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REPORT NO. 1181
NOVEMBER 1962

MICROWAVE INDUCED DISSOCIATION OF n-HEXANE

Arthur D. Coates

Department of the Army Project No. 512-10-001
BALLISTIC RESEARCH LABORATORIES

ABERDEEN PROVING GROUND, MARYLAND

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Terminal Ballistics Laboratory

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Report No. 1181

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Aberdeen Proving Ground, Md.
November 1962

THE MICROWAVE INDUCED
DISSOCIATION OF n-HEXANE

ABSTRACT

n-Hexane was dissociated by a 2450 megacycle per second microwave discharge maintained at one torr ambient pressure in a flow system. The products were collected in liquid helium and nitrogen-cooled traps, and were identified and determined quantitatively by gas chromatographic and spectroscopic methods. Twenty-five individual components were detected in the product mixture. Dissociation of the n-hexane results primarily from electron-molecule collisions, and from thermal reactions in the discharge zone. The type of dissociation products formed from the hexane suggest that free radical reactions assume an important role in the dissociation and product formation reactions. The relatively large number of branched products in the C_6 - C_8 category are attributed to the large concentration of isobutene and to the presence and stability of the isobutyl radical in the dissociation zone. The results indicate that the dissociation product distribution is independent of microwave input energy over the range of 25 to 125 watts at 2450 megacycles. An amber solid was formed in the reaction zone during the n-hexane dissociation. The material was removed and studied in KBr by infrared spectroscopy. Thermal decomposition of the amber solid was conducted in vacuum and the decomposition products were analyzed.

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INTRODUCTION

This is a report on the study of the effect of microwave discharge on n-hexane. Initial experiments performed in these Laboratories demonstrated that n-hexane is decomposed when passed through a microwave glow discharge under certain conditions. The purpose of this investigation was to identify and determine the abundance of products formed when n-hexane was thus dissociated. The paucity of published information on the mechanisms of microwave dissociation of hydrocarbons, precludes a direct comparison of these findings with those of similar experiments. It is desirable first, to review briefly a selected group of the more significant publications pertaining to n-hexane decomposition studies wherein the effect and interaction of other dissociation systems upon the hydrocarbon have been more thoroughly investigated.

The dissociation of n-hexane has been performed by others using various experimental conditions, systems and sources of energy. Norton and Andrews¹, and somewhat later, Haber² published two of the early studies of the thermal decomposition of n-hexane, performed at 550-700°C. They found that decomposition began to occur in significant amounts at 600°C and that the decomposition was accompanied by the formation of unsaturated products. Rice has published a series of papers in which the thermal decomposition characteristics of the n-hexane were described. A method³ was presented whereby the amount of decomposition products of n-hexane might be calculated. In a later paper Kossiakoff and Rice⁴ discussed the probability of the occurrence of hexyl radical isomerization, and the effect of such isomerization on the calculated and observed amount of products obtained from n-hexane.

The dissociation of n-paraffins by electrical discharge methods followed the initial thermal decomposition studies by several years. Some of the earliest studies of n-paraffins were performed by Losanitch,^{5,6} who observed that n-hexane⁷ exposed to an electrical discharge at atmospheric pressure was converted into a gas containing 40% hydrogen, 58% saturated hydrocarbons and 2% unsaturated hydrocarbons plus higher liquid products. Unsaturated products were found to be polymerized rapidly in the electrical discharge. When n-hexane was exposed to the same discharge at reduced pressure it was found to produce also a C₁₂ compound.

Some evidence of other addition reactions was found, and the presence of $C_{18}H_{36}$ and $C_{36}H_{64}$ was postulated. The high frequency electrical discharge was employed by St. Aunay⁸ for the dissociation of n-hexane vapor. The gaseous products were composed of 43% hydrogen, 12% methane, 6% ethane, 21% ethene and 11% propane. The liquid product collected at $-70^{\circ}C$ consisted of 70% propane and 30% propylene. The liquid removed from the discharge tube was found to contain approximately 5% of an unsaturated product attributed to 1-hexene. No evidence of 1-hexene had been found in the initial sample material.

The variation of breakdown voltage with time, distance from electrodes, temperature and pressure for liquid n-hexane exposed to electrode-type electrical discharge has been described by Inge and Walther.⁹ The behavior of n-hexane in low voltage electrical glow discharge has been reported by Linder.¹⁰ Experiments were performed over a pressure range of 0.2 to 4.5 torr using 0.5 to 2.5 milliamperes at 450 volts. The liquid product was not recovered. However, a wax-like substance was deposited on the electrodes. The yield of products was found to be proportional to current, and independent of voltage and vapor pressure for n-C₅, n-C₆, n-C₇, n-C₈, n-C₉, n-C₁₂ and n-C₁₄ materials. Quantitative analysis of the gaseous product was not performed. It has been shown by Conrad¹¹, that the action of electrical discharge on n-hexane results in the formation of a large number of molecular fragments, radicals and new compounds which originated in the discharge. The analyses were performed by mass spectrometer on the initial discharge products.

The action of cathode rays on n-hexane has been reported by Schoepfle and Fellows.¹² The products obtained from a 25 cc. sample which received a thirty-minute exposure using 0.3 milliamperes at 350,000 volts included 57.6 cc. of gas of which 66.3% was hydrogen and 5.3% methane. The remainder was not analyzed, but was noted to be primarily saturated in character. The reactions of hydrocarbons produced by cathode rays were found to be analogous with those produced by x-rays and corona discharge.

The nuclear radiation induced decomposition of n-hexane has been studied using alpha, electron and gamma radiation. Henri, *et al*¹³ examined the alpha induced decomposition of n-hexane in the gas phase by exposing hexane vapors directly to radon gas. Conversion rates of approximately 40% were obtained, and 73% of the

product was in the form of a non-volatile liquid. The gamma radiolysis of n-hexane at reduced pressure, utilizing a cobalt-60 source has been reported by Krenz.¹⁴ The principal products found were hydrogen, methane, ethane, and an unsaturated hydrocarbon with approximately the same volatility as n-hexane. C_3 and C_4 products were detected, but in amounts negligible compared to the principal products. It was found that the addition of ($10^{-3}M$) anthracene to the original material had little effect on the gas yield, but did cause a decrease in the yield of unsaturated product.

