REACTIONS OF HYDROGEN AND TRITIUM ATOMS WITH
BENZENE AND TOLUENE AT 77°K

by

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INTRODUCTION

Hydrogen atoms react with benzene and toluene giving abstraction, addition and radical-radical reaction products. The reactions of hydrogen atoms depend on the method of production and the energy they possess. In the present study hydrogen atoms possessing energies greater than the usual thermal energies but less than those of recoil atoms from nuclear reactions were produced by the atomization of hydrogen on a hot filament and reacted with solid benzene and toluene.

In order to prevent pyrolysis at the hot filament, the hydrocarbons used were cooled to 77°K by liquid nitrogen thereby allowing only hydrogen to come in contact with the hot filament. Also, low pressures were used to prevent hydrogen atoms from colliding with each other or with other molecules in the gas phase before reacting.

When hydrogen atoms react with solid benzene or toluene, free radicals are formed. A free radical thus formed usually reacts with another radical or hydrogen atom to give either more saturated or less saturated products. The composition of the reaction products varies with reaction conditions. Products of reactions were separated by gas chromatography and counted with a proportional counter placed in the effluent stream.

In the present study a free radical mechanism is proposed for hydrogen atom reactions with benzene and toluene. Also, a method of production of some of the intermediate, thermodynamically unstable, partially hydrogenated products of benzene and toluene was found.

LITERATURE REVIEW

Thermodynamic Properties of benzene and other Cyclic C_6 Compounds.
One of the important characteristics of aromatic compounds is their reson-
ance stabilization. Kistiakowsky (1) and coworkers measured the heat of
hydrogenation of benzene and its partially hydrogenated products. According
to their data the heats of hydrogenation at 355°K for cyclohexene, 1,3-
cyclohexadiene and benzene are -28.59, -55.37 and -49.80 kcal/mole. From
these figures one can see that the addition of one mole of hydrogen gas to
benzene to form cyclohexadiene would be endothermic by 5.6 kcal/mole.

Janz (2) calculated the Gibbs free energy changes involved in the hydro-
genation of benzene for the steps indicated below.
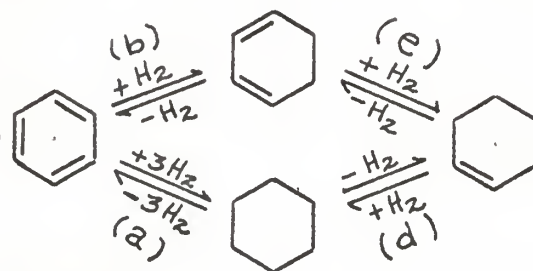
From the following table it is evident that the addition of the first
molecule of hydrogen is difficult, and further steps are spontaneous. Also,
it is seen that lower temperature is more favorable for hydrogenation of ben-

Table 1. Free energy changes for the hydrogenation of benzene.

	$\triangle$G° kcal/mole			
T°K	a	b	c	d
298.16	-23.40	+13.2	-17.9	-18.7
550.00	00.00	+19.6	-12.2	- 9.4
1000.00	+41.97	+31.3	+ 4.2	+ 6.5

zene. This is the reason why the intermediate compounds are produced in

minor amounts during the hydrogenation of benzene.

A consideration of the resonance structure of benzene shows its stability towards hydrogenation. Benzene is more stable than the hypothetical, non-resonant cyclohexatriene by 36 kcal/mole. The conversion of 1,3-cyclohexadiene into benzene and hydrogen is weakly exothermic and tends to proceed spontaneously with liberation of energy (5.6 kcal).

From these studies it is evident that cyclohexadiene would be an unstable intermediate. Also free energy values indicate that hydrogenation of benzene, and presumably other aromatic systems as well, is less favored thermodynamically than hydrogenation of nonresonating, unsaturated systems. The activation energy for the hydrogenation of benzene was found to be 7.5 kcal which is very close to heat of reaction (5.6 kcal) for the cyclic diene.

Catalytic Hydrogenation of Benzene. Benzene undergoes hydrogenation over a variety of catalysts. Two possible mechanisms have been suggested (4). 1) The adjacent interaction mechanism in which the two reacting molecules are adsorbed on adjacent sites in a chemisorbed monolayer, and after interaction in the monolayer, the product is desorbed and 2) the van der Waals chemisorbed layer interaction mechanism in which one reacting species is chemisorbed on the catalyst surface and the other molecular species reacts with it from the gas phase or van der Waals layer.

Madden and Kemball (5) found that hydrogenation of cyclohexene over nickel films proceeded 200 times faster than that of benzene at $-34°C$, and the difference increased with temperature. These authors concluded from absolute rate theory considerations that for benzene the slow step is the conversion of adsorbed benzene into adsorbed C_6H_8, but could not distinguish between the three possible mechanisms: 1) reaction of gaseous hydrogen with adsorbed benzene, 2) simultaneous addition of two chemisorbed hydrogen atoms,

or 3) reaction between a hydrogen atom and chemisorbed C_6H_7 radicals. From an Arrhenius plot they found the activation energy for hydrogenation of benzene to be 9.0 ± 0.5 kcal/mole.

Stability towards hydrogenation was shown not only by aromatic systems but also by certain olefins. Klein and Scheer (6) noted some olefins react at slower rates than others. This was explained to be due to differences in activation energy. Kang Yang (7) from the study of hydrogenation of 1,3-butadiene, ($C=C-C=C \leftrightarrow C\dot{=}C\dot{=}C\dot{=}C$) isobutene, benzene, etc., suggested that the main factor governing relative rates is the energy change that occurs in loosely bound π-electrons as attacking free radicals approach reaction centers.

Vapor Phase Hydrogenation of Benzene. In vapor phase hydrogenation of benzene (8) over evaporated films of nickel and tungsten, cyclohexene was detected as one of the intermediate products. This compound was rapidly hydrogenated on nickel, but the yield was reduced greatly by excess benzene. On a benzene poisoned surface, cyclohexene disproportionates to benzene and cyclohexane. The destructive hydrogenation of (9, 10, 11) of benzene to cyclohexane is considered to be a consecutive reaction. Hydrogenation at higher temperature and pressure gives higher molecular weight as well as lower molecular weight hydrocarbons. The lower hydrocarbons are formed from cyclohexane by first isomerization to methyl cyclopentane and then this is followed by cleavage of the isomerized product. It is considered that a direct cleavage of cyclohexane is impossible.

