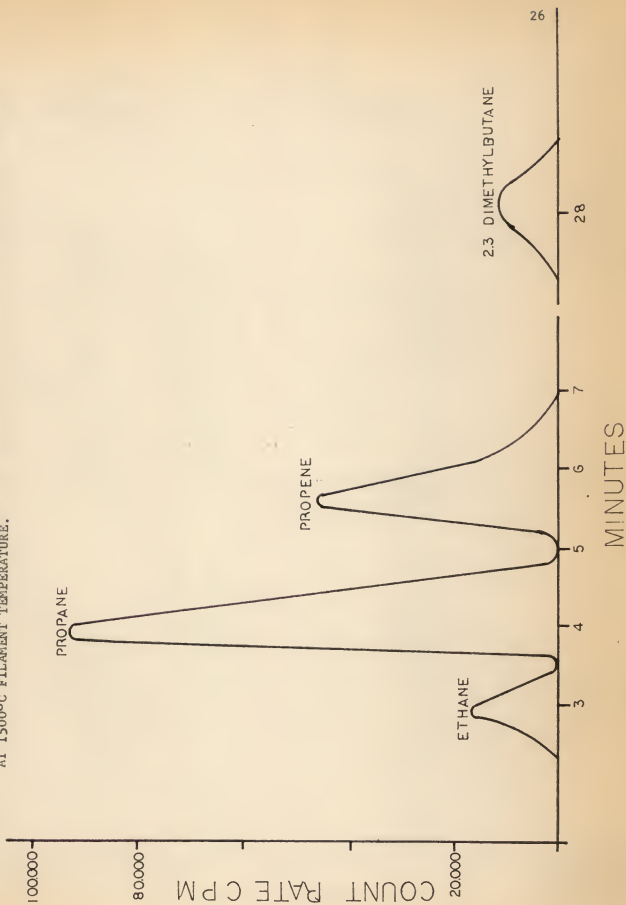




Table 14. Products of Reactions of Hydrogen Atoms with Varying Amounts of Propene<sup>1</sup>.

Moles of Propene ·10 <sup>6</sup>	ethane	Tritium Distribution, Percent		
		propane	propene	2,3-dimethylbutane
0.76	7.9	83	6.8	2.0
1.52	3.6	83	9.9	3.3
2.28	2.6	79	15.0	3.5
3.04	3.5	69	20.0	6.6
3.80	7.8	60	23	9.8
4.56	4.4	60	24	11.0
6.08	4.1	60	25	12
6.84	4.1	68	22	6
7.6	1.7	60	25	13
11.4	1.0	53	30	17
15.2	0	49	32	19
19.0	2.1	47	33	18
23.5	2.4	47	32	10
30.4	1.9	47	34	17
57.8	3.0	48	34	15

<sup>1</sup>Does not include methane.

Table 14 gives the results of reactions of  $10^{-7}$  mole hydrogen atoms with varying amounts of propene in an 8 cm diameter reaction flask and using a tungsten filament temperature of 1600°C. Reactions were continued until all of the hydrogen was used.

#### Effects of Varying the Number of Hydrogen Atoms

Table 15 gives the results of reactions of  $3.8 \cdot 10^{-6}$  mole of propene with various amounts of hydrogen atoms. An 8 cm diameter reaction flask and a filament temperature of 1500°C were used.

Table 15. Products of Reactions of Propene with Varying Amounts of Hydrogen Atoms<sup>1</sup>.

Moles Hydrogen ·10 <sup>8</sup>	Tritium Distribution, Percent			
	ethane	propane	propene	2,3-dimethylbutane
0.85	0	76	24	0
1.7	0	74	26	0
2.0	0	80	20	0
5.0	1.0	80	17	2
10.0	1.5	78	19	2
13.0	2.0	78	17	3
16.0	2.1	88	8	2.3
20.0	2.0	88	8	2.0

<sup>1</sup>Does not include methane.

Figure 2 is a chromatogram showing the reaction products from  $0.85 \cdot 10^{-8}$  moles hydrogen atoms with  $3.8 \times 10^{-6}$  mole of propene.

#### The Effect of Temperature of Filament

By varying the filament temperature of tungsten, the product distribution showed considerable change. Various combination products of radicals such as isopropyl, ethyl, n-propyl and methyl appeared at higher filament temperatures and thicker films of propene.

Propene and isobutane were not separated since their retention times were almost identical. Peaks from 2-methylpentane and 2,3-dimethylbutane overlapped, as is shown in Fig. 3.

Figure 3 shows the typical reaction products at 2020°C filament temperature. Table 16 gives the results of reactions with various filament temperatures in the range of 1200 to 2020°C.

FIG. 2. A CHROMATOGRAM OF THE DISTRIBUTION OF PRODUCTS FROM ONE OF THE THIN FILMS REACTIONS AT 1500°C FILAMENT TEMPERATURE.

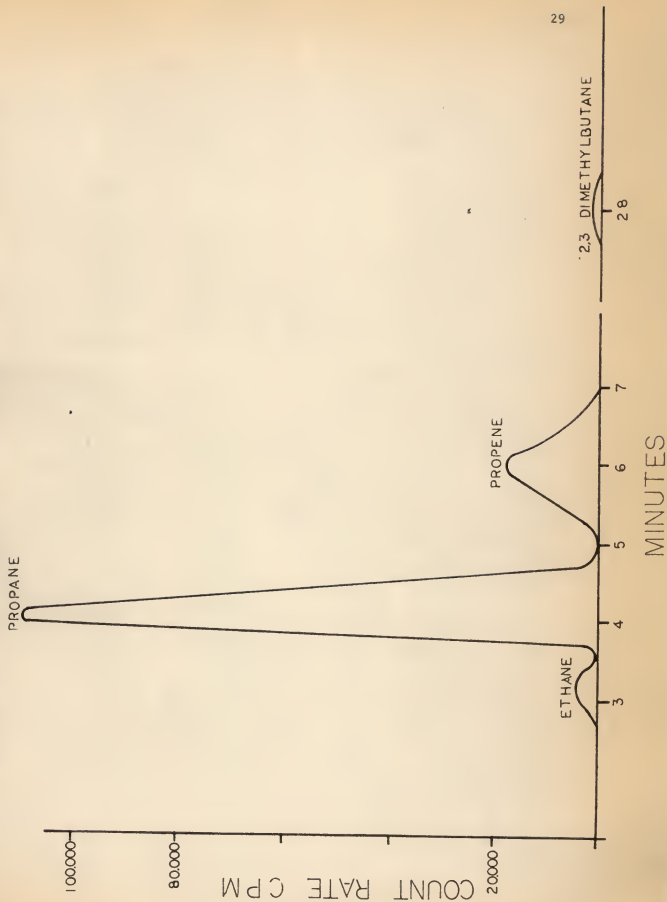


FIG. 3. A CHROMATOGRAM OF THE TYPICAL REACTION PRODUCTS AT 2020°C FILAMENT TEMPERATURE AND THE THICKER FILMS OF PROPENE.