Samples of n-hexane have been exposed in a nitrogen atmosphere to 800 kvp electrons by Dewhurst,^{15,16} who utilized a resonant transformer as the electron source. The gaseous and liquid products were studied as a function of the energy absorbed, temperature and presence of solutes. The yield of unsaturated product, mainly trans-vinylene, was independent of temperature, but was found in some cases to decrease in the presence of solutes, particularly oxygen and iodine. Volatile products consisted largely of hydrogen with smaller amounts of saturated and unsaturated hydrocarbons. An increase in irradiation temperature from -78 to $30^{\circ}C$ resulted in an increased hydrogen yield, whereas the hydrogen yield was found to be independent of temperature from $-120^{\circ}C$ to liquid nitrogen temperature. It was found that irradiated n-pentane, n-hexane, n-heptane and n-octane contained dimers of the original sample, i.e., n-decane, n-dodecane, n-tetradecane and hexadecane, respectively. No products with molecular weights larger than the respective dimers were detectable. Recently, the same author¹⁷ compared the radiolysis of n-hexane in both the liquid and vapor phases, and studied all products detected including those with boiling points higher than n-hexane. Excess amounts of hydrogen added to n-hexane vapors resulted in little change in the yield of low and intermediate molecular weight radiolysis products. However, the dimer yield was increased three-fold under the same conditions. The author discussed the relationship of the reactions occurring with ion-molecule, free radical and molecular reactions. A study of the high energy electron radiation chemistry of n-hexane in the liquid and vapor phase has been reported by Futrell,¹⁸ in which he determined hydrogen and the $C_1 - C_5$ hydrocarbon products. The author postulated that the products formed may be attributed to mechanisms based on very fast ion-molecule reactions of the hydride ion transfer type.

Mercury photosensitized decomposition of n-hexane in a flow system has been reported by Norrish and Purnell.¹⁹ Approximately one-third to one-half of the reacted hexane resulted in dodecane and other higher hydrocarbons. The remaining products primarily were lower alkanes and alkenes. The yield of decomposition products varied little with change of temperature, hexane pressure or time of reaction. The same authors²⁰ have studied the atomic hydrogen induced dissociation of n-hexane. It was found that hydrogen atoms, produced by mercury photosensitization, when reacted with hexane under flow conditions, resulted in a product mixture one-third of which had a molecular weight greater than hexane. Dodecane was the major component of this product. The effect of varying hydrogen concentration was studied, and significant decreases were found in the amount of unsaturated product as the hydrogen concentration increased. It was concluded that the initial product distribution was similar to that obtained by mercury photosensitization of n-hexane, and that the results indicated that the lower molecular weight products, i.e., below n-hexane derive almost completely from thermal decomposition of hexyl radicals. "Atomic cracking", the authors conclude, appears to be of little importance at the temperatures the experiments were conducted.

McCarthy²¹ utilized the 2450 megacycle magnetron oscillator to produce a microwave discharge to form free radicals and study their reactivity. It was found that the emission spectrum of a microwave discharge in methane shows a much more extensive band structure than that shown by a 60 cycle per second discharge in the same gas. This indicated increased molecular excitation and thus, greater potentiality for energy transfer from the electrical field to the molecules. Under the conditions of the experiments it was found that the production of free radicals per unit of input energy in a microwave discharge was approximately ten times that of low frequency or direct current discharges. When methane was passed into the microwave region both ethane and ethylene were found in significant quantities provided the effluent impinged directly on a surface cooled to liquid nitrogen temperatures. However, no ethane or ethylene was detected when the product flow was not permitted to impinge on the cooled surface.

It is conceivable that microwave induced reactions may offer a unique approach to dissociation and synthesis studies of basic scientific, as well as, potential commercial interest. The production of branched alkanes possessing a larger (CH_2) content than the starting material and the formation of compounds from other

normally unreactive elements or compounds, has synthetic potentialities. An additional advantage of the microwave induced dissociation is that free radical production per unit of input energy is ten times greater²¹ than that formed by low frequency electrical discharge. This adds to the economic attractiveness of this electrical discharge system for synthetic uses. With the development of gas chromatography, complemented by mass spectrometer and infrared spectrophotometer it has become possible to conduct complex analyses with a simplicity, speed and accuracy not available to the early investigators of n-paraffin dissociations. A study of the products formed by microwave induced dissociation of n-hexane becomes possible. The paucity of quantitative data for such relatively large molecules makes the study one of current interest.

EXPERIMENTAL

Material

Phillips Petroleum Co. "pure" grade n-hexane was used for the dissociation studies. The liquid hexane was purified by vacuum distillation, and the 10-90 percent fraction was used for the experimental studies.

Dissociation Apparatus and Procedure

A schematic drawing of the dissociation apparatus is shown in Figure 1. The sample container was a calibrated pyrex cylinder. This was connected perpendicularly near the center of the horizontal, 25mm tube in which the microwave plasma was maintained. A vacuum valve positioned between these two components provided sample flow regulation into the plasma region. Temperatures within the dissociation zone were monitored by a pyrex thermometer which was positioned in the center of the plasma region through a vacuum gland. The exterior wall temperatures of the dissociation region were obtained by iron-constantan thermocouples which were read on a direct reading potentiometer. The thermocouple junctions were attached to the exterior wall of the discharge tube by heat resistant pressure tape, and by imbedding the thermocouple directly into the pyrex surface.

Following the dissociation region, the products and intermediates flow toward and impinge directly on the vertically positioned liquid nitrogen cooled pyrex cold finger, located perpendicular to the product flow. All products except hydrogen and methane are retained at this point. Trap number one, the cold finger, extends eight inches below the area where the dissociation products strike.