Hydrogen Atom Reactions with Benzene. Brown and Rippere (16) found from the hydrogenation of benzene in a silent electric discharge, detectable amounts of 1,3-cyclohexadiene, 1,4-cyclohexadiene, cyclohexene, biphenyl, hydrogenated biphenyl and polymers along with other major products. In none

of the earlier works was there any indication of intermediate products. These authors carried out the reaction for 56 hours, and no intermediate compounds were present until 18 hours after the reaction was started. Some of these products were isolated and found to be biphenyl and a polymer con- sisting of a mixture of partially hydrogenated polyphenyls.

Howillers (17) found that atomic hydrogen produced in an electric dis- charge under high vacuum reacts with benzene vapor giving biphenyl. This was found to be a good method for the preparation of biphenyl. His sug- gested reaction mechanism is as follows:

$$C_6H_6 + H^{\bullet} \rightarrow C_6H_5^{\bullet} + H_2$$

$$2C_6H_5^{\bullet} \rightarrow C_6H_5C_6H_5$$
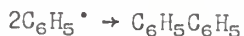
Shores (19) found that tritium atoms produced on a tungsten filament react with solid benzene at -195°C to form cyclohexane, cyclohexene cyclo- hexadiene and labeled benzene.

Schiff and Steacie (15) 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. They did not find any evidence for the formation of cyclohexane, cyclohexene or any dienes.

Radiation Induced Reactions of T_2 with Benzene and Toluene. Biance (3) and co-workers prepared radioactive toluene by istopic exchange with gaseous tritium under different radiation conditions. The distribution of the tracer in the molecule was examined and correlated as a function of reaction conditions. It was concluded that tritium distribution can be drastically changed in the presence of liquid phase. Their data are as follows:

Condition	methyl	ortho	meta	para
Liquid phase	26.0	25.3	19.9	13.3
Vapor phase	5.4	19.2	15.6	26.0

Wilzbach (12) has used the tritium gas exposure technique for tritium labeling: Organic compounds are exposed to curie amounts of tritium gas for several days. The energy released in the disintegration of tritium and adsorbed in the system provides the energy necessary to effect labeling.

The distribution of tritium in toluene labeled by the gas exposure technique has been determined from the activities of appropriate derivatives. Wilzbach found that the tritium appears at all positions in the molecule, but is preferentially incorporated in the aromatic ring and particularly at the ortho position in the ring. The results are as follows:

	% of Tritium at each position
Methyl position	= 8.5
Two ortho positions	= 27.2
Two meta positions	= 12.2
Para position	= 12.7

Melander (14) studied the kinetic isotopic effect of hydrogen exchange between benzene or toluene and concentrated acid. Three milliliters of labeled hydrocarbon was treated with 20 ml aqueous 80% sulphuric acid at 25°C for various time intervals and the relative exchange rates of hydrogen at the ortho, meta and para positions in toluene were determined from the initial slopes. He found relative exchange rates of 47,1 and 41 respectively for tritium and 51,1 and 46 for deuterium. The meta position in toluene was somewhat more reactive than a single position in benzene.

Recoil Tritium Atom Reactions with Benzene. Nesmeyanov and Dzantiviev (18) studied the reactions of recoil tritium atoms with liquid benzene. The

results were as follows:

Labeled Products	% Tritium Distribution
Benzene	26.70
1,4-Cyclohexadiene	2.50
1,3-Cyclohexadiene	1.25
Cyclohexene	0.10
Open ring compounds	0.30

Two reaction mechanisms were proposed to account for labeled benzene form-
ation: 1) Direct interaction of T atoms with H atoms in benzene. 2) Indirect
mechanism in which T reacts first with the aromatic bond forming a complex
from which the labeled benzene is formed by detachment of an H atom. They
also suggested that when a benzene molecule is excited, it forms a biradical
which would accept one T atom and detach one H atom from another benzene
molecule.

Garland (20) studied the reaction of recoil tritium atoms with gaseous
benzene. In case of non-moderated tritium the author found benzene, cyclo-
hexane and an open chain compound, and in case of moderated tritium atoms
he found, in addition to the above, 1,3-cyclohexadiene. The chemical differ-
ences between the radiation chemistry and the recoil tritium systems for
aromatic compounds were indicated, and this difference is that in radiation
chemistry the basic radical to be considered is the phenyl type radical,
while in recoil tritium experiments the basic radical is the cyclohexadienyl
type radical. Therefore, a large part of the radiation chemistry of benzene
is the chemistry of phenyl radicals, which are hydrogen poor relative to
benzene, while a large part of the recoil reaction chemistry of benzene is
the chemistry of cyclohexadienyl radicals, which are hydrogen rich relative
to benzene. He also stated that although biphenyl is a major product of the

radiation chemistry of benzene, it is a rather unlikely product of recoil tritium reaction with benzene. The reaction of labeled cyclohexadienyl radical or phenyl radical should give tetrahydrobiphenyl or dihydrobiphenyl. Addition of a cyclohexadienyl radical to benzene would lead to hydrogenated biphenyl or to higher polymers.

Hydrogen Atom Production

There are several methods available for production of hydrogen atoms: thermal methods, electrical methods, photochemical methods, nuclear reactions, and dissociation of hydrogen at heated filaments.

Heated filaments. The chemical experiments of Langmuir (21) were the first example of this kind. Langmuir showed that the hydrogen was dissociated into atoms on a very hot filament. When the pressure was low enough, the hydrogen atoms produced on the filament reached the wall of the reaction vessel and their reactivity was shown by the reduction of metallic oxides.

In the gas phase the recombination of two hydrogen atoms to form a molecule results in such an excited state that dissociation occurs. Therefore, recombination requires a third body for removal of excess energy. Thus, hydrogen atoms can be produced in one part of a system and pumped into another part of the system for reaction.

Klein and Scheer (22, 23, 24, 27, 28) used this method of thermal dissociation for producing hydrogen atoms. They used a hot tungsten ribbon located in the center of a vessel containing gaseous hydrogen. Hydrogen atoms thus produced reached the frozen hydrocarbons coated inside the vessel before recombining and reacted with them giving products. When olefins were reacted under Klein and Scheer's experimental conditions they found alkanes and alkyl radical dimers.