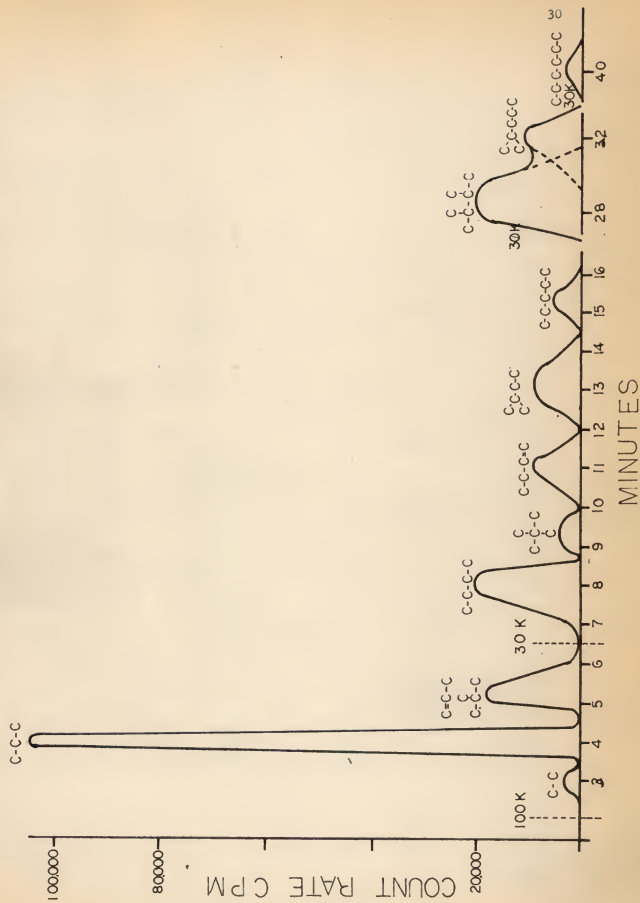


Table 16. Reaction Products of Hydrogen Atoms and Propene at Various Filament Temperatures<sup>1,2</sup>.

Filament Temperature °C	2020	1800	1600	1400	1300	1200
Moles H Atoms·10 <sup>8</sup>	7.52	5.40	3.76	12.0	7.52	3.76
	Tritium Distribution (Percent)					
Ethane	2.0	2.1	0.5	1.1	0.6	0
Propane	58.0	58.0	55.0	63.0	59.0	61.5
Propane & isobutane	15.3	19.0	20.0	17.0	19.0	25.5
n-Butane	1.6	1.6	1.2	1.7	1.5	0
Butene-1	1.3	1.2	1.7	0.3	0.2	0
Isopentane	0.8	0.9	1.4	0.6	0.1	0
n-Pentane	0.5	0.3	0.2	0	0	0
2,3 dimethylbutane	16.0	11.0	13.0	14.0	16.0	10.0
2 Methyl pentane	3.0	4.0	6.0	1.7	2.0	2.0
n-Hexane	1.6	1.9	2.0	1.4	1.0	1.0

<sup>1</sup>Does not include methane.<sup>2</sup>The conditions used were: Reaction flask in diameter 4.3 cm, 3.76·10<sup>-8</sup> moles hydrogen atoms (mostly), 7.6·10<sup>-6</sup> moles propene.

Table 17. Products of Reactions of Hydrogen Atoms and Propene at Various Filament Temperatures<sup>1,2</sup>.

Filament Temperature °C	2030	1850	1700	
Moles Propene. $10^4$	3.0	1.9	1.9	
<u>Tritium Distribution (percent)</u>				
Ethane	1.3	5.0	5.0	0.4
Propane	66.0	65.0	74.0	60.0
Propene and isobutane	9.0	6.9	9.0	27.0
n-Butane	4.0	4.4	1.0	0
Neopentane	1.0	0.7	0.3	0
Butene-1	3.3	2.5	0.7	0
Isopentane	3.3	3.4	0.8	0
n-Pentane	1.7	1.5	0.1	0
2,3 Dimethylbutane	6.0	7.0	7.0	11.0
2 Methylpentane	3.3	3.4	1.0	1.0
n-Hexane	1.0	0.3	0	1.0

<sup>1</sup>Does not include methane.

<sup>2</sup>The conditions used were: An 8 cm reaction flask,  $9.68 \cdot 10^{-8}$  moles hydrogen,  $1.9 \cdot 10^{-4}$  moles propene (mostly).

#### The Rate of Reactions

As described in the previous section for measurement of reaction rate, the reduction in hydrogen pressure was recorded continuously. The rates of pressure decrease corresponded to the rate of hydrogen atom reaction with solid propene plus that absorbed by condensed inert solids such as the glass wall.

Table 18. The Rate of Reaction with Varying Amounts of Propene at 1300°C Filament Temperature<sup>1,2</sup>.

	Moles propene × 10 <sup>6</sup>	Initial rate × 10 <sup>9</sup> moles/sec	$\frac{1}{2}$ Hydrogen decomposed	$\frac{3}{8}$ H <sub>2</sub> decomposed	$\frac{1}{2}$ Hydrogen decomposed
1.	0.76	0.87	0.73	0.58	0.48
2.	1.52	1.03	0.83	0.65	0.52
3.	2.28	1.20	0.87	0.69	0.57
4.	3.04	1.20	0.83	0.68	0.56
5.	3.8	1.40	1.10	0.92	0.76
6.	5.32	1.38	1.10	0.92	0.79
7.	6.84	1.30	0.97	0.84	0.73
8.	11.1	1.40	0.97	0.89	0.76

<sup>1</sup>Used a 4.3 cm diameter reaction flask.<sup>2</sup>Initial hydrogen 5.68·10<sup>-8</sup> moles.Table 19. The Rate of Reaction with Various Amounts of Propene at 1550°C and 1440°C Filament Temperature<sup>1</sup>.

	Moles propene × 10 <sup>6</sup>	Initial rate × 10 <sup>9</sup> moles/sec	$\frac{1}{2}$ Hydrogen decomposed	$\frac{3}{8}$ H <sub>2</sub> decomposed	$\frac{1}{2}$ Hydrogen decomposed
1.	0.76	1.29	0.47	0.37	0.30
2.	2.28	1.99	0.96	0.74	0.58
3.	3.80	2.20	1.14	0.86	0.64
4.	5.32	2.30	1.23	0.87	0.56
5.	6.08	2.42	1.07	0.80	0.60
6.	13.68	2.42	1.13	0.82	0.54

<sup>1</sup>At 1550°C filament temperature and using an 8 cm diameter reaction flask. Initial hydrogen 9.68·10<sup>-8</sup> moles.

7.	0.76	0.40	0.19	0.19	0.12
8.	1.52	0.70	0.23	0.23	0.14
9.	3.04	0.49	0.26	0.21	0.17
10.	4.56	1.45	0.78	0.78	0.40

<sup>1</sup>At 1440°C filament temperature and an 8 cm diameter reaction flask. Initial hydrogen 9.68·10<sup>-8</sup> moles.



Table 18 gives the rate of reaction on thicker films (about  $10^{-6}$  cm) and Table 19 gives the rate of reaction on thin films (about  $10^{-8}$ ). The relationship between the rate and condition such as thickness will be discussed in a later section.

Table 20. Effect of Filament Temperature on the Rate of Reaction<sup>1</sup>.

Filament temperature °C	Initial rate molecules/sec. $10^{-14}$	
	first run	second run
1470	16.20	19.50
1350	3.62	4.26
1290	1.97	2.42

<sup>1</sup>At  $7.6 \cdot 10^{-6}$  moles propene and  $9.68 \cdot 10^{-8}$  moles hydrogen atoms.

From Arrhenius rate expression,

$$\text{Rate} = A \exp -E_a/RT$$

The activation energy for reaction can be calculated by plotting the logarithm of the rate verse  $1/T$ .

#### The Effect of Dilution with Propane

When a mixture of propene and propane reacts with hydrogen atoms, propane does not react appreciably since the activation energy for reaction with hydrogen atoms is larger than that for reaction with olefin. Hence, we do not observe exchange reactions with alkanes when present in the mixture with olefins.