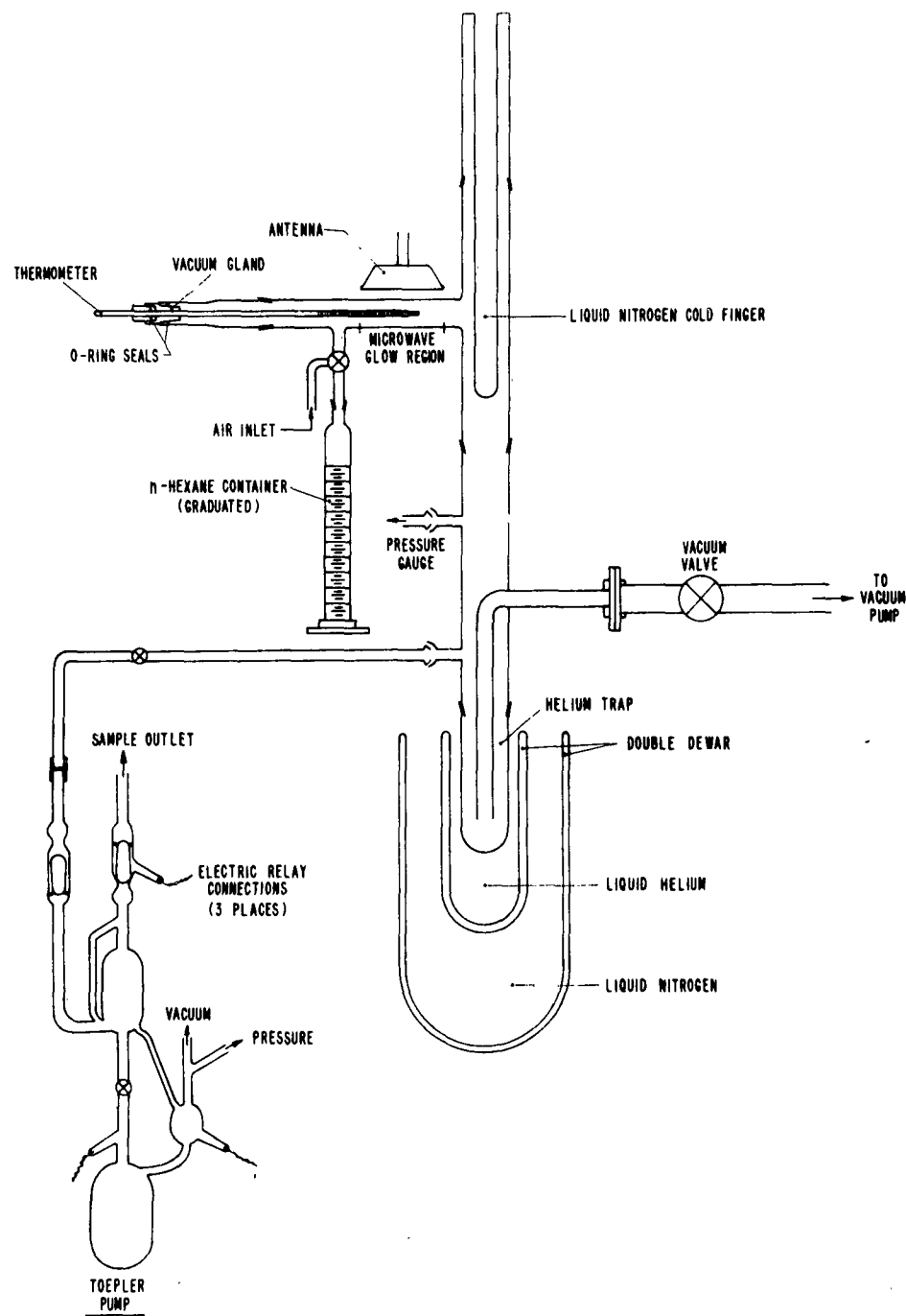


FIG. 1-THE MICROWAVE GLOW DISSOCIATION SYSTEM

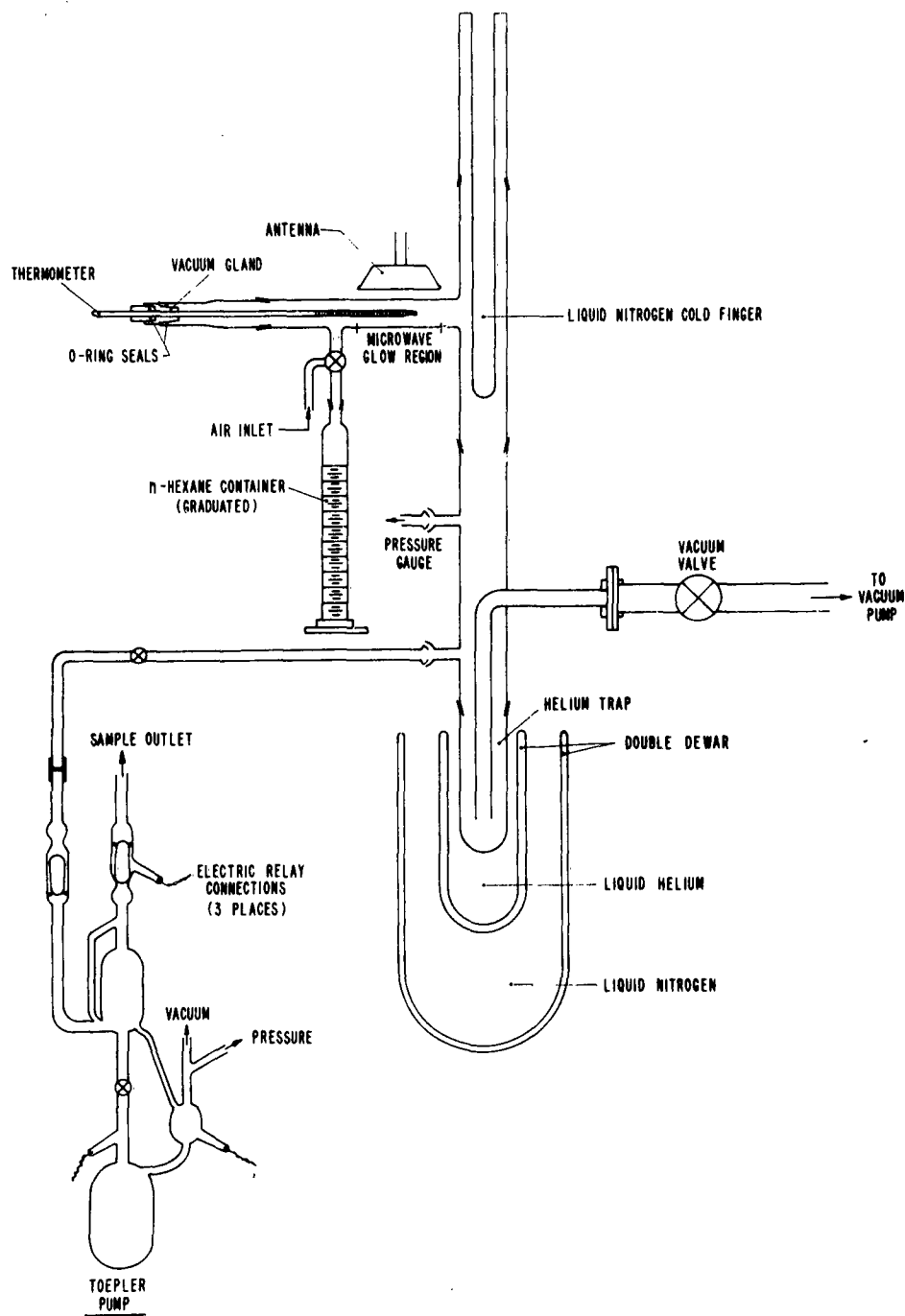


FIG. 1-THE MICROWAVE GLOW DISSOCIATION SYSTEM

Since the products must pass by this extensive cooled surface, as the gases travel toward the vacuum pump, the efficiency of the trapping action is enhanced. Trap number two is located in line, directly below the cold finger. Hydrogen and methane are retained in this trap when refrigerated with liquid helium. Upon completion of a dissociation experiment, the volatile products were removed first from the helium trap and then from the cold finger by toep-ler pump. When desired, the cold finger refrigerant may be removed and all products condensed in trap number two. Provision was made to weigh the products condensed in the second trap. For experiments not conducted with liquid helium, trap number two was filled with liquid nitrogen. No products were condensed in this second trap if refrigerant remained in the cold finger. This attests to the condensing efficiency of the cold finger, as well as successful elimination of vacuum pump oils from the product sampling region.

Pressures in the dissociation system were maintained with a 432 liter per minute mechanical vacuum pump, having the distinct advantage of very high pumping capacity at the experimental operating pressure. The system was evacuated to 1×10^{-3} torr for one hour prior to each dissociation experiment.

