

THE MERCURY PHOTSENSITIZED REACTIONS
OF SOME HYDROCARBONS

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OF SOME HYDROCARBONS

THESIS

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CHAPTER I

THE NATURE OF PHOTOCHEMISTRY

Ordinary chemical reactions are the results of molecular collisions. Such reactions require from 10 to 100 kilocalories per mole so that only those molecules having a high amount of energy can obtain this activation from collision. Reaction is especially difficult if the activation energy is high and the temperature low. However, molecules may be activated by some external source of energy such as heat or radiation.

Radiant energy is emitted as discrete particles of matter containing a quantum or photon of energy.¹ Absorption of such radiations can produce a chemical change although not all absorption of light is accompanied by a chemical reaction. The study of this type of reaction, that is one which receives energy from an external radiant source, is known as photochemistry.

When a photon of a frequency that can be absorbed and that has sufficient energy to produce a reaction comes near a molecule that is to be activated, several things may happen. (1) There may be a transfer of energy from the photon to the molecule with production of heat as a result of the conversion

¹ Frank L. Robeson, Physics, p. 359.

of radiant energy to kinetic energy. (2) The molecule may dissociate. (3) Fluorescence, the Compton effect, or the Raman effect may result from the transformation. (4) The molecule may retain its energy. In the last case, it is known as an excited molecule and may either react itself or serve as a carrier to transmit this activation energy to another molecule which does react.²

The degree of excitation of a molecule is dependent upon the frequency and the energy of the radiation absorbed. The energy of one quantum is given by the relationship

$$E = hv$$

where E is the energy in ergs per photon, h is the universal Planck constant, 6.547×10^{-27} ergs seconds, and v is the frequency of vibration. The energy per mole of photons is found by multiplying by Avogadro's number N. The frequency is calculated by dividing the velocity of light, c, by the wave length, l, of the radiation. By dividing the energy in ergs per einstein by 4.183×10^7 ergs per gram calorie, the calories of energy per mole of photons may be obtained.

It can be seen from

$$E = \frac{hc}{l}$$

that the energy of radiation would vary as the wave length. E would be small in the part of the spectrum where the wave

length is long and large where the wave length is short. For example, radiations in the far infrared having a wave length of 200,000 Å would contain energy of the order of 1000 gram calories per mole. Since this is less than the usual quantity of energy needed for reaction, radiations in this region would not be expected to possess enough energy to act as an external source. Experimentally, absorption of the far infrared has been found to cause rotation and vibration of the molecule. On the other hand, radiations in the other end of the spectrum, that is, x-rays and alpha particles, having a wave length of 1 Å or less, contain energy of the order of a hundred million to 10^{10} gram calories per mole. This exceeds the amount of energy commonly required so that as would be expected, electrons deep inside the atom or even particles within the nucleus are displaced. In the region of the visible and ultraviolet, absorption is accompanied by 35,000 to better than 150,000 gram calories of energy per mole depending on where between the limits 8,000 to 2,000 Å the wave length lies. Radiations absorbed in this region contain enough energy to produce ordinary reactions. In addition to meeting the energy requirement, absorption of these radiations also may displace an outer electron from the molecule.

The calculated energy of ultraviolet radiation of 2536 Å is 111.2 kilogram calories per mole which is sufficient to

rupture a C-H bond requiring 100 kilogram calories per mole or a C-C bond requiring 83 kilogram calories per mole. Similarly, the calculated energy of visible light of 4358 Å wave length, 64.6 kilogram calories per mole, does not meet the energy requirement necessary to rupture a carbon-to-hydrogen⁴ or a carbon-to-carbon bond.

As has been stated, molecules which absorb light rays sometimes react directly. For example, the 64.6 kilogram calories per mole of visible light is sufficient to produce a number of polymerization reactions.

Blythe and Hofman noted that polymerization of styrene to polystyrene required three weeks in the summer sun, three days in a sealed tube at 100° C., but only one half hour in a sealed tube at 200° C. No reaction was observed on a sample of styrene kept in a sealed tube at room temperature in the dark.⁵

Fritzsche polymerized anthracene to a white solid hydrocarbon by exposure to the sunlight.⁶

Other molecules are sensitized or excited by light and act as carriers. Several metal vapors such as those of mercury and cadmium are examples of photosensitized carriers.