The effects of dilution should tell us something about the possi-

bility of radical diffusion in the solid and also something about the surface effect of radical reactions in condensed states. Table 21 shows the product distributions for dilution with various amounts of propane and constant propene concentration.

Table 21. The Effect of Dilution with Inert Propane on the Product Distribution.<sup>1</sup>

1. Filament temperature 1400°C;  $9.68 \cdot 10^{-8}$  moles hydrogen; 8 cm diameter reaction flask.

Moles Propene $\cdot 10^6$	0.76				
Moles Propane $\cdot 10^6$	0	0.7	1.4	3.6	7.0
Ethane	1.0	3.6	1.9	11.0	3.5
Propane	81.0	86.0	84.0	82.6	92.0
Propene	13.0	9.0	10.0	6.6	4.6
2,3 Dimethylbutane	4.9	1.8	3.8	0	0

Moles Propene $\cdot 10^6$	3.8				
Moles Propane $\cdot 10^6$	0	1.0	2.1	3.6	
Ethane	5.9	11.0	4.7	8.6	
Propane	85.0	79.0	79.3	86.2	
Propene	5.9	7.0	12.0	3.5	
2,3 Dimethylbutane	3.2	3.0	5.3	7.7	

2. Filament temperature 1400°C;  $7.6 \cdot 10^{-7}$  moles propene  $5.68 \cdot 10^{-8}$  moles hydrogen; 4.3 cm diameter reaction flask.

Moles Propane $\cdot 10^6$	0.71	1.43	3.56	3.56	7.13	14.26
Initial rate Moles <sup>2</sup>						
H.Atoms/Sec. $\cdot 10^9$	2.18	2.03	1.50	1.30	0.98	0.86

Tritium Distribution (percent)

Ethane	0	1.5	0	1.6	3.2	4.5
Propane	57.0	61.0	60.0	75.4	73.0	70.0
Propene	27.0	23.0	14.0	13.0	12.0	17.0
n-Butane	2.4	4.0	15.0	3.3	4.0	4.5
Butene-1	0	1.5	3.0	0	0	0
Isopentane	0	1.0	1.4	0	0	0
2,3 diMebutane	13.0	9.0	7.0	7.0	8.0	4.5

<sup>1</sup>Does not include methane.

<sup>2</sup>Until half of the hydrogen was decomposed.

## DISCUSSION

## Chemical Mechanism

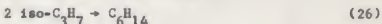
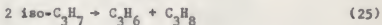
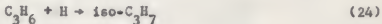
When a hydrogen atom reacts with an olefin, the corresponding alkyl radical is usually formed.



Under the conditions of the present study, the free radical formed can either react with another radical or another atom.

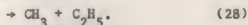
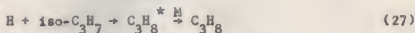
In the reaction of alkyl radicals with hydrogen atoms the reaction products vary with the method of producing H atoms and chemical conditions involved.

Using the method of hydrogen atom production from a tungsten filament centrally located in a vessel, Klein and Scheer (16) assumed, for condensed propene reactions with hydrogen atoms, that the olefin was uniformly deposited on the reaction flask and that the hydrogen atoms reached the walls without recombining. They (18) proposed the following mechanism on the basis of their experiments:



Heller and Gordon (13) have investigated the reactions of hydrogen atoms with  $\text{iso-C}_3\text{H}_7$  in the gas phase. At pressures high enough to get some quenching of vibrationally excited propane, they have interpreted

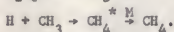
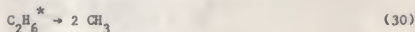
their results principally by



Methane and ethane result from



The ethane yield is reduced and methane are increased by



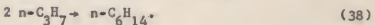
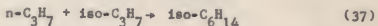
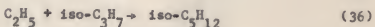
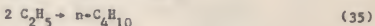
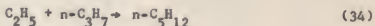
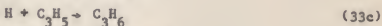
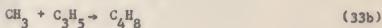
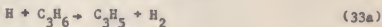
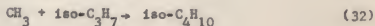
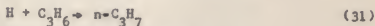
Products given in equations (24) to (30) include all those observed in our experiments except at higher filament temperature where products were observed from various combinations of iso-C<sub>3</sub>H<sub>7</sub>, n-C<sub>3</sub>H<sub>7</sub>, C<sub>2</sub>H<sub>5</sub> and CH<sub>3</sub> radicals.

On the assumption that equations (24) to (30) are appropriate, the fractions of iso-C<sub>3</sub>H<sub>7</sub> radicals reacting by paths (25) to (28) were calculated from the counting data. (See Table 13 to 15 and Appendix I). Corrections were made for the difference in specific activities of the various fractions neglecting isotope effects. For example, C<sub>3</sub>H<sub>8</sub> resulting from combination of iso-C<sub>3</sub>H<sub>7</sub> and H atoms would be expected to have about twice the activity of C<sub>3</sub>H<sub>8</sub> resulting from disproportionation (2:1.17 used in the calculation). Figures 4, 5, and 6 give the fractions of reactions occurring by path 25, disproportionation; path 26, combination;

path 27, addition; and path 28, cracking.

With the thicker films ( $7.6 \cdot 10^{-6}$  moles propene on 4.3 cm flask and high filament temperatures of  $1800^{\circ}$  and above), appreciable yields were found for n-butane, butene-1, iso-butane, isopentane, n-pentane, 2-methylpentane, n-hexane, methane and ethane beside the main products: propene, propane and 2,3 dimethylbutene.

At less than  $1800^{\circ}\text{C}$  down to  $1200^{\circ}\text{C}$  filament temperature, iso-butane, isopentane, butene-1 and n-pentane were not observed (Table 16). Similar results were observed for thin films ( $1.9 \cdot 10^{-4}$  moles propene on an 8 cm diameter flask) when the filament temperature was in the range of  $2030$  to  $1700^{\circ}\text{C}$ . Evidently the following reactions occurred in addition to those forming the major products.



Judging from the products observed, it is quite evident that  $\text{n-C}_3\text{H}_7$  radicals were formed at higher filament temperature.

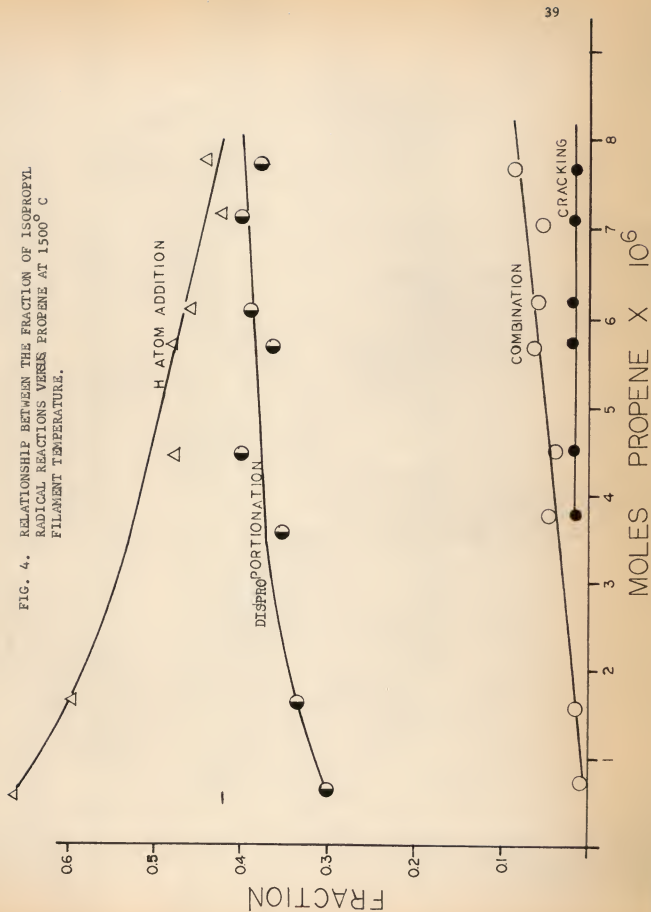


FIG. 5. RELATIONSHIP BETWEEN FRACTION OF ISOPROPYL RADICAL REACTIONS VERSUS PROPENE CONCENTRATION AT 1500°C FILAMENT TEMPERATURE.