Reactions of Alkyl Radicals.

A hydrogen atom can react with a hydrocarbon to give a free radical, which is a very highly reactive molecular fragment. Its reactivity is attributed to its unpaired electron. Under proper conditions free atoms and low molecular weight radicals can be trapped for relatively long periods of time in solidified gases at low temperature. This is known as the 'matrix isolation method.'

Diffusion in a solid is strongly temperature dependent. Similarly, free radical diffusion in a matrix also is temperature dependent. A rule of thumb stated by Pimentel (29) is that reactive species cannot be preserved if the temperature of the matrix substance is higher than approximately $T_m/2$, where T_m is the melting point of the substance.

Klein and Scheer have proposed that reactions of hydrogen atoms with solid olefins provide a method for the preparation of alkyl radicals. Their mechanism implies that hydrogen atoms react on the surface producing alkyl radicals, which diffuse readily through solid hydrocarbons reacting with other radicals or even molecules giving the final products.

EXPERIMENTAL

Compounds Reacted. In the reaction system used, either liquid or gaseous hydrocarbons could be handled. The compounds reacted were all cyclic compounds. Benzene (spectrograde, Eastman Organic Chemicals) and toluene (Allied Chemicals. Meets A.C.S. Specifications) were the two main reactants although cyclohexane, cyclohexene (Aldrich Chemicals) and 1,4-cyclohexadiene (Aldrich Chemicals) were reacted to give evidence for reaction mechanisms.
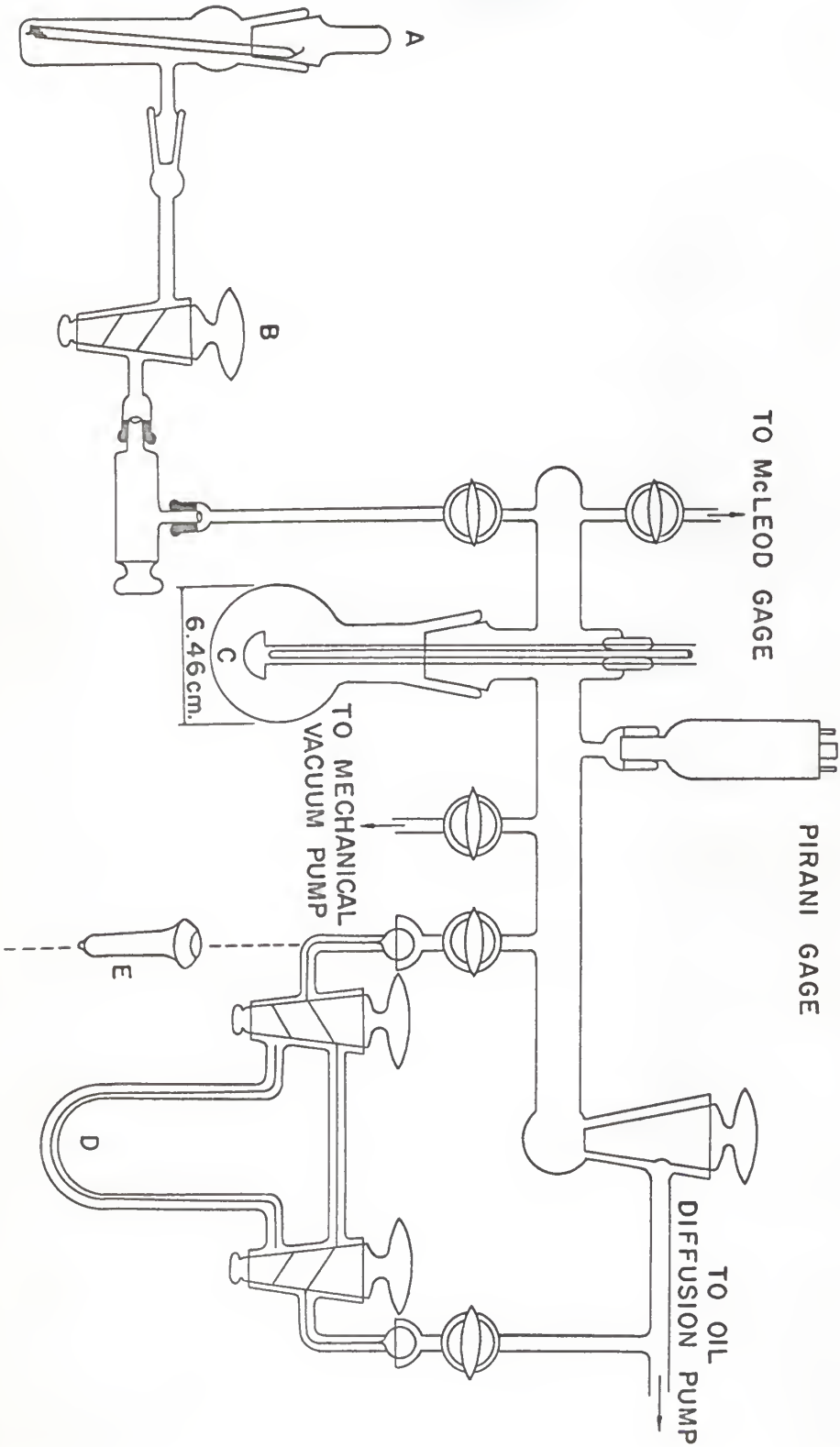
Preparation of Tritium. Molecular hydrogen containing tritium was prepared by heating tritiated water (specific activity 18 mc/m mole) in the

presence of metallic zinc for one hour in an evacuated Pyrex (No. 1720) fusion tube at 650°C. The fusion tube was placed in chamber A (Fig. 1). This tube was broken open after evacuation of the chamber, and the hydrogen thus released was stored in the same chamber. From this chamber hydrogen was transferred into the system whenever necessary through a high vacuum needle valve.

Measurement of Pressure and Temperature. During the reaction, the pressure variation was followed by a Pirani gauge (Consolidated Vacuum Model GP-110). Calibration of the Pirani gauge was found necessary, and a daily calibration was made with the use of a McLeod gauge. A liquid nitrogen trap was placed between the McLeod gauge and the system in order to prevent mercury vapor from getting into the system. The McLeod gauge was opened to the rest of the system and both were evacuated to a pressure of 0.05μ or less by using an oil diffusion pump. To this evacuated system hydrogen was introduced and the readings were noted on both the Pirani gauge and the McLeod gauge. After calibration the McLeod gauge was shut off from the system and the Pirani gauge was used for following the pressure during reaction.