The microwave energy was supplied by a Raytheon Manufacturing Company unit, model number CMD4. The output of the unit was variable from 0-125 watts at 2450 megacycles, and was delivered through a conventional antenna.

Gas Chromatography Analysis

The analyses of the dissociation products were accomplished by the use of both isothermal and programmed temperature vapor phase chromatography complemented by infrared spectrophotometry and mass spectrometry. The identification of each component by vapor phase chromatography was performed by peak enhancement of the unknown product, utilizing pure standard samples as references. The concentrations of the individual products were determined from the integrated areas under the chromatogram peaks.

To simplify and increase the accuracy of the identification of the complex liquid product mixture by chromatographic analysis, the liquid product mixture of several dissociations were combined and distilled into smaller boiling point ranges containing fewer hydrocarbons. Table I illustrates the ten distillation temperature ranges into which the liquid was separated.

TABLE I

Distillation of the Higher Boiling Point Products from the Microwave
Induced Dissociation of n-Hexane

<u>Fraction</u>	<u>Temperature Range °C</u>
1	23.5 - 30
2	30 - 50
3	50 - 60
4	60 - 65
5	65 - 67
6	67 - 69
7	69 - 70
8	70 - 72
9	72 - 74
10	74 - E.P.

The products were determined quantitatively in three separate lots. These were: (1) products condensable only in liquid helium, (2) products condensed by liquid nitrogen, but volatile at dry ice temperature, and (3) products with boiling points above dry ice temperature. The C_2 and C_3 products represent the sum of two analyses, since some of each was found in both product groups two and three listed above. Hydrogen and the $C_1 - C_2$ hydrocarbons were analyzed using a two meter gas chromatography column 6.4 mm in diameter. The column was packed with 24-80 mesh silica gel. Hydrogen and the $C_1 - C_2$ hydrocarbons were determined using argon as the chromatography eluent. For the determination of the dissociation products C_3 and above, the partitioning column was 6.4 mm in diameter and six meters in length, packed with 30-60 mesh fire brick which had been impregnated with 40 per cent by weight of tri-m-tolyl-phosphate. The helium eluent flow was maintained at twenty milliliters per minute.

Infrared Spectroscopy

The dissociation products up to the C_6 hydrocarbons were identified by vapor phase chromatography. The identification of products above C_6 presented a more complex problem since the number of possible isomers and the number of hydrocarbon standards required were significantly greater. To facilitate the chromatographic analysis of C_7 and C_8 hydrocarbons and to decrease the number of standard samples

required, the following procedure was utilized. Samples of the higher boiling range products, Table I, were charged into the gas chromatography unit. As the components were separated and emitted from the chromatography unit the unknown product under study was trapped. Several injections of each fraction, into the partitioner, were required for each unknown component. Only one component was collected during each chromatography run.

After sufficient product had been isolated, an infrared spectrum of the sample was obtained. The absorption regions present in the infrared spectrum attributable to the sample were compared with those in the American Petroleum Institute series on the infrared spectra of hydrocarbons. With this procedure one may tentatively identify the hydrocarbon isolated or limit the number of possible isomers responsible for the infrared spectrum. The infrared determinations were performed on a Perkin-Elmer model 13 spectrophotometer. This procedure was repeated for each dissociation product above n-hexane on the chromatogram of dissociation products. The possible products were tabulated, and samples of each were obtained from the National Bureau of Standards. The positive identification of each product, C₇ and above, was performed by the gas chromatography peak enhancement method described earlier in this section.

During the dissociation process an amber colored solid material deposited on the inside of the discharge tube. Several grams of the material were collected from the discharge region. The amber solid was mixed with KBr in a ratio of one part amber solid in 199 parts KBr by weight. This mixture was ground and pressed into pellet form by conventional procedures. An infrared spectrum of the prepared pellet was then obtained.

Mass Spectrometer Analysis

During the initial phase of this study a mass spectrometer was utilized to identify the products formed during the dissociation process. The large number of products found discouraged such use, and it was evident that gas chromatography was more suitable for the analysis of the complex mixture. The use of the mass spectrometer was continued to complement vapor phase chromatography analysis for the detection and determination of hydrogen and methane present in the product mixture.

To characterize further the nature of the amber solid formed in the reaction zone, ten gram samples were collected for decomposition studies. An investigation of its thermal decomposition was performed to obtain information on the decomposition products of this solid material. The amber solid was placed in a quartz container that was attached to a high vacuum system. The sample container was evacuated to 1×10^{-5} torr and maintained at that pressure for twenty-four hours to facilitate removal of volatile material that may have been adsorbed on the surface of the solid. The vacuum system was then isolated from the sample container. The evacuated cylinder and amber solid were then heated to 400°C and this temperature was maintained for twenty minutes. Provision was made to obtain samples of the vapors evolved, for mass spectrometer analysis.

RESULTS

The products trapped when passing n-hexane through the microwave plasma, at a flow rate of fifteen milliliters per minute, a pressure of one torr and with the microwave power output at 100 watts are listed in Table II. The amount of each product detected also is included, with the exception of the amber solid formed in the reaction zone. The dissociation products are listed as moles of product detected for each 100 moles of n-hexane passing into the microwave region.

The products may be divided into three groups. (1) Products with molecular weight less than n-hexane, (2) products with molecular weight of n-hexane and greater, and (3) the amber solid formed in the reaction zone. The division is convenient because of the large diversity of vapor pressures, the analytical methods used in the analyses, and methods of sample collection and storage. Group one contained hydrogen and lower olefin and paraffin hydrocarbons, while group two contained n-hexane, three other six-carbon, four, seven-carbon, and two, eight-carbon compounds. Group three was the amber solid, the specific composition of which is speculative. No acetylene or hexene was detected in the products by any of the three analytical methods used in these studies.

Hydrogen, the most volatile dissociation product has a melting point of -259°C and should be retained in the liquid helium trap. The trapping efficiency of the liquid helium trap was not studied specifically, and the loss of small amounts of hydrogen is not inconceivable. The reported amounts of the extremely volatile hydrogen thus are subject to larger potential experimental error than are any of the other reported products.

TABLE II
Microwave Dissociation Products of n-Hexane

<u>Product</u>	<u>Moles/100 Moles Hexane Exposed</u> *
Hydrogen	29.4
Methane	12.3
Ethane	16.6
Ethene	6.4
Propane	9.0
Propene	8.8
n-Butane	5.8
Isobutane	1.0
Isobutene	7.5
Cis-2-Butene	1.5
Trans-2-Butene	1.5
n-Pentane	2.1
2-Methylbutane	0.6
2-Methyl-1-Butene	0.8
2-Pentene	1.6
2,2-Dimethylbutane	2.4
2,3-Dimethylbutane	0.6
3-Methylpentane	1.1
n-Hexane	41.7
2,2,3-Trimethylbutane	2.6
3,3-Dimethylpentane	2.7
3-Methylhexane	1.4
3-Ethylpentane	1.5
3,4-Dimethylhexane	0.9
3-Methylheptane	0.7

* Moles of n-hexane exposed is defined as the total mass flow of a n-hexane into the discharge region.