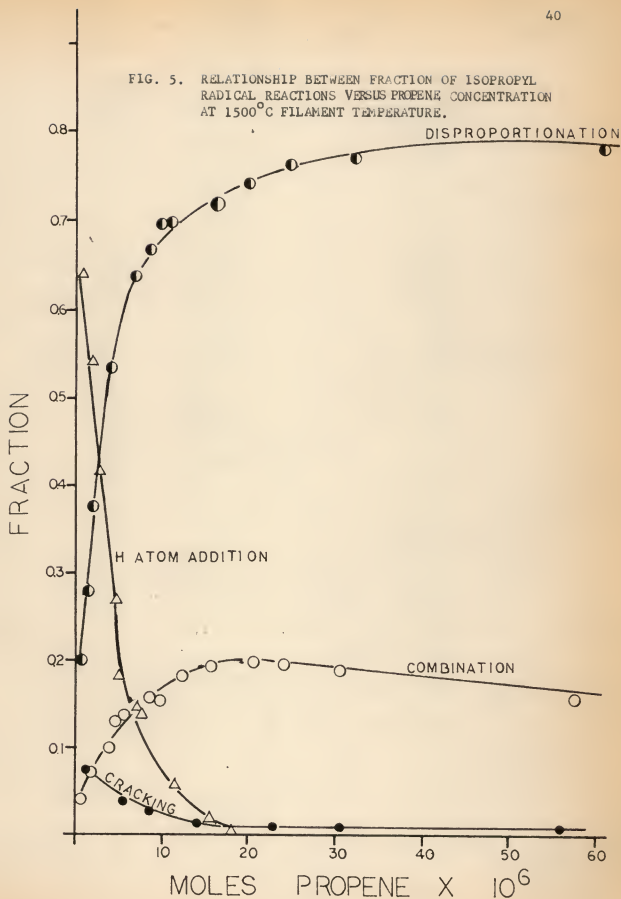
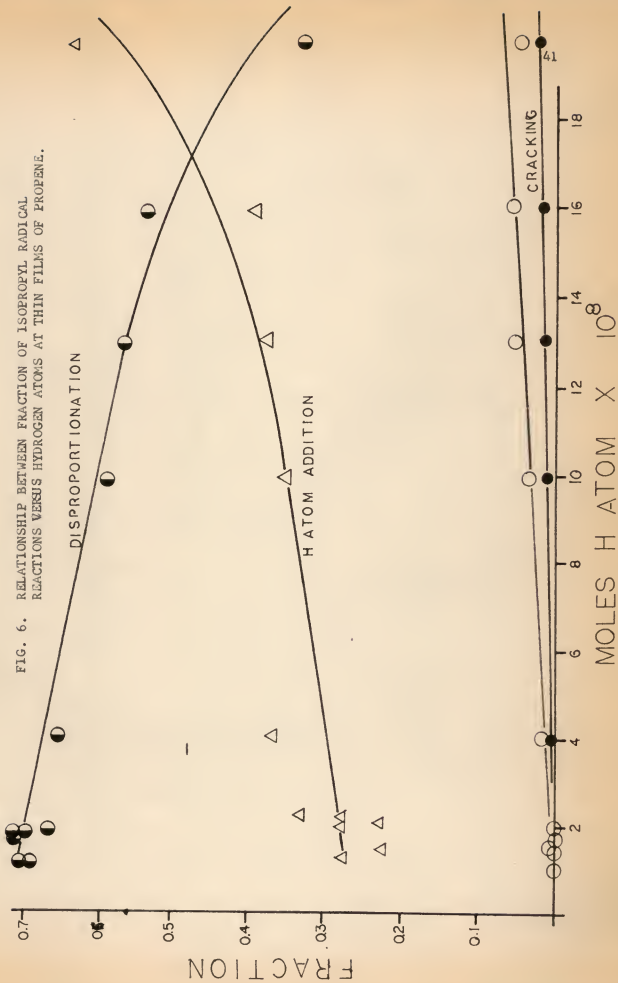




FIG. 6. RELATIONSHIP BETWEEN FRACTION OF ISOPROPYL RADICAL REACTIONS VERSUS HYDROGEN ATOMS AT THIN FILMS OF PROPENE.



Using a similar method involving deuterium instead of tritium, Klein and Scheer (17) strongly proposed that hydrogen atoms add only to the terminal carbon of the primary olefin to form secondary alkyl radicals.

Moore and Taylor (23), as discussed in the previous section, explained that the failure to obtain any evidence for the occurrence of a  $n\text{-C}_3\text{H}_7$  probably is due to a difference in the activation energies  $E_2 - E_1$  for the addition of a hydrogen atom to the middle versus addition to the terminal carbon in propene.

There is little reason to suppose that there is any difference in entropy of activation so that a minimum difference of 2.4 Kcal/mole in activation energies is reasonable. However in the gas phase, using a discharge method for producing H atoms, Robb, et al. (4) observed 2-methylpentane, 2,3 dimethylbutane, and n-hexane, and estimated that the difference between  $\Delta E_a$  for the formation of  $n\text{-C}_3\text{H}_7$  and  $\text{iso-C}_3\text{H}_7$ , was 1.5 Kcal/mole.

Since tritium atoms would be energetic at higher filament temperatures, we can conclude that the formation of  $n\text{-C}_3\text{H}_7$  is due to reactions of energetic tritium atoms.

#### Effects of Film Thickness and Number of Hydrogen Atoms

Effects of increasing the film thickness can be seen in Figs. 4 and 5. Experimental conditions were not identical in both cases, but the same behavior was evident. Apparently the most important factor

influencing the product distribution is a competition between reaction (27), addition and the combination of (25) and (26), disproportionation and radical-radical combination. In thinner films (27) should be favored because of a relatively larger contribution with (24), the reaction for production of more iso-C<sub>3</sub>H<sub>7</sub>. In thicker films (24) is the main reaction of hydrogen atoms and (25) and (26) are the principal reactions of iso-C<sub>3</sub>H<sub>7</sub>.

Disproportionation, reaction (25), likely occurs to the greatest extent on the surface where reaction can occur before complete quenching of excited iso-C<sub>3</sub>H<sub>7</sub>. The activation energy for disproportionation has been estimated at 0.3-0.5 Kcal/mole (27) while that for combination is probably nearly zero. There is further justification for proposing a predominately surface process for disproportionation. At very low hydrogen atom concentrations (Fig. 6) disproportionation is the major reaction followed by addition. Little if any combination occurred in thin films. The major change is the increasing role of addition compared to disproportionation.

In thicker films there is an increase in the yield from radical-radical combination reactions which would be expected to accompany deeper penetration of hydrogen atoms to form iso-C<sub>3</sub>H<sub>7</sub> in the interior layers.