Filament temperatures were measured with an optical pyrometer. Part of the measurements were made with a Pyrometer Instrument Company Model 95 Pyrometer and in the remaining experiments a Leeds and Northrup Company, Cat. No. 8622-C pyrometer was used. The filament was made of tungsten wire, 3.1 cm long and 0.003" diameter. This was suspended at the center of the reaction vessel of 6.5 cm diameter by two molybdenum leads. Two variable transformers connected in series were used to control the filament voltage.

Procedure for Reaction. The reaction vessel consisted of a round, thin-walled, Pyrex glass flask of 100 ml capacity. The maximum filament to wall distance was about 4 cm, which was about the estimated mean free

A

B

TO McLEOD GAGE

6.46 cm.

C

TO MECHANICAL VACUUM PUMP

PIRANI GAGE

E

D

TO OIL DIFFUSION PUMP

path of hydrogen atoms at $5\,\mu$.

Since all the reactants used were liquids, a small glass tube, E, shown on Fig. 1 was used for introducing the reactants into the system. This tube was also used for collecting the products from the system except when the samples were very small, in which case the products were collected back in the sampler D and used directly for analysis. The sampler E was dried, and with a measured quantity of sample, it was cooled in liquid nitrogen while on the vacuum system and evacuated to less than $0.05\,\mu$ pressure. The hydrocarbon was transferred to the coldfinger by evaporation and condensation and likewise to the glass wall of the reaction vessel at 77°K. In this way a uniform coating of frozen compound was obtained, hydrogen was introduced into the system to the required pressure and the reaction was carried out in most cases for 15 seconds. Most of the hydrogen was used up within this time. The products of the reactions were transferred back to the sampler E for analysis. For high molecular weight product analysis, the reaction flask was removed from the vacuum system while it was still cool, and ether was used to rinse out the products.

Analysis of Products. Small aliquots of products were separated at room temperature on a seven foot gas chromatographic column packed with β, β'-oxydiproprionitrile liquid phase on Chromosorb P and detected by using a gas flow proportional counter. The He carrier gas emerging from the column was mixed with methane in a ratio of 1:1 before passing through the counter. In case of small samples the loop D was directly connected to the gas flow and was flushed with He to remove air before the sample was allowed to flow into the column.

For higher molecular weight product analysis a four foot column with Apiezon-L grease as liquid phase was used at 190°C to separate the products. A fractional distillation was also carried out. A small aliquot (5μ) was added to a mixture of 10 ml benzene, 10 ml toluene and 10 ml decane. This was fractionated by distillation, and the different fractions were counted in a liquid scintillation counter. For study of hydrogen atom reactions with toluene the same experimental technique was followed as that used for benzene. Separations were made with the use of a five foot column using benzyl diphenyl as liquid phase. Labeled toluene was collected from the column and used for tritium position analysis. Benzoic acid was prepared from the toluene by oxidation with alkaline $KMnO_4$.

EXPERIMENTAL RESULTS

Effect of Filament Temperature. Table 1 shows the effect of filament
temperature on product distribution for the reaction of hydrogen atoms with
benzene at 77°K. Fifteen microliters of benzene were condensed on the inside
surface of a Pyrex reaction flask (diameter 6.5 cm). The reaction was car-
ried out for 15 seconds with an initial hydrogen pressure of $4\,\mu$. Each
result listed represents an average of 8 to 10 reactions. The temperatures
shown have been corrected for emissivity. Deviations listed are standard
deviations.

Table 1. Effect of filament temperature. Products of hydrogen
and tritium atom reactions with benzene at 77°K.

Filament Temperature (°C)	1527	1607	1892	2007	2137
Product	% Tritium Distribution				
Cyclohexane	8.9±0.5	10.1±1.9	10.6±2.4	8.5±2.0	8.0±1.2
Cyclohexene	61.5±4.3	59.8±1.1	59.0±2.5	56.5±4.0	56.5±2.1
1,3-Cyclohexadiene	7.2±0.5	7.8±0.5	7.7±1.7	9.7±1.7	10.0±1.2
1,4-Cyclohexadiene	20.4±2.2	22.9±3.4	20.2±2.9	23.1±3.1	22.7±1.4
Benzene	1.9±0.4	2.2±0.3	2.6+0.4	2.6±1.4	2.9+0.8

Effect of Length of Reaction Time. Table 2 shows the effect of length
of reaction time on product distribution for the reaction of hydrogen atoms
with benzene at 77°K. The reaction was carried out in a 6.5 cm diameter
flask with an initial hydrogen pressure of $4\,\mu$. A 15 microliter sample of
benzene was reacted, and the filament temperature was 1927°C, corrected for
emissivity. Each result listed represents an average of 2 to 4 reactions.

Table 2. Effect of length of reaction time. Products of hydrogen
and tritium atom reactions with benzene at 77°K.

Length of Reaction Time	1sec.	3sec.	5sec.	10sec.	15sec.	20sec.
Product			% Tritium Distribution			
Cyclohexane	6.0	9.2	12.4	13.8	20.5	19.1
Cyclohexene	62.6	63.9	59.4	60.6	60.3	59.1
1,3-Cyclohexadiene	9.3	6.8	5.6	5.9	4.8	5.1
1,4-Cyclohexadiene	20.1	19.8	19.7	16.6	13.0	12.4
Benzene	1.8	1.2	2.9	2.4	1.5	2.0

Effect of Film Thickness. Table 3 shows the effect of hydrocarbon coating thickness on product distribution for the reaction of hydrogen atoms with benzene. A reaction flask of 6.5 cm diameter was used for the reaction. The reaction was carried out for 15 seconds with an initial pressure of 4μ, and a filament temperature of 1977°C. Each result listed represents an average of 8 reactions. Deviations listed are standard deviations.

Table 3. Effect of film thickness. Products of hydrogen and tritium atom reactions with benzene at 77°K.