Variation of Experimental Conditions

The products reported are for experiments conducted at a pressure of one torr with 100 watts output of microwave power to the antenna. Under these conditions maximum stability of the microwave glow discharge and minimum variation of experimental results were attained. When the power output was varied between 30 and 125 watts and the n-hexane flow maintained at constant rate, the same hydrocarbons were found in the dissociation product mixture. Though the fraction of n-hexane converted, decreased as the microwave power was decreased, the ratio of the individual products remained essentially constant.

The flow of n-hexane vapor into the discharge region was then varied in five milliliter increments from five to thirty milliliters per minute, at 100 watts output. At flow rates above 15 milliliters per minute the amount of n-hexane detected in the product began to increase. As in the study of power variation, if the n-hexane concentration in the product mixture is neglected the change in the relative amount of each of the other products detected was small, but the n-hexane found in the product increased with increasing flow rate. The increase in flow rate was accompanied by a decrease in reaction zone temperature, along with a change in color of the microwave induced glow. At flow rates of 10 milliliters per minute of n-hexane vapor, the color of the discharge was a pale blue, while at 30 milliliters per minute the glow was red. At intermediate flow rates the color of the glow was a mixture of red and blue.

Characterization of Amber Solid Deposit

In the electrical discharge, used for hydrocarbon dissociation studies, it has been reported that one of the major losses of radicals is to the wall of the discharge tube region. This applies for studies conducted at low pressures, such as the one reported herein. The major loss of electrons from an electrodeless discharge²² zone also is to the wall of the reaction vessel. Since both radical and electron population are probably significant at the wall of the reaction zone, the amber solid formed may well be attributed to the reaction or dissociation of hexyl or other radicals at this surface. The wall temperature of the pyrex dissociation region also may influence the dissociation of the n-hexane vapor, the products formed, or a combination of both. To decrease these wall effects, efforts were made to perform dissociations in very clean apparatus. Despite these efforts the amber polymeric material continued to deposit on a four inch length of the

inner wall of the dissociation region. This material adhered tenaciously to the pyrex and could be removed only partially by mechanical scraping or completely by operation of the discharge with the sample removed and a small air flow through the discharge region. One additional experiment was conducted which had as its object, to eliminate or decrease the amount of amber deposit formed. The interior of the reaction tube was coated with meta-phosphoric acid, a compound with established radical recombination inhibiting characteristics. While the rate of deposition appeared to remain low at the beginning of the experiment, the meta-phosphoric acid coating could not be maintained and the region was soon covered with the solid deposit. Thus it was not possible to ascertain the effectiveness of the compound for decreasing wall reactions, or to affect product variation in the dissociation mixture.

The microwave induced amber solid formed during the dissociation of n-hexane is insoluble in all common laboratory solvents. Upon heating the solid decreases in volume. Products detected when the deposit was heated to 400°C at 1×10^{-5} torr were hydrogen, $\text{C}_1 - \text{C}_5$ alkanes and $\text{C}_2 - \text{C}_4$ olefins. No hexane or any other compound with a molecular weight above pentane was detected in the evolved products of the amber solid. The identifications were performed by mass spectrometer. Figure 2 shows the infrared spectrum of the solid deposit in KBr. The ESR spectrum of the amber solid also was obtained and indicated the absence of trapped radicals.

Trace Products

A mass analysis of the higher boiling range products revealed the presence of very small amounts of three compounds, in addition to those listed in Table II. These products were found in the 90-110 mass region. One interesting product was that of mass 92 most likely attributable to toluene. The significance of this observation is that an aromatic hydrocarbon may have been produced by exposing a n-paraffin to a microwave discharge. The two other products were of the mass regions of 102 and 108.

DISCUSSION

The microwave glow has been described by McCarthy²¹ as one of the most effective electrical discharge dissociation sources. He utilized it for dissociation studies of nitrogen, oxygen, hydrogen, and methane. Several other electrical discharge techniques and devices have been reported by other authors for dissociation and free radical studies. The three most frequently used types of electrical

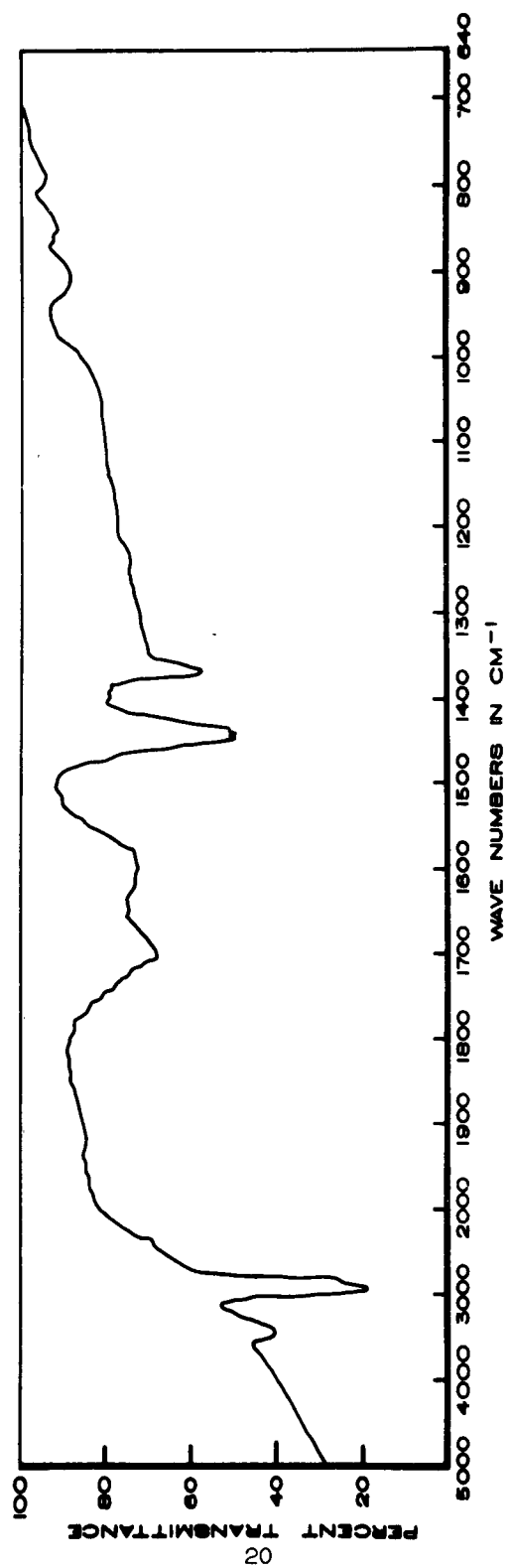


FIG. 2 - INFRARED SPECTRUM OF SOLID FORMED IN REACTION ZONE
0.5% SAMPLE IN KBr

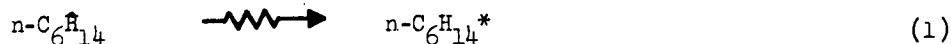
discharge units ²² for dissociation studies are the low frequency, radio frequency and microwave discharge. In an electrical discharge, the generally accepted picture of low pressure, gaseous dissociation process by electron-molecule collisions, postulates a swarm of electrons moving through the gas under the influence of an applied electrical field.²² The majority of electrons arise from ionizing collisions in the discharge. To sustain the discharge, the rate of electron production must balance the rate of electron loss. In the high frequency discharge, electrons are lost primarily by diffusion to the walls of the containing vessel. Dissociation by means of electron-molecule collisions may be the direct result of electron impact or may occur indirectly by the production of a metastable intermediate following the electron impact. Dissociation then occurs following a secondary encounter between the metastable intermediate and a neutral molecule or free radical. In a polyatomic molecule, the processes become quite complex, and it is probable that at least two modes of dissociation are occurring simultaneously.