By comparing Fig. 6 with Fig. 5 a conclusion can be made regarding the diffusion of iso-C<sub>3</sub>H<sub>7</sub> radicals. If diffusion were rapid resulting in a homogeneous distribution of iso-C<sub>3</sub>H<sub>7</sub> throughout the films, similar products would be expected for the two different situations: (1) low

hydrogen atom concentration and (2) thicker films. Both cases would involve a low concentration of iso-C<sub>3</sub>H<sub>7</sub> radicals. Because there is a large difference between these situations, we may conclude that extensive diffusion does not occur.

#### Effect of Filament Temperature

The effect of filament temperature is very critical. Yields of various compounds containing four to six carbon atoms increased with filament temperature and concentration of propene. Examination of Tables 16 and 17 shows that relative yields of only propane and 2,3 dimethylbutane are unchanged regardless of the filament temperature, but the relative yield of propene varies inversely with the filament temperature. This indicates that some hydrogen atoms attach to middle carbon atoms in propene and produce n-C<sub>3</sub>H<sub>7</sub>. The radicals (CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, n-C<sub>3</sub>H<sub>7</sub> and iso-C<sub>3</sub>H<sub>7</sub>), formed by reaction of hydrogen atoms with propene, react by radical-radical combination rather than H atom addition or radical-radical disproportionation, at higher filament temperature and higher radical concentrations. The extent of propyl radical disproportionation is influenced by this condition. The amount of excited propane which is formed by energetic H atoms (Eq. 28) at higher temperature would increase and the number of propane molecules that crack would also increase. The propyl radicals likely combine with methyl and ethyl radicals rather than react by radical disproportionation, and combination of ethyl radicals likely occurs also.

The activation energy for disproportionation is higher than that for combination, and the activation energy for combination of different radicals is a little higher than that for identical radicals (35).

Table 22. Yields of  $n\text{-C}_3\text{H}_7$  for Various Filament Temperatures<sup>1,2</sup>.

Filament temperature °C	Moles hydrogen $\cdot 10^8$	Yield of $n\text{-C}_3\text{H}_7$ in percent of total $\text{C}_3\text{H}_7$
2020	7.52	3.38
	5.40	4.04
	3.76	5.28
1800	12.0	2.22
	7.52	2.16
	3.76	2.01
1600	3.76	1.70
1400	3.76	1.65
1300	3.76	1.75
1200	3.76	0.98

<sup>1</sup>From Table 16 ( $7.6 \cdot 10^{-6}$  moles propene and a 4.3 cm. diameter reaction flask.)

<sup>2</sup>Yields of  $n\text{-C}_3\text{H}_7$  are approximately equal to yield percent of  $n\text{-hexane} + \frac{1}{2}$  2-methylpentane +  $\frac{1}{2}$   $n\text{-pentane}$ .

Table 23. Yields of  $n\text{-C}_3\text{H}_7$  for Various Filament Temperatures<sup>1,2</sup>.

Filament temperature °C	Moles propene $\cdot 10^4$	Yield of $n\text{-C}_3\text{H}_7$ in percent of total $\text{C}_3\text{H}_7$
2020	3.0	3.15
	1.9	2.70
1850	1.9	1.85
1700	1.9	1.35

<sup>1</sup>From Table 17 ( $9.68 \cdot 10^{-8}$  moles hydrogen and an 8 cm. diameter reaction flask.)

<sup>2</sup>Yields of  $n\text{-C}_3\text{H}_7$  are approximately equal to yield percent of  $n\text{-hexane} + \frac{1}{2}$  2-methylpentane +  $\frac{1}{2}$   $n\text{-pentane}$ .

### Analysis of Rate of Reaction

Klein and Scheer (17) assumed that hydrogen atom diffusion through thin layers of hydrocarbons is rapid and does not control the rate and that all the hydrogen atoms formed at the tungsten ribbon reach the olefin surface. Also they measured the hydrogen uptake by solid butene-1 as a function of tungsten temperature and calculated an activation energy of about 58 Kcal per mole of hydrogen atoms. This activation energy is the value that would be expected for the dissociation of hydrogen at the hot filament. The slope in Fig. 11 gives an activation energy of 57.2 Kcal per mole of hydrogen atoms.

Figures 9 and 10 show that the plot of logarithm hydrogen pressure versus time gives straight lines except on thicker films of propene where rates were faster. These plots are taken from Tables 18 and 19. Some initial rates of hydrogen pressure drop give non-linear plots in Figs. 9 and 10. This is reasonable, because initially hydrogen atoms must overcome the activation energy for reaction by addition to form propyl radicals. (1.5 Kcal/mole)

The straight lines in Figs. 9 and 10 indicate that the rate of reaction depends on first power of hydrogen pressure rather than a half power. On thicker film and lower filament temperature, Fig. 9 showed that rate is proportional to one half power of hydrogen pressure. This may be caused by some experimental error such as electronic response on the recorder. Also it may be because recombination of hydrogen atoms is reduced in thicker films, and the number of reacting H atoms would be

increased.

Table 24 gives ratios of observed and calculated rates of reactions and shows a maximum of 0.1 for thick films and 0.02 for thin films of propene. Surface recombination of atomic hydrogen may occur or hydrogen

Table 24. Calculated and Observed Rates of Reaction.

	Observed rate molecules/sec.	Calculated rate of atomization <sup>1</sup>	Ratio of obs. to calc.
Figure 10			
(1)	$1.27 \cdot 10^{14}$	$1.07 \cdot 10^{16}$ at 1300°C	0.012
(2)	$5.9 \cdot 10^{14}$		0.055
(3)	$7.4 \cdot 10^{14}$		0.070
(5)	$1.3 \cdot 10^{15}$		0.121
(6)	$1.32 \cdot 10^{15}$		0.123
(7)	$1.12 \cdot 10^{15}$		0.105
Figure 11			
(1)	$3.76 \cdot 10^{14}$	$3.2 \cdot 10^{17}$ at 1550°C	0.0012
(2)	$7.0 \cdot 10^{14}$		0.0022
(3)	$7.62 \cdot 10^{14}$		0.0024
(7)	$2.06 \cdot 10^{14}$	$8.6 \cdot 10^{16}$ at 1400°C	0.0024
(8)	$1.98 \cdot 10^{14}$		0.0023
(10)	$1.685 \cdot 10^{15}$		0.0195

<sup>1</sup> Expression of Brennen and Fletcher: (4)

$$V_a = 18 \cdot 10^{24} P_{H_2}^{\frac{1}{2}} \exp -52600/RT \text{ atoms/ sec} \cdot \text{cm}^2$$

may be absorbed by solid in the atomic state, because the pressure gauge



indicates complete use of hydrogen during reaction. Recombination of atomic hydrogen is highly exothermic,



This energy may be available to activate molecules or radicals on the surface.

The rate of reaction is not proportional to the propene concentration in all cases, but it appears to be at relatively low concentration (See Figs. 7 and 8). This indicates that the rate of reaction is controlled by H atom addition to propene and rate of atomization is not the controlling step.

#### Effect of Dilution with Saturated Hydrocarbon

The effect of dilution with saturated hydrocarbon gives indication of the extent of surface reactions and radical migration in the solid. Klein and Scheer (19) observed for dilution with butane on propene that above a certain thickness (about  $3 \cdot 10^{-4}$  cm) the rate was independent of thickness and yields of main products (propane, propene and 2,3 dimethylbutane) were invariant. Further they proposed extensive diffusion of iso-C<sub>3</sub>H<sub>7</sub> in solid propene and applied a one dimensional diffusion equation to their data.