4

Howard J. Lucas, Organic Chemistry, p. 21.

5

Annalen der Chemie, 53 (1845), 311, cited by Gustav Egloff, Reactions of Pure Hydrocarbons, (American Chemical Society Monograph Series, No. 73), p. 580.

6

Journal fur Praktische Chemie, (1), 33, (1867), 101, as cited by Egloff, ibid., p. 602.

Similar results were obtained by Landau with light from a mercury lamp.⁷ Ethylene underwent 85% photopolymerization in 134 hours with a 100-volt lamp. A 500-volt lamp completely converted the ethylene into higher boiling products.

Ethylene also polymerized in the presence of cadmium vapor at 225-260° C. by exposure to radiation from a cadmium-quartz lamp.⁸

Tolloczko exposed ethane to ultraviolet light and obtained liquid and gaseous products. The liquid was largely hexane while the vapor was a mixture of hydrogen and methane.⁹

Bates and Taylor observed that when n-hexane was exposed to the mercury resonance line in a "sufficient concentration" of mercury, the reaction rate was 1000 times larger than when mercury vapor was absent.¹⁰

Walker worked with the mercury sensitized reaction of isopentane to ultraviolet radiations of 2536 Å and observed that a number of hydrocarbons were produced. The desired 3,3,4,4-tetramethyl hexane was present but a number of isomers and products of fragmentation were also there. Gas analysis

⁷ M. Landau, "Application of Light Energy to the Study of Some Questions of Chemical Analysis," Compt. Rend., 155, (1912), 403.

⁸ J. Am. Chem. Soc., 50, 771, (1928).

⁹ S. Tolloczko, "Condensation of Ethane Under the Action of Ultraviolet Rays," Przemysł Chem., 11 (1927), 245; Chem. Abs., 22 (1928), 4380.

¹⁰ J. R. Bates and H. S. Taylor, "Studies in Photosensitization," J. Am. Chem. Soc., 49 (1927), 2438.

showed a large percentage of hydrogen and a smaller percentage of methane. Small amounts or traces of other low molecular weight gases were present.

¹² Gary ¹³, Rohrer ¹⁴, and Oliver ¹⁵ subjected mixtures of isobutane and isobutene to ultraviolet radiation of 2536 Å in the presence of mercury vapor to determine whether there was a reaction. They found that a higher boiling fraction resulted from such treatment. The physical properties of this obtained product approximated those listed in the literature for the anticipated hydrocarbon.

Darwent and Winkler investigated mercury photosensitized reactions of isobutane. They reported that hydrogen, octanes, and dodecanes were the main products. The rate of reaction was not affected by the working pressure at the temperature of the experiment. The temperature affects

¹¹

Russell Walker, "Photochemical Reactions of Isopentane" (Unpublished Master's Thesis, Dept. of Chemistry, North Texas State Teachers College, August, 1945).

¹²

Felice Gary, "Mercury-Sensitized Photochemical Action on a Mixture of Isobutane and Isobutene" (Unpublished Master's Thesis, Dept. of Chemistry, North Texas State Teachers College, June, 1939.)

¹³

Vern Rohrer, "The Effect of Photo-Sensitized Mercury on Mixtures of Isobutane and Isobutene" (Unpublished Master's Thesis, Dept. of Chemistry, North Texas State Teachers College, August, 1940).

¹⁴

Bob M. Oliver, "The Photo-Alkylation of C₄ Hydrocarbons" (Unpublished Master's Thesis, Dept. of Chemistry, North Texas State Teachers College, August, 1942).

the nature of the product but not the reaction rates.¹⁵

Mercury is the photosensitizer for the above alkylations and polymerizations. The mercury vapor receives the radiant energy of the mercury lamp to form a sensitized or excited mercury which possesses enough energy to break the H-H bond as well as to decompose ammonia and many different organic compounds.¹⁶ The equation



shows the formation of the excited mercury Hg*.

¹⁵

B. de B. Darwent and C. A. Winkler, "The Mercury-Photosensitized Reactions of Isobutane," J. Phys. Chem., 49, No. 2, (1945), p. 159.