Dissociation Mechanisms

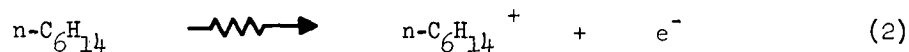
The microwave induced dissociation of n-hexane represents an extremely complex process. The production of twenty-five products in readily detectible amounts virtually precludes critical consideration of reaction mechanisms. In addition, the amber solid deposit which cannot be quantitatively recovered negates the usefulness of a material balance. However, it is constructive to consider certain features of the dissociation pattern.

Microwave radiation will sustain a discharge in the reaction zone and although dissociation is attributable in part to ionization, it is not implied that the results are identical with interactions of ionizing radiation of nuclear origin. It is believed, that the initial reactions of n-hexane with both microwave plasma and ionizing radiation are not completely dissimilar, and that the microwave plasma dissociation reactions resembles electron-molecule and high energy electron reactions such as those described by Dewhurst ¹⁷ and Futrell¹⁸.

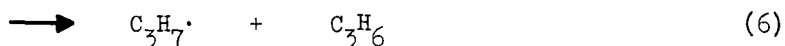
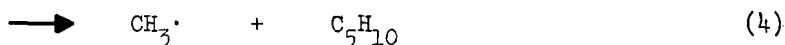
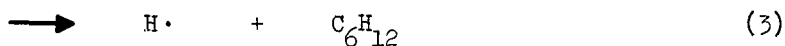
The interaction of ionizing radiation and paraffin hydrocarbons leads to both excited and ionized atoms and molecules.²³ It is believed that the initial reactions involved in the microwave dissociation of n-hexane are:



and

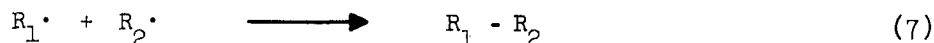


Subsequent reactions of the excited molecules are different from those of the ions. The former leads primarily to hydrogen atoms, methyl radicals and hexyl radicals while the latter leads mostly to hydrogen molecules, olefines etc.²³ The hexyl radicals that fragment during the initial dissociation process are believed to follow the dissociation pattern shown below.



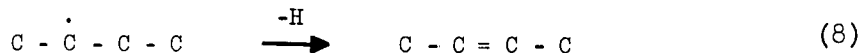
It has been suggested by Dewhurst,¹⁷ that vapors of n-hexane subjected to high energy electron bombardment show a greater yield of products which must result, ultimately from C-C bond cleavage, while liquid hexane exposed to the same type of radiation shows a higher proportion of products, attributable to C-H bond cleavage. It is assumed that a similar pattern exists in the vapor phase studies of n-hexane exposed to the microwave plasma zone. It is believed that hexene, if formed, is reacted with other intermediates present in the reaction zone. The absence of 1-pentene reaction (4) in the microwave product mixture may be attributable to microwave induced reaction causing the olefin to dissociate further, to rearrange into the 2-pentene product, or to react with the hydrogen, methyl or ethyl radicals in the reaction zone. The similar amounts of both propane and propene found in the product mixture lends credence to the assumption that reaction (6) may occur in the product formation pattern. Reactions (3), (4), (5) and (6) are presumed to occur with different probabilities.

The majority of the products listed in Table II may be attributed to formation from hydrogen, methyl, ethyl or propyl radicals, which probably result from secondary reactions involving excited molecules, ions and radicals. It is probable that products attributable to formation from two components in the reaction zone, resulting from an initial encounter between a metastable intermediate and a radical, ion or excited molecule is much more likely to occur than that of three components resulting from the addition of two radicals,



followed by reaction of $R_1 - R_2$ with another radical, ion or excited molecule. It is believed that reactions outside of the plasma region are limited to atoms and radicals, and that ions and electrons do not exist beyond the microwave region²⁴.

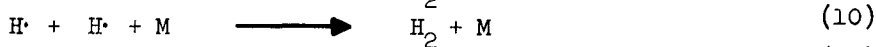
The formation of cis and trans-2-butene, 2,2,3 trimethylbutane, 3,3 dimethylpentane and 2,4 dimethylhexane are not explained readily, by conventional radical reactions, although cis and trans-2-butene may be attributed to formation from the olefin radical, the transient existence of which has been postulated by Buckley and Swarc²⁵. The same authors have found that the affinity of both cis and trans-2-butene for reacting with methyl radicals is quite low, and attributed this characteristic to steric hindrance. Thus the presence of the hindered cis and trans-2-butene and the absence of the less hindered 1-butene in the microwave product mixture is reasonable. The two butene isomers also may result in part from the loss of a hydrogen atom from the sec-butyl radical by electron or metastable intermediate collision, followed by rearrangement to form



the butene isomers. The similar amount of each isomer formed in the product mixture is indicative of similar probabilities of formation in the rearrangement processes.

Dissociation of n-Hexane by Mercury Photosensitization

The reactions of the C_1 , C_2 and C_3 alkyl radicals are reasonably well established. However, little information is available concerning the specific reactions of the hexyl radical. A series of reactions have been shown in a detailed study of the photolysis of n-hexane using 2537 Å light. Norrish and Purnell,¹⁹ who performed this series of experiments, conclude that hexyl radicals are produced, and that the following reactions are important in the n-hexane dissociation process when performed at 300°C, as well as, in the subsequent product formation.



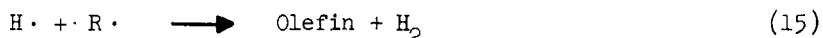
(Where R = hexyl radical)

It was assumed that the rates of reaction of (9) and (11) are comparable, and that the reaction of:



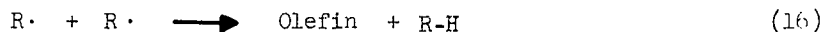
is very rapid and well known. Hydrogen atoms in the reaction zone, it was postulated, react only by (10) (11) and (12).