Sample Volume (μl)	5	10	15	20	25
Product	% Tritium Distribution				
Cyclohexane	14.8±1.3	12.9±0.7	10.4±0.4	9.2+0.9	9.9+0.5
Cyclohexene	59.9+3.0	58.4+0.6	56.8+0.2	56.3+0.5	58.1+0.5
1,3-Cyclohexadiene	9.3±0.6	8.0±0.5	9.2±0.2	9.4±0.2	8.9±0.1
1,4-Cyclohexadiene	18.4±1.0	18.1+0.0	19.9±0.3	21.8+0.8	19.9±0.2
Benzene	3.4±0.2	2.7±0.4	3.5±0.1	3.4+0.7	3.2±0.2

Effect of Hydrogen Pressure on Product Distribution. Table 4 shows
the effect of pressure on hydrogen atom reactions with benzene. The reaction
was carried out in a 6.45 cm diameter flask for 15 seconds. A 15 microliter
sample was used, and the filament temperature was 1977°C, corrected for
emissivity. Each result listed represents an average of 8 reactions. Devi-
ations listed are standard deviations.

Table 4. Effect of varying initial pressure. Products of hydrogen and
tritium atom reactions with benzene at 77°K.

Pressure (microns)	3	5	8	15
Product	% Tritium Distribution			
Cyclohexane	8.3±0.0	15.2+0.3	21.5+0.3	39.5±1.4
Cyclohexene	57.7+0.0	58.3+0.4	57.3+0.2	48.7+1.3
1,3-Cyclohexadiene	9.4+0.0	6.7+0.5	5.2+0.2	3.3+0.2
1,4-Cyclohexadiene	21.7+0.0	17.1+0.1	13.7+0.1	7.6+0.2
Benzene	2.9+0.0	2.7+0.0	2.3+0.2	0.8+0.1

A Comparative Study of Hot and Thermal Hydrogen Atom Reactions. Table 5 shows results of a comparative study of hot and moderated hydrogen atoms with benzene. The atoms were moderated by collisions with He gas. The reaction flask contained 4μ hydrogen and 86μ He initially. A 15 microliter sample of benzene was reacted for 15 seconds with a filament temperature of 1977°C. Each result listed represents an average of 4 reactions.

Table 5. Products of hot and thermal hydrogen and tritium atom reactions with benzene.

Gas Phase Composition	H_2 alone	H_2 + He
Product	% Tritium Distribution	
Cyclohexane	10.3	29.0
Cyclohexane	62.4	62.0
1,3-Cyclohexadiene	6.9	1.9
1,4-Cyclohexadiene	18.3	6.6
Benzene	1.9	0.0

Cyclohexane Reactions with H Atoms. Fifteen microliters of cyclohexane were reacted at 4 μ pressure for 15 seconds with a filament temperature of 1970°C. The products were cyclohexane and cyclohexene.

Table 6. Products of hydrogen and tritium atom reactions with solid cyclohexane.

Gas Phase Composition	H_2 + HT (4 μ)	H_2 + HT (4 μ) He (86 μ)
Product	% Tritium Distribution	
Cyclohexane	90.0	95.7
Cyclohexene	8.6	0.0
n-Hexane	0.8	3.5

A Comparative Study of Benzene and Cyclohexene. Benzene and cyclohexene were reacted under similar conditions. The temperature used was high and hence a few unidentified peaks were noted. Thirty microliter samples were used with an initial pressure of 4 μ, and the reactions were carried out for 15 seconds with a filament temperature of 2110°C. Cyclohexene gave cyclohexane, cyclohexene, 1,3-cyclohexadiene and 1,4-cyclohexadiene. Each result listed represents an average of two reactions.

Table 7. Products of hydrogen and tritium atom reactions with benzene and cyclohexene.

Compound Reacted	Benzene	Cyclohexane
Product	% Tritium Distribution	
n-Pentane	1.0	1.5
n-Hexane	0.1	0.0
Cyclohexane	8.7	43.1
----------	0.1	13.0
Cyclohexene	46.6	32.4
----------	2.3	1.9
1,3-Cyclohexadiene	10.4	1.6
----------	5.8	1.1
1,4-Cyclohexadiene	19.8	5.5
Benzene	1.8	0.0

1,4-Cyclohexadiene Reaction. 1,4-cyclohexadiene samples at 77°K were reacted with hydrogen atoms produced at a filament temperature of 1977°C and 1670°C for 15 seconds with an initial hydrogen pressure of 4 μ. Fifteen microliter samples were reacted.

Table 8. Products of hydrogen and tritium atom reactions with 1,4-cyclohexadiene.

Filament Temperature (°C)	1670	1977
Product	% Tritium Distribution	
Cyclohexane	25.2	33.8
Cyclohexene	42.4	51.3
1,3-Cyclohexadiene	5.9	2.8
1,4-Cyclohexadiene	20.1	11.8
Benzene	1.3	0.3

[a]The listed results represent an average of five reactions.

High Molecular Weight Products. Several high molecular weight compounds were produced by the reaction of Hydrogen and Tritium atoms with solid benzene. Three different techniques were used for this analysis: 1) Ordinary vacuum transfer of sample followed by gas chromatographic analysis, 2) Ordinary vacuum transfer of sample followed by fractional distillation of sample plus a mixture of 10 ml benzene, 10 ml toluene and 10 ml n-decane, and 3) Removal of sample from reaction flask by rinsing followed by gas chromatographic analysis.

Table 9. High molecular weight concentration.

Method of Analysis	1	2	3	3
Filament Temperature (°C)	2000	2000	2000	1300
Product	% Tritium Distribution			
L.M.W.	97.0	96.5	84.9	100
H.M.W.	3.0	3.5	15.1	none detected

Effect of Filament Temperatures. Table 10 shows the effect of filament temperatures on the product distribution for the reaction of hydrogen atoms with toluene at 77°K. Fifty microliters of toluene were condensed on the inside surface of a Pyrex reaction flask (6.5 cm diameter). The reactions were carried out for five minutes with a constant hydrogen pressure of 5μ. The temperatures shown have been corrected for emissivity.

Table 10. Effect of filament temperature. Products of hydrogen and tritium atom reactions with toluene at 77°K.