¹⁶

Taylor, "Treatise on Physical Chemistry," 1931, pp. 1480-1482, cited by Getman and Daniels, op. cit., p. 587.

CHAPTER II

THE PROBLEM

The problem was to study the behavior of several hydrocarbons when they were subjected to ultraviolet light of 2536 Å⁰ in the presence of mercury vapor.

It would be expected from the work of Stallings that the rupture of any tertiary hydrogen bond in the molecule would be the predominant effect.¹ However, secondary and primary bond splitting would occur as well as some C-C bond rupturing, but these would be expected to a lesser degree than the first, since the t-hydrogen has the greatest reactivity.

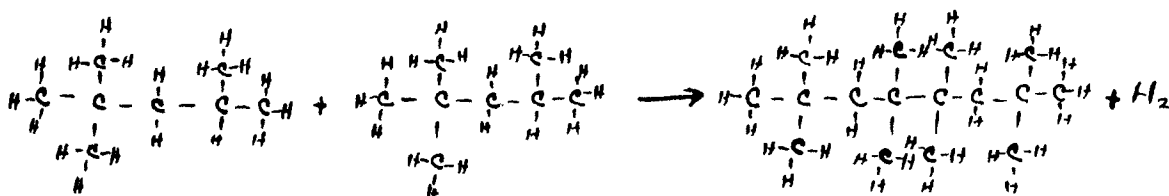
Although there are no data for the maximum absorption of many of the hydrocarbons, it is known that in general their absorption spectra are in the far ultraviolet. Carr and Stüeklen give the value of 1500 Å⁰ for hexane and heptane so probably the maximum absorption for isooctane and other hydrocarbons of about the same chain length should be near that value.² Since the absorption band is so far from that

¹ James C. Stallings, "The Mercury-Sensitized Photo-Reactions of Isobutane" (Unpublished Master's Thesis, Dept. of Chemistry, North Texas State Teachers College, May, 1943).

² E. P. Carr and H. Stüeklen, "Absorption Spectrum of Some Hydrocarbons in the Schumann Region," H. Phys. Acta., 6, (1933), 261.

of the mercury resonance line, mercury vapor must be used to transport the energy to the hydrocarbon. Thin layers of mercury vapor are very effective for this purpose.

In the case of the isooctane, 2,2,4-trimethyl pentane, one would obtain 2,2,4,4,5,5,7,7-octamethyl octane, say, as indicated by the reaction below.



This would involve a removal of two t-hydrogens and reaction of the octyl radicals. However, one would also expect other reactions due to the "splitting off" of the less active secondary and primary hydrogens with combination reaction of these radicals following. For example, there are ten structural isomers of hexadecane that may be formed from C-8 radicals produced by "splitting off" of either tertiary, secondary, or primary hydrogens. Of these isomers, one is a tetramethyl diisopropyl hexane, one is a hexamethyl isopropyl heptane, three are octanes (one octamethyl octane and two pentamethyl isopropyl octanes), two are heptamethyl nonanes, and three are hexamethyl decanes.

The number of possibilities is increased even further by the possibility of dissociation of the molecule into fragments. An interaction between fragments may follow with the formation of lower molecular weight and consequently, lower boiling substances than the anticipated sixteen-carbon compounds; or as has been pointed out, the excited mercury has enough energy to rupture the H-H bond to produce hydrogen atoms. This atomic hydrogen may combine with fragments to form more low molecular weight or probably gaseous hydrocarbons. But, in light of previous investigations, it would seem that the octamethyl octane would be the chief product with all or some of these other compounds present in smaller quantities.

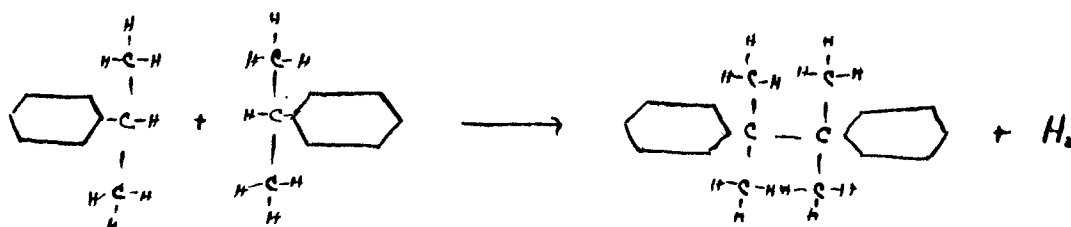
The hydrogens that are split off would form molecular hydrogen. As the reaction proceeds, the amount of hydrogen should increase as indicated by a rise in pressure. It would seem unlikely that unsaturated products would exist to any appreciable extent in this atmosphere of largely hydrogen at relatively high operating pressure.