While the reactions:

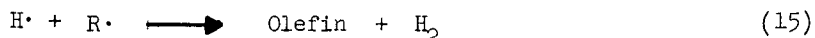


are of little consequence to the overall product formation mechanisms.

Disproportionation of two radicals:



has been postulated elsewhere in connection with paraffin decompositions. However, Smith, Beatty, Pender and LeRoy²⁶ as well as Bradely, Melville and Robb²⁷ have shown that the importance of this disproportionation reaction has been over-emphasized. In addition, it is believed that in the reaction of the hexyl radical at 300°C, disproportionation is negligible compared to the amount of thermal cracking that is occurring. Additional evidence against disproportionation of hexyl radicals is that if:



does occur, hexene should be formed, and should be found in the product mixture. However, no hexene was detected in the final product mixture.

From these results, one might assume that when a n-alkane undergoes photolyzed dissociation, the corresponding olefin is rarely detected in the ultimate products. Previous investigators have found this to be true. Bywater and Steacie^{28,29} studying n-alkane dissociations, found large yields of propylene but no butylene from n-butane. Propane likewise yielded ethylene but no propylene. Thus when one compares the results of mercury photosensitized dissociation of n-hexane with those of the microwave studies reported herein, certain similarities do appear. First, in each of the two series of experiments, temperatures in the dissociation regions are in the order of 300°C and it has been established that the thermal stability of

the hexyl radical at 300°C is poor.¹⁹ Thus, hexyl radicals formed in each series of experiments are subject to influences which may result in further dissociations. Second, a series of alkane radical reactions are established in which the most favored reactions are separated from the less important reactions. Third, the C₁-C₅ products formed in each series of experiments while not identical are somewhat similar, although the product distributions are not correlatable. Fourth, no hexene was detected in the product mixture of either series of experiments. This fact gives added support to the concept that disproportionation reactions of the hexyl radical are of little importance in the dissociation product reactions. Fifth, in both series of experiments it was found that an increase of n-hexane flow into the dissociation region caused a decrease in the conversion rate of the hexane. However, in both cases only very small changes were found in the relative distribution of all other products. The residence time of the n-hexane molecule in the microwave region is estimated to be 0.08 of a second which is probably much shorter than the time of exposure of the n-hexane in the photolytic dissociation apparatus. However, the microwave method has been established as a very efficient dissociation and energy transfer system, attributable in part to the efficient coupling that is obtained readily between the microwave induced glow and the dissociation sample. Thus it is believed that the residence time of the n-hexane in each system may not be directly correlated with dissociation efficiency or hexyl radical stability.

A major difference in the products of the two systems concerns the formation of dimers of the hexyl radical. n-Hexane dissociated by mercury photosensitized reaction yielded a significant amount of the C₁₂ hexyl dimer, while n-hexane subjected to microwave discharge resulted in no detectable C₁₂ product.

Dissociation of n-Hexane by Atomic Hydrogen

It has been shown²⁰ that n-hexane exposed to atomic hydrogen will dissociate and yield products similar to those noted for mercury photosensitized¹⁹ dissociation of n-hexane. Norrish and Purnell²⁰ found that both ethylene and propylene disappear from the dissociation product mixture when the hydrogen to n-hexane ratio was raised to ten to one respectively, and no olefins were detected at hydrogen-hexane ratios above twenty-five to one. Experiments were conducted at ratios up to fifty-five to one, but only the olefin content was affected significantly. Little change in the distribution of saturated products was observed as

hydrogen atom concentration increased, although the percentage of n-hexane dissociated does vary with increasing hydrogen concentration.

It is assumed that hydrogen atoms are present in the n-hexane microwave plasma region. Since, both ethylene and propylene were detected in the microwave products, the hydrogen atom concentration in the dissociation region apparently is small. It has been established that increasing hydrogen atom concentration decreases the olefin content in the n-hexane studies of Norrish and Purnell.²⁰ Thus it is assumed that the relatively large olefin content present in the microwave product, indicates a hydrogen concentration that is quite small. Since the hydrogen concentration in the reaction zone is low, this dissociation process contributes less significantly to the microwave dissociation reaction than do the electron-molecule reactions and thermal reactions.

Thermal Dissociation of n-Hexane

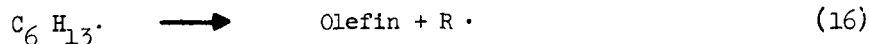
When a straight chain hydrocarbon is decomposed thermally, it yields a lower paraffin and an olefin, where the saturated fragment is the shorter of the two.³⁰ The probability of C - C bond rupture is greatest at the link between the number one and number two carbons, methane being formed in the highest proportion. The probability of rupture at the link between the second and third carbon is lower, although the proportion of ethane formed is considerable. The amounts of propane and higher paraffins that are formed are much smaller. The probability of thermally induced C - C bond scission is shown in Table III.

TABLE III

Relative Probability of Carbon to Carbon Bond Rupture³⁰ for
Thermal Dissociation of n-Alkanes

<u>Hydrocarbon</u>	<u>C₁₋₂</u>	<u>C₂₋₃</u>	<u>C₃₋₄</u>
n-Pentane	1.0	0.78	
n-Hexane	1.0	0.5	0.25
n-Heptane	1.0	0.64	0.35

Norrish¹⁹ has found the hexyl radical to be thermally unstable above 290°C., with the decomposition following the path,



where the olefin is the larger of the two products. When the n-hexane is

dissociated by the microwave discharge, the hydrocarbon and the initial dissociation products are exposed to temperatures of greater than 300°C at the center of this dissociation region. Since it has been established that the hexyl radical is thermally unstable at 300°C , it is probable that thermal dissociation of the hexyl radical would occur near the center of the discharge region.

The thermal dissociation of n-hexane has been studied by Rice.³ The experimental conditions under which that study, and these microwave investigations were conducted precludes critical comparison of the two. However, there exists one similarity which has an interesting aspect. This is the similarity of the thermal dissociation products of n-hexane as reported by Rice, and the products detected when the microwave produced amber solid deposit was decomposed when heated in vacuum. The products found in each study are listed in Table IV. Products from the plasma region deposit, were analyzed by mass spectrometer. The individual C_4 olefins, butane and pentane isomers were not identified.

While one has no substantial evidence that the solid deposit is attributable to a C_6 material, the lack of C_5 and C_6 olefins and the overall product distribution does not preclude this postulation, since it has been established that the corresponding olefin of a saturated hydrocarbon undergoing dissociation is rarely detected in the reaction products. The infrared spectrum of the amber solid in KBr, shown previously in Figure 2 indicates some unsaturation but negligible aromatic content. Solid deposits have been described by previous investigators^{7,8,12} using electrical discharges for the dissociation of n-alkanes. In those studies the solid was deposited on the electrodes, of the electrode type discharge tubes, or on the inner pyrex or quartz surface of the discharge regions used for electrodeless discharge experiments. The microwave induced solid deposit also has been observed recently, by Walker, Vastola and Wightman²⁴ on the inner surfaces of their reaction tubes. However, little information is available concerning the characteristics of these solid deposits which may contain a clue to the microwave induced dissociation reaction mechanisms of organic materials.