Our experiments with propane diluent showed (Table 21) that the products are methane, ethane, propane, propene, and 2,3 dimethylbutane. There were no products of reactions of n-C<sub>3</sub>H<sub>7</sub>. With increasing amounts

FIG. 7. RATE OF REACTIONS DEPENDENCE AGAINST PROPENE CONCENTRATION AT THICK FILMS.

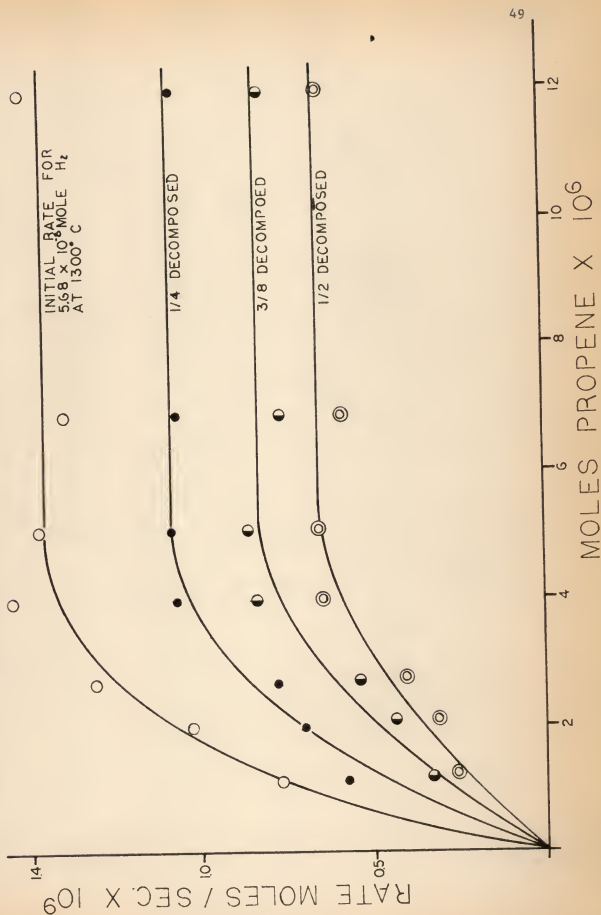
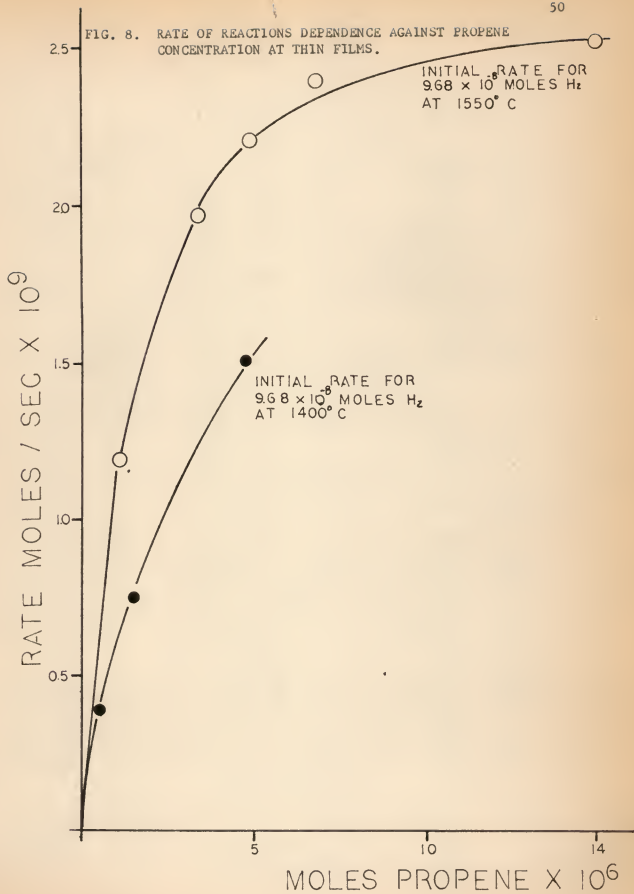
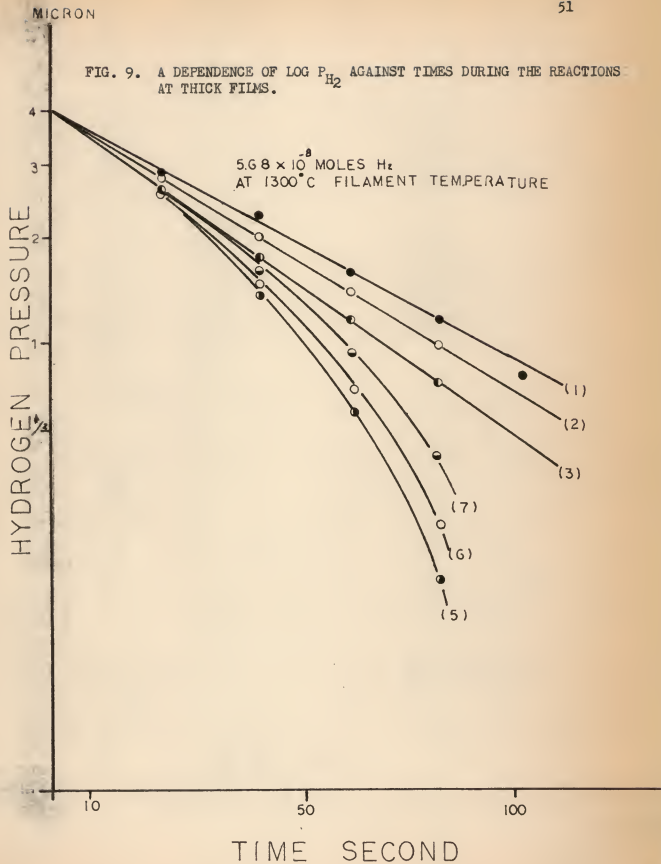


FIG. 8. RATE OF REACTIONS DEPENDENCE AGAINST PROPENE CONCENTRATION AT THIN FILMS.





MICRON

FIG 10. A DEPENDENCE OF  $\log P_{H_2}$  AGAINST TIMES DURING THE REACTIONS AT THIN FILMS.