The desired product was not listed in the literature, but it should be closely related to 2,2,3,3,6,6,7,7-octamethyl octane. Whitmore lists 74.2° C. for the melting point of that hexadecane.⁴

⁴James Whitmore, J. Amer. Chem. Soc., 63 (1941), p. 1626.

In a similar manner, one would look for the formation of longer chain compounds if cumene, 2,4-dimethyl pentane, and 2,3-dimethyl butane underwent the same kind of photochemical treatment.

A high boiling, or even solid, product may be obtained when, say, cumene reacts. Toluene also should yield a related, unalkylated ethane derivative.



No data are available concerning the tetramethyl derivative of diphenyl ethane. However, the properties of the two predicted products are likely to be nearly the same due to the similarity in structure. A Handbook of Physics and Chemistry gives a boiling point of 272° C., refractive index of 1.5761 at 20° C. when a sodium D-line is used, and a specific gravity of 1.00 $\frac{21}{4}$ for diphenyl ethane.

Dimethyl butane and dimethyl pentane would probably react in an analogous fashion so that dodecanes and tetradecanes would be formed. But the structure, that is two tertiary hydrogens in each molecule, suggests the possibility of cyclization. If cyclization should occur 1,1,3,3,4,4,6,6-octamethyl cyclohexane

might be the main fraction from dimethyl pentane, while 1,1,2,2,3,3,4,4-octamethyl cyclobutane would be expected from dimethyl butane.

Cyclization products could be easily separated and identified because of the difference in physical constants of alkanes and cycloparaffins. Use of the refractivity intercept is made in distinguishing the hydrocarbon types which differ in this physical constant. The refractivity intercept b is defined by the equation

$$n_D^{20} = 0.5 d_4^{20} + b.$$

The low boiling naphthenes have a refractivity intercept of 1.0400 while paraffins have a value of 1.0461.

Reaction products obtained as described above, if they form as predicted, would be of particular interest to industry in which the hydrocarbons related to those cited are light ends of petroleum refining. The reasonably low boiling points and extensive branching suggesting high octane numbers are of interest for they may be utilized as high octane fuels for internal combustion engines or for blending agents in making such fuels. The increasing demand for better fuel might partially be met by a commercial photochemical process.

CHAPTER III
THE APPARATUS AND PROCEDURE
The First Unit

The first apparatus consisted of a small quartz reaction vessel connected to a mercury-sealed stirrer by means of a rubber sleeve. The electrically driven stirrer was extended almost to the bottom of the flask to continuously agitate the mercury there, thus keeping the hydrocarbon layer saturated with the metallic vapor. The unit was mounted on a flexiframe so that the light from a Braun Florolight, also supported by the frame, would furnish the ultraviolet radiation, 2536 ⁰ A.

After the reaction vessel had been charged to the neck with about 30 cc. of liquid, the lamp was turned on and the stirrer motor started. Two runs were made using cumene (isopropyl benzene) for a 24 hour and a 120 hour run. A third run was made using 2,4-dimethyl pentane. It was allowed to run 75 hours.

At the end of each run, the hydrocarbon layer was removed by disconnecting the reaction flask at the rubber sleeve and pouring the contents into a glass-stoppered container. The refractive index was recorded as read from the scale of the Abbe Refractometer. If there were sufficient difference in the index of refraction of the charge and the product to

indicate a reaction, the product was fractionated in a small fractionating column which consisted of a glass spiral enclosed in a glass tube. The column was jacketed to prevent excessive heat losses to the air.

The index of refraction, n_D^{20} , the micro boiling range, and the specific gravity were determined for each fraction. The constants were compared to those of the charge as well as those of the anticipated product. In case the product sought was not listed in the literature, comparison was made to physical constants for a closely related compound.