Effect of Experimental Conditions on n-Alkane Dissociations

The effect of ambient pressure variation on the activation energy of thermal dissociation reactions has been discussed by previous investigators.^{31,32} It was found that one of the interesting characteristics of n-paraffin decompositions is that from n- C_4 to the higher homologs, the activation energy of the molecular

TABLE IV
Thermal Decomposition Products of n-Hexane³ and the Microwave
Formed Amber Solid

<u>n-Hexane Products</u>	<u>Amber Solid Products</u>
Hydrogen	Hydrogen
Methane	Methane
Ethane	Ethane
Ethene	Ethene
Propane	Propane
Propene	Propene
n-Butane	Butanes
1-Butene	
2-Butene	Butenes
Isobutene	
n-Pentane	Pentanes

reaction becomes a well defined function of pressure. However, the relative proportions of the saturated hydrocarbons formed in the decomposition of n-pentane, n-hexane and n-heptane are independent of ambient pressure.³⁰ It is assumed that there are kinetically different modes of activation, corresponding to different relations between total energy of the molecule, energy required in a critical location, and the dissociation probability of the energized molecule. From *prima facie* evidence it is postulated that at low pressures, large total energy accumulations in the molecule have time for redistribution, and cause dissociation when an appropriate part is concentrated in the specific bond,³⁰ as in the classical theory of unimolecular reactions. There is little difficulty with molecules the size of butane and the higher paraffins in accounting for an energy accumulation rapid enough to provide the necessary activation rate.^{31,32} The extrapolated activation energies of some representative n-paraffins at both high and low pressures are given in Table V. It is suggested that if the microwave plasma could be maintained at pressures of 700-800 torr, the n-hexane conversion rate might be appreciably increased. At the present time, the author has not been successful in these experiments.

TABLE V
Variation of Activation Energy with Pressure³⁰

Hydrocarbon	E, K cal	
	Lowest Pressures	High Pressures
n-Butane	69	58
n-Pentane	93	63
n-Heptane	88	59

CONCLUSIONS

The qualitative and quantitative determination of the products of microwave dissociated n-hexane are difficult, because of the wide spread of product vapor pressures and the techniques required for the identification and determination of the amount of each component in the product mixture. A material balance is virtually impossible since the solid deposit formed during the dissociation

reaction is extremely difficult to remove from the inner walls of the reaction tube. The formation of at least twenty-five products during the dissociation process precludes critical comparison of reaction mechanisms.

The results indicate that n-hexane subjected to microwave discharge is decomposed primarily by electron-molecule reactions yielding an active molecule and a free radical. The reactants then dissociate further by electron collision, or recombine with other reactants present in the dissociation region or are caused to react further because of other environmental influences in the microwave plasma region. It is assumed that the reaction of all intermediate products occurs between the plasma region and the liquid nitrogen cold finger trap.

The products formed in the range C_1 to C_3 are similar to products formed when n-hexane is dissociated by high energy electron irradiation, thermal decomposition, hydrogen atom reactions and mercury photosensitization. It is more important to note, however, that the microwave product distribution for products $> C_4$ is not similar to that of any other energy system.

Dimers of the hexyl radical were not detected in the reaction product mixture. This indicates that hexyl radicals, in the reaction zone, dissociated into smaller products or that the hexyl dimers formed, were unstable in the plasma region and dissociated again into other products. It is more probable that the former statement approximates the actual conditions existing in the plasma region. The relatively large number of C_5 - C_7 branched alkanes and the relatively large amount of isobutene present in the reaction products indicates that some isomerization occurred. Similar amounts of propane and propene in significant quantities, suggests that C_3 - C_4 carbon-carbon bond scission is prevalent in the dissociation process.

It has been established that the hexyl radical is thermally unstable at the temperatures existing at the center of the plasma region, and dissociates to form a free radical and an olefin. Electron-molecule reactions of n-hexane also produce a free radical as one of the products. Therefore, the free radical concentration in the reaction zone is believed to be significant, and it is felt that where reaction intermediates do recombine it is primarily by free radical mechanisms. The variation of microwave power, over the range of 25-125 watts, to the plasma region caused no change in either the number or the type of products isolated. However, a decrease in power decreases the hexane conversion, and

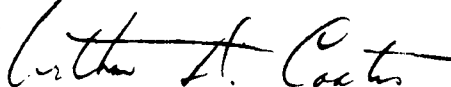
one finds increasing amounts of hexane in the product mixture as microwave power is decreased. When the power input to the plasma region is held constant, an increase in n-hexane flow rate into the plasma region affects the product mixture in the same manner as does a decrease in microwave power.

The amber solid formed in the dissociation region is a very stable substance, is insoluble in all conventional laboratory solvents, and appears somewhat polymeric in character. The deposit may be decomposed thermally, in vacuum, into at least nine species. The amber deposit removed from the reaction zone contains no radicals. The large number and structural variation of the microwave products indicates that the microwave plasma is a more efficient dissociation source for n-hexane than any other type of electrical discharge. Product distribution is dissimilar to that reported for any other energy system.

It became evident as this initial study of the microwave dissociation products of n-hexane progressed, that information on other facets of the microwave induced changes in organic materials would be useful, in addition to the commercial and syntheses potentialities. Future studies for instance might include the effects of additives to inhibit, promote or control specific product formation. The effect of pressure variation on the dissociation conversion efficiency. Further characterization of the amber solid and the determination of the product variation caused by hydrogen atom and methyl radical addition into and just beyond the microwave plasma region would aid in determining the characteristic reactions that do occur.

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ARTHUR D. COATES

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n-Hexane was dissociated by a 2450 megacycle per second microwave discharge maintained at one torr ambient pressure in a flow system. The products were collected in liquid helium and nitrogen-cooled traps, and were identified and determined quantitatively by gas chromatographic and spectroscopic methods. Twenty-five individual components were detected in the product mixture. Dissociation of the n-hexane results primarily from electron-molecule collisions, and from thermal reactions in the reaction zone. The type of dissociation products formed from the hexane suggest that free radical reactions assume an important role in the dissociation and product formation reactions. The relatively large number of branched products in the C ₆ -C ₈ category are attributed to the large concentration of isobutene and to the presence and stability of the isobutyl radical in the dissociation zone. The results indicate that the dissociation product distribution is independent of microwave input energy over the range of 25 to 125 watts at 2450 megacycles. An amber solid was formed in the reaction zone during the n-hexane dissociation. The material was removed and studied in KBr by infrared spectroscopy. Thermal decomposition of the amber solid was conducted in vacuum and the decomposition products were analyzed.	Accession No. Ballistic Research Laboratories, APG THE MICROWAVE INDUCED DISSOCIATION OF n-HEXANE A. D. Coates ERL Report No. 1181 November 1962 DA Project No. 512-10-001 UNCLASSIFIED Report
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