Filament Temperature (°C)	1747	1987	2207	2497
Product	% Tritium Distribution			
Methylcyclohexane	60.7	50.7	32.3	30.5
4-Methylcyclohexene	14.5	12.5	15.1	15.5
1-Methyl-1-cyclohexene	16.1	15.6	19.3	21.8
1-Methyl-1,4-cyclohexadiene	00.0	3.5	6.3	4.6
Toluene	8.9	17.5	26.6	27.5

Effect of Reaction Time on Distribution of Tritium on Toluene Molecule.
Table 11 shows the effect of reaction time on tritium distribution within
the toluene molecule at 77°K. Fifty microliters of toluene were condensed
on the inside surface of a Pyrex reaction flask (6.5 cm diameter). Reactions
were carried out with a filament temperature of 2000°C and 1μ pressure.

Table 11. Percent tritium distribution on toluene molecule after
tritium atom reactions with toluene.

Reaction Time (min.)	3	5	7	10
Position of Tritium	% Tritium Distribution			
Methyl position	79.2	79.7	78.1	81.2
Ring	20.8	20.3	21.8	18.8

DISCUSSION

From the products observed, the primary reactions of hydrogen atoms with solid benzene appear to be those which give $C_6H_5{}^\bullet$ and $C_6H_7{}^\bullet$ radicals. These radicals might result from the following reactions:

$$H + C_6H_6 \rightarrow C_6H_5{}^\bullet + H_2 \tag{1}$$

$$H + C_6H_6 \rightarrow (C_6H_7{}^\bullet) \tag{2}$$

In this discussion reaction (1) will be referred to as an abstraction reaction while reaction (2) will be referred to as an addition reaction.

A phenyl radical from (1) can react further with a T atom to give labeled benzene or it can react with another phenyl radical to give biphenyl as the combination product.

$$C_6H_5{}^\bullet + T \rightarrow C_6H_5T \tag{3}$$

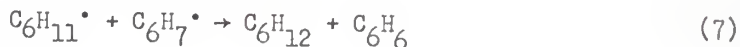$$C_6H_5{}^\bullet + C_6H_5{}^\bullet \rightarrow C_6H_5C_6H_5 \tag{4}$$

Both benzene and biphenyl were observed indicating the occurrence of reactions 1, 3, and 4. Labeled benzene might also be formed through another path indicated by reaction (5).

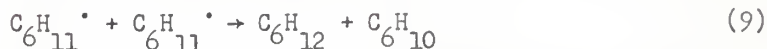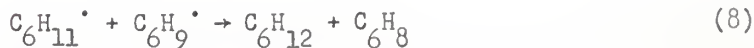$$(C_6H_7{}^\bullet) \rightarrow C_6H_6 + H \tag{5}$$

This mechanism was proposed by Rowland and coworkers (20) for reactions of recoil tritium atoms with cyclopropane or benzene and by Melander (14) for proton exchange between benzene and acid solution.

Study of the Effect of Length of Time of Reaction on Product Distribution. In most reactions cyclohexene is the most abundant product, and its percentage yield is almost time independent (Table 2). Cyclohexane could be formed from any of the following reactions:

$$C_6H_{11}{}^\bullet + H \rightarrow C_6H_{12} \tag{6}$$

$$C_6H_{11}{}^\bullet + C_6H_7{}^\bullet \rightarrow C_6H_{12} + C_6H_6 \tag{7}$$

$$C_6H_{11}{}^{\bullet} + C_6H_9{}^{\bullet} \rightarrow C_6H_{12} + C_6H_8 \tag{8}$$

$$C_6H_{11}{}^{\bullet} + C_6H_{11}{}^{\bullet} \rightarrow C_6H_{12} + C_6H_{10} \tag{9}$$

All these reactions involve the same intermediate $C_6H_{11}{}^{\bullet}$. Reaction (6) is part of a series of consecutive hydrogen atom addition reactions, and reactions (7 to 9) are disproportionation reactions. The series of consecutive addition reactions are:

$$C_6H_6 + H \rightarrow C_6H_7{}^{\bullet} \tag{2}$$

$$C_6H_7{}^{\bullet} + H \rightarrow C_6H_8 \tag{10}$$

$$C_6H_8 + H \rightarrow C_6H_9{}^{\bullet} \tag{11}$$

$$C_6H_9{}^{\bullet} + H \rightarrow C_6H_{10} \tag{12}$$

$$C_6H_{10} + H \rightarrow C_6H_{11}{}^{\bullet} \tag{13}$$

$$C_6H_{11}{}^{\bullet} + H \rightarrow C_6H_{12} \tag{6}$$

This kind of simple addition of H atoms probably occurs more frequently than radical-radical reactions since there are large numbers of H atoms available in the system. Therefore, the chance of an encounter of an H atom with a radical on the surface is greater than that of radical-radical encounter, since most of the H atoms are in the gas phase and the hydrocarbon radicals are restricted to a relatively immobile solid phase. Therefore, the major reactions are consecutive addition reactions which occur on the surface although disproportionation also could lead to the same products.

$C_6H_{11}{}^{\bullet}$ is mainly formed through reaction (13) and since the yield of C_6H_{10} is essentially time independent the loss of C_6H_{10} leading to the formation of C_6H_{12} is balanced by the formation of C_6H_{10} from dienes.

The yield of labeled benzene also seems to increase with time of reaction. The observed yield is much lower than what was observed by other workers. Steacie (25) and coworkers (25) have noted an average exchange of 40%. This probably was due to the incomplete separation of other hydrogenated products,

like cyclohexadiene, in their work.

Study of the Effect of Filament Temperatures. Although the effect of temperature on product distribution is small, it is seem from the data (Table 1) that yields of cyclohexane and cyclohexene decrease at higher temperature while yields of benzene and dienes increase. At higher temperatures more hydrogen atoms are produced, and they have more energy. Disproportionation reactions probably still occur, but since the hydrogen atom production rate is faster, more hydrogen atom-radical reactions take place. A radical like ⬡• could react mainly in two ways.

$$R^{\bullet} + H \rightarrow RH \tag{3}$$

$$R^{\bullet} + R^{\bullet} \rightarrow R\text{-}R \tag{4}$$

Possibly both mechanisms contribute at higher temperatures. Products from reaction (4) were found to be more favorable at higher temperatures (Table 9) than at lower temperatures.