The Second Unit

The second apparatus was designed as a simplified unit to allow a vapor phase reaction with the mercury supplied by metallic mercury in the boiler.

The diagram, Figure 1, is a schematic representation of the unit. A 500 ml. Kjeldahl flask was used for the boiler. It was sealed to a glass tube (inside diameter of 39 mm.) that contained a Westinghouse No. WL-782-30 Sterilamp. The lamp contained a mixture of neon and argon at an absolute pressure of 16 mm. Eighty-five per cent of the radiations were 2536 Å long. The metal electrode ends of the 34.5 inch Sterilamp were fitted into sockets. A copper wire spiral connected one of the sockets to a nonex electrode. The other was spliced to a length of No. 22 iron wire which lead through

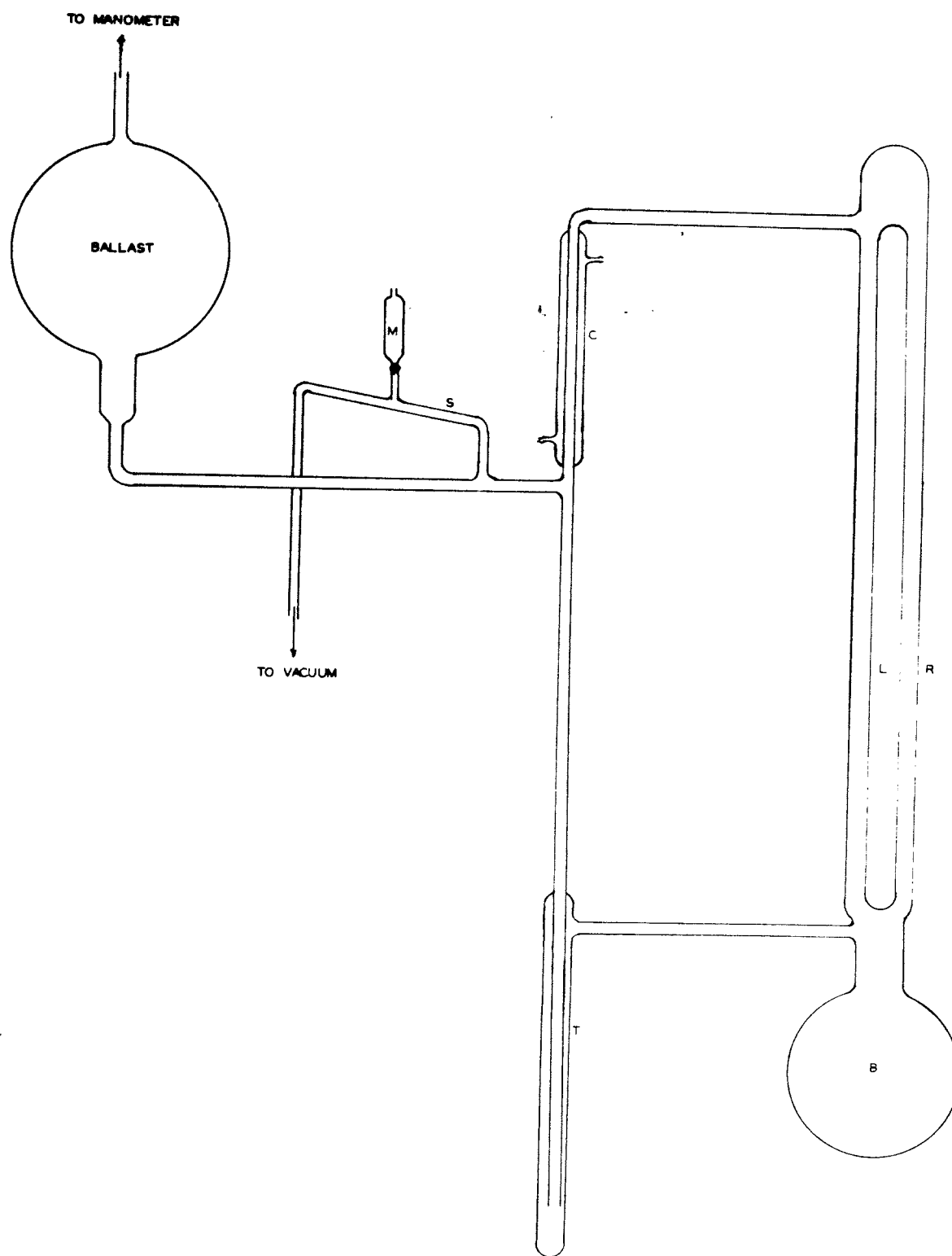


Fig. 1. The Second Apparatus

the condenser and ballast to the mercury manometer. The mercury served as the other electrode. A Westinghouse ST-70 transformer supplied a current of 50 milliamperes at an operating voltage of about 450 volts.

A water condenser C condensed the hydrocarbon vapor as it flowed from the reaction vessel. The condensate was lead back to the still pot through a trap T which prevented back-flow.

A take-off just below the condenser lead to the open mercury manometer which could be used to measure absolute pressures up to three and one-half atmospheres. A ballast in the line was for volume to take care of the gas that resulted from the reaction.

Heat was supplied to the boiler by a Cenco electric heater controlled by an autotransformer. A spiral of No. 26 nichrome wire was used to heat the reaction tube. The temperature, observed from a thermometer attached to the Sterilamp, was controlled by another autotransformer.