$9.68 \times 10^{-6}$  MOLES  $H_2$

AT  $1550^\circ C$   
FILAMENT TEMPERATURE

TIME SECOND

HYDROGEN PRESSURE

$9.68 \times 10^{-6}$  MOLES  $H_2$   
AT  $1400^\circ C$  FILAMENT TEMPERATURE

TIME MINUTES

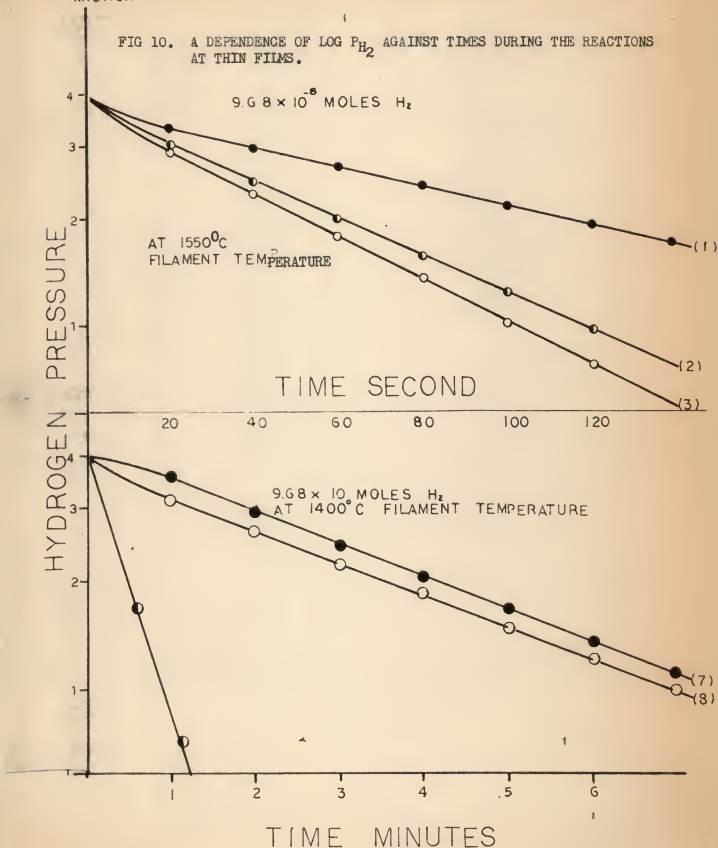
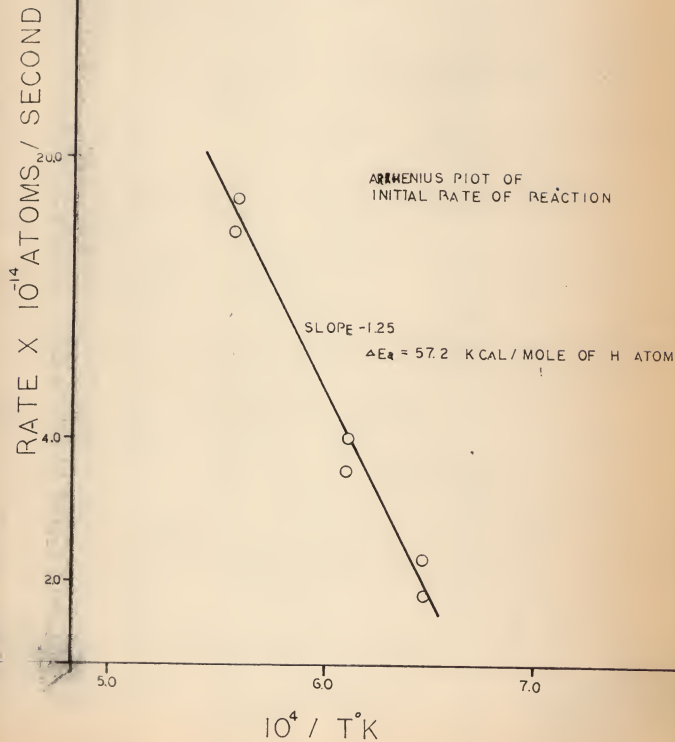


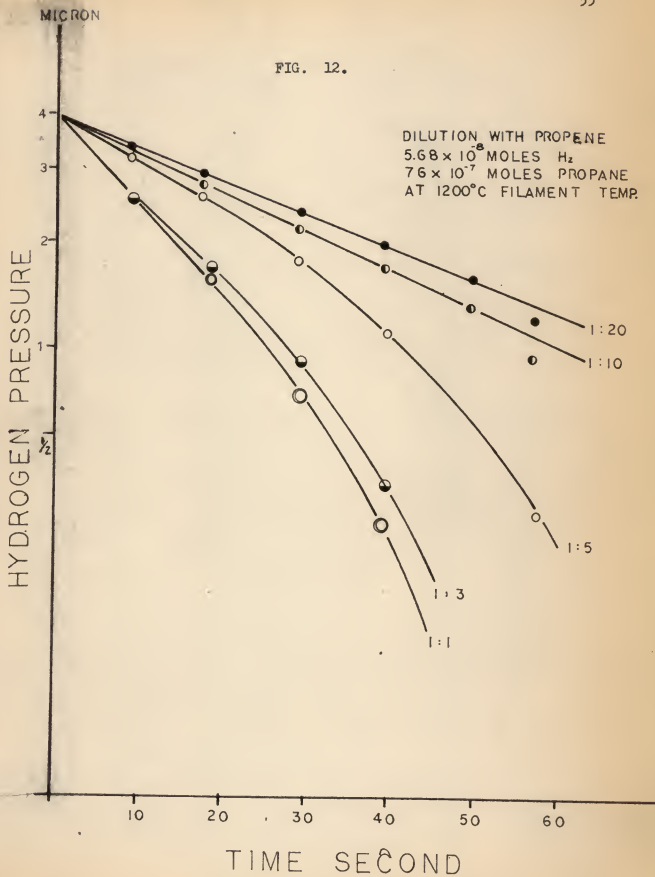
FIG. 11.



of dilution with propane, the fraction of radicals that react by combination with H atoms increases while the fraction of iso-C<sub>3</sub>H<sub>7</sub> that react by disproportionation and radical-radical combination decreases. Therefore we can conclude that (1) reactions occur on or near the surface, because otherwise the extent of dilution would not affect the product distribution, and (2) hydrogen atoms diffuse much faster than iso-C<sub>3</sub>H<sub>7</sub> radicals, because the yield of radical-radical reactions is reduced while the yield of H atom addition reactions is increased. Figure 12 showing the effect of dilution on the reaction rate also supports the above conclusions.



FIG. 12.



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## LITERATURE CITED

1. Berlic, M.R. and D.J. LeRoy  
The reactions of hydrogen atoms with ethane. *Dissc. Farad. Soc.* 14, 50 (1953).
2. Bonhoeffer, K.F. and P. Hartick  
*Z. Physik. Chem. A* 139, 64 (1928).
3. Bradley, Melville and Robb  
*Proc. Roy. Soc. (London)* 236 A (1956). The kinetics and chemistry of the interaction of alkyl radicals. p. 318. The disproportionation and combination of ethyl radical. p. 333. The collision efficiency for interaction of ethyl radical. p. 339. The disproportionation and combination of propyl radical.
4. Brenner, W.E. and A.F. Fletcher  
The atomization of hydrogen on tungsten. *Proc. Roy. Soc. A* vol. 256, p. 389 (1959).
5. Bywater, S. and E. W. R. Steacie  
The Hg photosensitized reaction of ethane at high temperature. *J. Chem. Phys.* 19, 326 (1951).
6. \_\_\_\_\_ and \_\_\_\_\_  
The Hg photosensitized decomposition of propane at high temperature. *J. Chem. Phys.* 19, 319 (1951).
7. \_\_\_\_\_ and \_\_\_\_\_  
The Hg photosensitized decomposition of n and iso-butane at high temperature. *ibid.* 19, 172 (1951).
8. Durham, R.W., G.R. Martin and H. C. Sutton  
*Nature*, 164, 1052 (1949).
9. Durham, R.W. and E.W.R. Steacie  
The photolysis of azo isopropane. *Can. J. Chem.* 31, 377 (1953).
10. Frakas, S.  
The thermal interaction of deuterium and ammonia. *J. Chem. Soc.* 26 (1936).
11. Freeman, A.E.  
The absorption of active hydrogen by platinum. *J. Am. Chem. Soc.* 35, 927 (1912).