Variation of Hydrocarbon Thickness. Matrix thickness affects the diffusion of radicals and hence probably influences radical-radical reactions the most. From the present experimental data there is no way of finding ratios of yields of disproportionation to combination or ratios of yields of disproportionation to consecutive addition reactions, since there is no way of knowing how much of a specific product results from disproportionation and how much results from hydrogen atom addition reactions.

Radical-radical reactions can take place in the matrix or on the surface and the latter is probably predominant. Radicals formed have freedom to move into the matrix or on the surface layer before they react. Since there is extra energy required for penetration into the matrix, it is reasonable to assume that more of the radical-radical reactions occur on the surface than in the matrix.

The product distribution reveals that only the yield of cyclohexane shows a significant variation. For very thick films this yield is low. This can be explained by diffusion properties. Before hydrogen atom addition reactions can occur some of the intermediate radicals diffuse and undergo radical-radical combination reactions. Neither disproportionation of C_6H_{11}· nor H atom reaction can be used to explain the decrease in cyclohexane yield because in both cases the cyclohexane and cyclohexene yield should increase. This might be an indication for the lack of availability of H atoms inside the matrix. Also, since the yield of dienes do not change with film thickness, it is reasonable to assume that the dienes are produced on the surface by simple addition reactions. On the other hand C_6H_7· could diffuse into the matrix and undergo disproportionation or combination reactions.

It is suggested that benzene reacts first to give dienes by simple H atom addition reactions and further reactions are a combination of consecutive addition reactions and radical-radical reactions. The presence of high molecular weight products definitely shows that consecutive addition is not the only reaction mechanism.

A Comparative Study of Hot and Thermal Hydrogen Atoms. No labeled benzene was observed for reactions run with helium added to thermalize the hydrogen atoms to 77°K. Hydrogen atoms thermalized to 77°K do not have enough energy for abstraction reactions, and this is probably the reaction by which labeled benzene is produced. Another point supporting the occurrence of the abstraction reaction is the slightly higher yield of benzene at higher filament temperatures.

When hydrogen atoms thermalized to 77°K were used it was noted that the cyclohexane concentration increased and the diene concentrations decreased. The radicals do not have enough energy to diffuse away and therefore react

by simple hydrogen atom addition reactions. If the cyclohexane increase
was from disproportionation reactions the yield of dienes and cyclohexene
should increase simultaneously. This was not observed. Therefore, more
consecutive hydrogen atom addition reactions must have occurred in case of
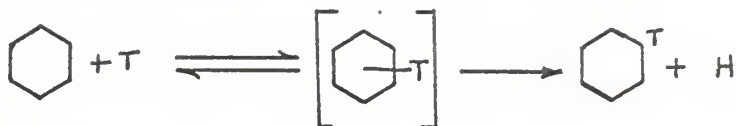hydrogen atoms thermalized to 77°K.

A small sample (one microliter) in the presence and in the absence of
He was reacted to measure the yield of open chain products which are formed
by the cracking processes. Even in the case of thermal hydrogen atoms open
chain compounds were observed. However, a reproducible quantitative study
was not possible because with such small amounts irregularities occurred.
From the above study it is concluded that H atoms thermalized to 77°K can
react to give cracking products but do not have enough energy for abstraction.
The products of cracking reactions were identified as n-hexane and n-pentane.
The precursor for these cracking products must be cyclic C_6H_{12}. Kalechits
and Pavlova (9) had suggested that cyclohexane isomerizes first to methyl
cyclopentane and then the five membered ring ruptures to give the open chain
products. In the present work it was noted that more open chain products
were obtained as the film thickness was decreased. Therefore, the glass wall
participates in cracking process directly or indirectly. Due to the energy
evolved from the C-H bond formation the new species formed has excess energy.
This energy is sufficient to rupture the ring if the species do not have a
chance to transfer the energy to some other molecule. In case of thick films
this energy is transferred to other molecules while in thin films, transfer
of energy does not take place except to the wall and this transfer may not
be as efficient as to the molecules.

Cyclohexane Reaction with H Atoms. The main products observed were
cyclohexane and cyclohexene (Table 6). $C_6H_{11}\cdot$ radicals must have been pre-

sent in the system since cyclohexene was one of the products. If all the cyclohexane and cyclohexene come from disproportionation reactions their yields should be in a 1:1 ratio. But the product analysis showed about 90% cyclohexane and 10% cyclohexene. Therefore, cyclohexane which is in excess must be formed through some path in addition to disproportionation. This can be formed either by an abstraction reaction or a complex formation. The abstraction method is as follows:
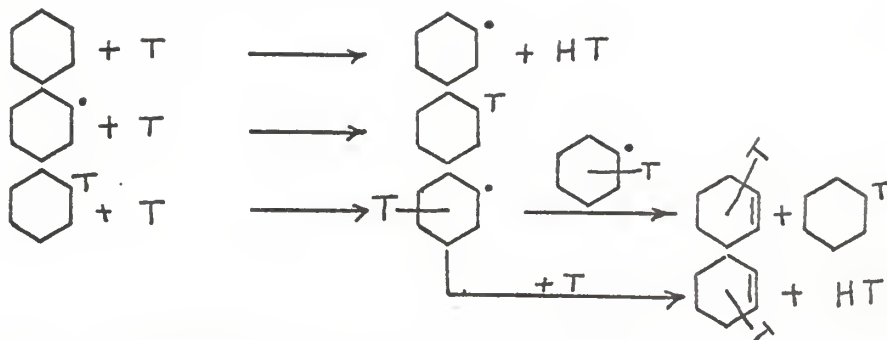
and the complex formation can be represented as shown below.

Cyclohexane was reacted also with helium moderated hydrogen atoms. This did not give any cyclohexene but gave cyclohexane, although the yield was very low. Thermal hydrogen atoms did not have enough energy for abstraction and the small yield of cyclohexane must have come from the second mechanism or from an impurity of the cyclohexane used. The sample was tested for purity by gas chromatography using a thermal conductivity detector and was found to be pure.

Cyclohexene and Cyclohexadiene Reactions with Hydrogen Atoms. The product analysis showed the presence of cyclohexane, cyclohexene, 1,3-cyclo-hexadiene and 1,4-cyclohexadiene from cyclohexene reactions and cyclohexane, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene and benzene from 1,4-

cyclohexadiene reactions. The products observed can be explained with abstraction as well as disproportionation reactions. With cyclohexadiene the $C_6H_7^{\cdot}$ radical can be formed only through an abstraction reaction, and since more addition can occur than abstraction the chances of benzene formation is low.