The hydrocarbon was charged to the evacuated system which had been checked for leaks with a high voltage Tesla coil. A few milliliters of liquid was left in the funnel M each time to prevent an air influx into the system. The hydrocarbon was contained in the trap T and boiler B. The unit was sealed off just below the funnel to remove stopcocks from the system.

The heaters and the Sterilamp were turned on, and initial manometer readings were made. The temperature of the reaction vessel was adjusted so that flow was established and maintained through-out the run. At intervals during the run, pressure differences were recorded, along with the barometric pressure, and temperature at that time.

Three hydrocarbons, cumene, toluene, and isooctane, were run on this unit. The average time for each run was 96 hours. At the end of that time, the product was withdrawn. The charge was recovered by fractional distillation on a large fractionating column made of nichrome gauze spiral in a glass tube and operating at an equivalent of 20 plates under total reflux.

The physical constants were determined for the fractions and used again to detect a reaction and identify some of the products formed--if any--and their nature.

The Third Unit

The apparatus used in this set of experiments was essentially the same as Walker used in his work with isopentane.¹ The modifications in design were: (1) increase in boiler volume to enable a larger amount of hydrocarbon to be handled per run, (2) addition of another reaction vessel in series with the other one, (3) use of a ballast to take care of the large volume of gases formed.

¹
Walker, op. cit., p. 10.