12. Geib, K.H. and E.W.R. Steacie  
Austauschreaktionen mit deuterium atomen. Z. Physik. Chem.  
B 29, 215 (1935).
13. Heller, G.A. and A.S. Gordon  
Isopropyl radical reactions. III. Reactions with hydrogen  
atoms. J. Phys. Chem. 64, 390 (1960).
14. Hickmott, T.W.  
Interaction of hydrogen with tungsten. J. Chem. Phys. 32,  
810 (1960).
15. Hickmott, T.W.  
Interaction of atomic hydrogen with glass. J. Appl. Phys.  
Vol. 31, p.128 (1960).
16. Klein, R. and M.D. Scheer.  
The addition of hydrogen atoms to solid olefins at  $-195^{\circ}$ .  
J. Am. Chem. Soc. 80, 1007 (1958).
17. Klein, R. and M.D. Scheer.  
The reaction of hydrogen atoms with solid olefins at  $-195^{\circ}$ .  
J. Phys. Chem. 62, 1011 (1958).
18. Klein, R. and M.D. Scheer.  
Hydrogen atom reactions with propene at  $77^{\circ}\text{K}$ . J. Phys.  
Chem. 65, 324 (1961).
19. Klein, R. and M.D. Scheer  
The reaction of hydrogen atoms with solid propene at low  
temperature. J. Phys. Chem. 64, 1247 (1960).
20. Langmuir, I.  
A chemically active modification of hydrogen. J. Am. Chem.  
Soc. 37, 417 (1915).
21. Langmuir, I. and G.M. Mackay  
The dissociation of hydrogen into atoms. Part II. Calculation  
of the degree dissociation and heat of formation. J. Am. Chem.  
Soc. 36, 1708 (1914).
22. Lee, J.K., B. Musgrave and F.S. Rowland.  
Hot atoms reactions and radiation induced effects in the  
reactions of recoil tritium with cyclopropane.
23. Moore, W.J. and H.S. Taylor  
The mercury photosensitized hydrogenation of propane,  
ethane and n-butene. J. Chem. Phys. 8, 504 (1940).

24. Moore, W.J.  
The mercury photosensitized hydrogenation of propene. J. Chem. Phys. 16, 916 (1948).
25. Rabinowitch, B.S., S.G. Davis and C.A. Winkler  
Can. J. Research. B 21, 251 (1943).
26. Schiff, H.I. and E.W.R. Steacie  
The reaction of hydrogen and deuterium atoms with cyclic and paraffin hydrocarbons. Can. J. Chem. 29, 1 (1951).
27. Shaw, T.M.  
Dissociation of hydrogen in a microwave discharge. J. Chem. Phys. 29, 1366 (1958).
28. Shores, R.D. and H.C. Moser.  
The reaction of tritium atoms with frozen hydrocarbons. J. Phys. Chem. 65, 570 (1961).
29. Shores, R.D.  
M.S. thesis, Kansas State University, 1962. Reaction of tritium atoms with frozen hydrocarbons.
30. Steacie, E.W.R.  
Atomic and free radical reactions. Vol. 1. New York. Reinhold Publ. Corp. 1952.
31. Steacie, E.W.R.  
Atomic and free radical reactions. p. 496. Vol. II, Reinhold Publ. Corp.
32. Steacie, E.W.R. and N.W.F. Phillips.  
The reaction of deuterium atoms with methane and ethane. J. Chem. Phys. 4, 461 (1936).
33. Steacie, E.W.R.  
The kinetics of elementary reaction of the simple hydrocarbons. Chem. Rev. 22, 311 (1938).
34. Trenner, N.R., K. Morikawa and H.S. Taylor  
The reactions between atomic deuterium and the saturated aliphatic hydrocarbon. J. Chem. Phys. 5, 203 (1957).
35. A.F. Trotman-Dickenson  
Free Radicals. p. 120. Methuen and Co. London, England.
36. Wolfgang, R.W. and F.W. Rowland  
Radioassay by gas chromatography of tritium and carbon labeled compounds. Anal. Chem. 30, 903 (1958).

37. Wood, R.W.

Proc. Roy. Soc. (London) A 97, 455 (1920). Proc. Roy. Soc.  
(London) A 102, 1 (1922). Phil. Mag. 42, 729 (1921). Phil.  
Mag. 44, 538 (1922).

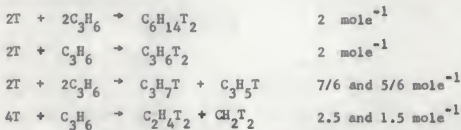
## APPENDIX 1



Calculation for Fractions of iso-C<sub>3</sub>H<sub>7</sub> Radicals on Figs. 5, 6 and 7.

Let us use A, B, C and D as the integrated counts for propane, propene, 2,3 dimethylbutane and ethane respectively.

Neglecting isotope effects the relative specific activities of the products should then be:



The relative molar amounts of propyl radicals responsible for the respective counting rates should be then:

Compound	Count	No. of isopropyls required for formation	Relative amount of iso-C <sub>3</sub> H <sub>7</sub> used in formation
2,3 Dimethylbutane	C	2	$\frac{C}{2} \cdot 2$
Ethane	D	1	$\frac{D}{2.5}$
Propane	A	1	$\frac{1}{2} \frac{B}{5/6} + A \frac{-B}{-5/6} \cdot 7/6 = \frac{1}{2} A + B$
Propene	B	1	$\frac{B}{5/6}$

Therefore the fractions of isopropyl reacting by the various path are:

Combination	C/S
Disproportionation	B(1 + 7/5)/S
Addition to H atom	$\frac{1}{2}(A + 7/5B)/S$
Cracking	D/2.5/S

where S is total sum of relative amount of isopropyls used in formation

which is  $C + D/2.5 + 6B/5 + \frac{1}{2}(A + B)$ .

REACTION OF HYDROGEN ATOMS WITH PROPENE AT 77°K

by

HAN BO YUN

B. S., Yonsei University, Seoul, Korea, 1958

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AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1962

Reactions of tritium and hydrogen atoms with propene at liquid nitrogen temperature were studied. The 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 1200 to 2030°C were used. Reaction flasks were used that had a maximum filament to wall distance of approximately one mean free path at 5 $\mu$  pressure. Products were separated by gas chromatography and counted with a proportional counter placed in the effluent stream. Propane, propene and 2,3 dimethylbutane were major products. Also identified in small amounts were methane and ethane for lower filament temperature and thin film reactions (less than 10<sup>-7</sup> cm thick). At elevated filament temperatures and thicker films (5 x 10<sup>-6</sup> cm) methane, ethane, isobutane, n-butane, butene-1, isopentane, n-pentane, isohexane, and n-hexane were produced in addition to the major products.

The primary reaction of an H atom with propene is considered to be addition to form an iso-C<sub>3</sub>H<sub>7</sub> radical or a n-C<sub>3</sub>H<sub>7</sub> radical. Principal reactions of propyl radicals are considered to be radical-radical disproportionation and combination and H atom addition. Cracking of excited propane is considered as the initial process in the formation of methane and ethane. As the filament temperature is increased and with higher concentrations of propene, the yields of cracked radicals (methyl and ethyl) increase. Methyl and ethyl radicals predominantly reacted with identical radicals and propyl radicals rather than by H atom addition reactions.

Disproportionation of propyl radicals is less favorable than radical-radical combination.

An Arrhenius plot for the rate of reaction as a function of filament temperature gave an activation energy  $5.2$  Kcal/mole of H atoms, which is approximately equal to half of the dissociation energy of molecular hydrogen. The rate of reaction was proportional to the first power of the hydrogen pressure and propene concentration for thin films. However, the rate of reaction for thick films was proportional to the one half power of the hydrogen pressure and nearly independent of the amount of propene. The rate of reaction was less than the rate of atomization and it was concluded that H atom addition to the olefin was the rate controlling step.

Results of the reaction of H atoms with propene using propane as a diluent showed that reactions took place mostly on or near the surface and H atoms diffused much faster than isopropyl radicals.