Effect of Pressure on Hydrogen Atom Reactions with Benzene. From the data (Table 4) it is seen that the effect of pressure on product distribution is more prominent than any other variation studied. A major part of the variation results from a slight change in pressure. Another important factor is the non-uniform film coating. The cyclohexene percentage remains almost constant with increment in pressure while cyclohexane increases greatly with increment in pressure while cyclohexane increases greatly with pressure. The yields of the other compounds decrease as the pressure is increased. At higher pressures more hydrogen atoms are produced. Therefore, the major processes in the system are consecutive H atom addition reactions which takes place on the surface.

High Molecular Weight Compositions. None of the gas chromatographic columns used were found adequate for a study of all the products. The observed high molecular weight products consisted of more than one compound. The only compound which was identified was biphenyl. Since the chances of an abstraction reaction compared with addition is low and the chance of an abstraction occurring on a labeled molecule is still less, the biphenyl yield should be very small. But there are other types of radical reactions which can take place in the system to form high molecular weight compounds. For example:

(14)

Probably this would be the major high molecular weight product since $C_6H_7^{\cdot}$ radicals are thought to be the major ones existing in the system. A higher filament temperature and thicker film showed higher yield of high molecular weight (Table 9) products. The results obtained agreed with those of Shores (26) when the same sampling technique was used. But with the improved sample collection technique, the high molecular weight yield increased to 15% on the average.

Hydrogen Atom Reactions with Toluene. The present study was carried out to determine the site of H atom substitution reaction in the toluene molecule. Wilzbach's study (12) involving exposure of toluene to T_2 (2.33 curie-days/mmole) showed the following result:
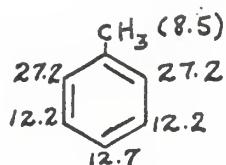
Ingalls (13) found that in the abstraction reaction of toluene with hydrogen atoms, the activation energy for abstraction from the methyl position was lower by 3-5 kcal/mole than from any other position on the molecule and hence abstraction from methyl position is the most probably site of an abstraction reaction. Tritiated toluene prepared by exposure to T atoms was oxidized to benzoic acid and the methyl position activity was found to be about 80% of the total activity in the molecule. This result agrees with Ingall's conclusion. An attempt to find out the activities in other positions failed due to exchange reactions that occurred in hot acidic medium between tritium on the ring and protons in the solvent. This kind of acidic exchange was observed by Melander and other workers (14).

An attempt was made to see how much exchange took place in the presence of oxidizing conditions. A 3 ml sample of toluene of known activity was

treated with 10 ml concentrated sulfuric acid for 55 minutes with continuous shaking. Seventy-four percent of the activity was lost to the solvent. Hence it was concluded that reactions involving acidic media are not suitable for determining the site of the tritium atoms in the ring.

Only five peaks were identified by a chromatographic analysis. The products identified were methylcyclohexane, 4-methylcyclohexene, 1-methyl-1-cyclohexene, 1-methyl-1,4-cyclohexadiene and toluene. A study of the effect of temperature is shown in table 10. A free radical mechanism similar to that proposed for benzene could be suggested here, although it is difficult to draw any conclusion from this data. With an increase in temperature a decrease in the yield of methyl-cyclohexane was observed. At higher temperatures more abstraction reactions should take place, especially in the methyl position producing more benzyl radicals, which would undergo combination reactions. The yield of labeled toluene was also found to increase with temperature. This should be another indication that more abstraction reactions occurred at higher temperatures.

<div align="center">SUMMARY</div>

The following conclusions are drawn from the results of this study of hydrogen atom reactions with solid benzene and toluene. 1) A fraction of hydrogen atoms produced have enough energy for abstraction reaction, and the labeled benzene is formed by the addition of hydrogen atoms to the phenyl radicals thus produced. The formation of labeled benzene through a complex intermediate has very little or no part in the mechanism. 2) A major part of the hydrogenated products results from consecutive addition reactions on the surface. 3) Disproportination and combination reactions also occur in the system mostly on the surface although there is only slight evidence that

any radical diffusion takes place. 4) The reactions do not stop with the formation of a saturated hydrocarbon. If the newly formed molecule is not able to transfer its excess energy formed through the formation of C-H bonds, to other molecules, it will vibrate apart. 5) The high molecular weight products consist of more than one compound and one of them is biphenyl. 6) In case of toluene the main abstraction site is the methyl position which contains about 80% of tritium in labeled toluene. 7) Toluene also gives hydrogenated products and possibly some combination products.

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REACTIONS OF HYDROGEN ATOMS WITH
BENZENE AND TOLUENE AT 77°K

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AN ABSTRACT OF A THESIS

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Reactions of tritium atoms with frozen benzene and toluene were studied. Tritium atoms were produced at a hot tungsten filament by the dissociation of a mixture of H_2 and HT. The pressure of hydrogen was usually kept low, so that the atoms produced at the filament could reach the benzene or toluene surface before colliding with other atoms or molecules in the gas phase.

Thin films of benzene and toluene at 77°K were reacted under these conditions, and the products were separated by gas chromatography and counted with a proportional counter placed in the effluent stream. In the case of benzene the products detected were: cyclohexane, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, benzene, n-pentane, n-hexane, and high molecular weight products. The following types of reactions are proposed to account for the formation of the products.

1) Abstraction of a hydrogen atom to form a free radical.

2) Addition of a hydrogen atom to a free radical or unsaturated molecule.

3) Radical-radical and/or H atom-radical disproportionation.

4) Combination of free radicals.

5) Decomposition of excited molecules.

By comparing results of reactions of both hot and thermal (77°K) hydrogen atoms it was concluded that labeled benzene was formed by a process with an activation energy of several kcal. A two step process involving hydrogen abstraction as the initial reaction is proposed.

The main reactions taking place in the system appear to be those classed as type 2 above. These reactions occur mainly on the surface and lead to a sequence of cyclic C_6 products ending with fully saturated cyclohexane. However since the pressence of high molecular weight products can be explained only by radical-radical combination reactions, radical-radical and hydrogen atom-radical disproportionation reactions may contribute also. Most of the