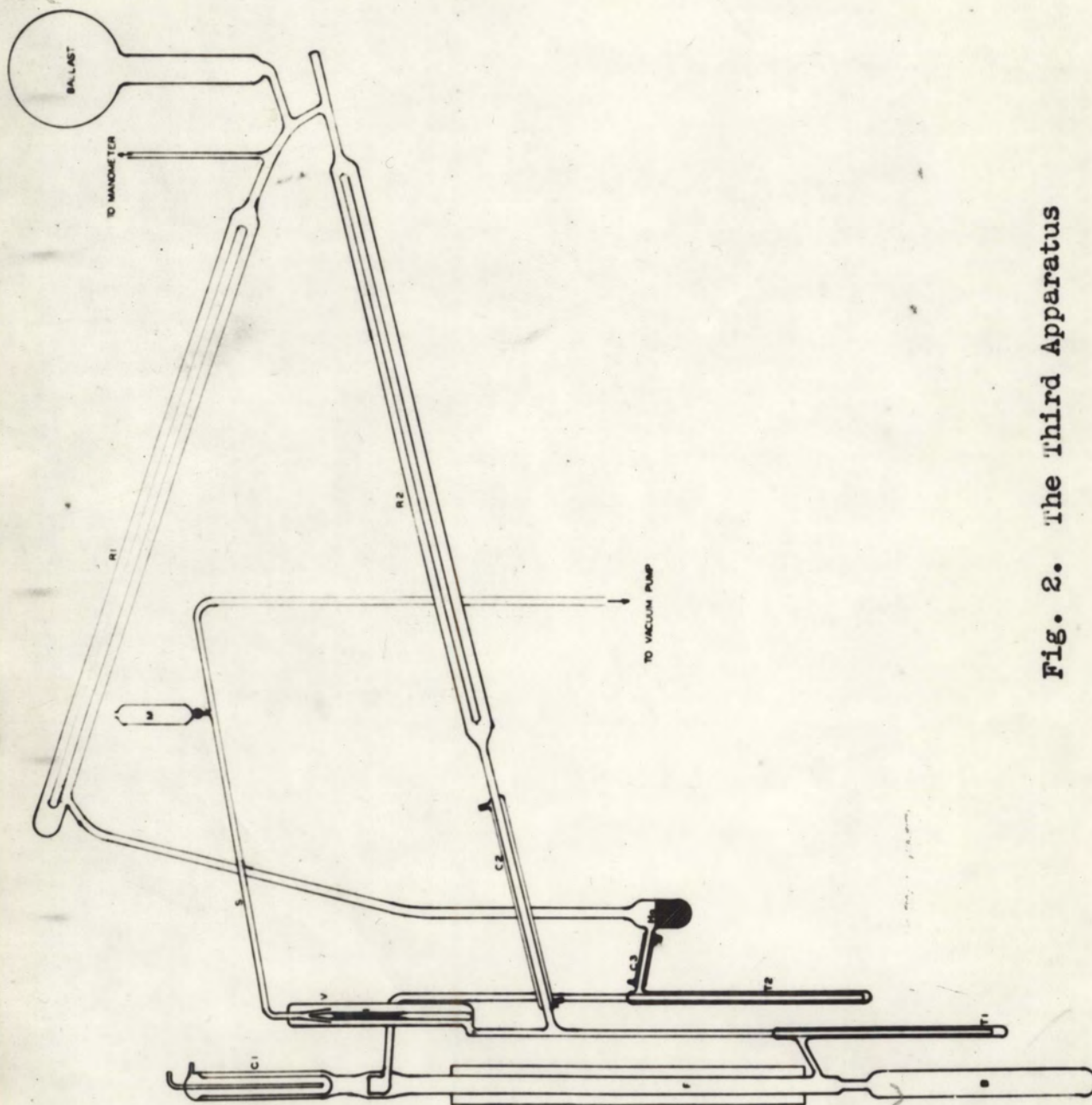


Fig. 2. The Third Apparatus

Figure 2 is the diagram of the apparatus. About 200 ml. of the hydrocarbon was charged to the evacuated system by means of the funnel M. Flow was controlled and air kept out of the system as described in the procedure for charging unit two. The charge entered the system through the electromagnetic trap V which was made by sealing a piece of metal I in the lower part of a ground glass joint. A solenoid operated by a transformer was used to raise the lower part thus closing the system after introduction of the hydrocarbon. With a vacuum still on the line, the stopcocks were sealed out by collapsing the small diameter tubing S.

The charge was collected in the trap T_1 and boiler B. T_1 was designed primarily to prevent backward flow. The boiler was sealed to the fractionating column F made of a nichrome gauze spiral packing in a glass tube. A nichrome spiral heated the column to prevent flooding, while an asbestos sheet surrounding the tube insulated the column. The heaters were regulated so partial condensation occurred along the gauze spiral to increase the effectiveness of the fractionation. At total reflux, the column operated at an equivalent of 20 plates. The hydrocarbon vapors condensed on a Friedrich cold finger at the top of the column. The temperature of the condenser C_1 was maintained low enough to condense the vapors of the hydrocarbon of that particular charge. The condensate dropped into the receiver and flowed into the trap T_2 which controlled

the rate of flow. T_2 was connected by a condenser C_3 to a heated mercury saturator containing about 50 ml. of mercury. A head made by the increased pressure from the boiler heater forced the hydrocarbon into the saturator where it evaporated from the hot mercury surface. The mercury-saturated vapor flowed to the first reaction vessel R_1 through a 13 mm. glass tube heated to keep the mercury and hydrocarbon in the vapor phase.

The reaction vessels R_1 and R_2 were constructed of 39 mm. pyrex tubing connected by smaller diameter tubing. Each contained a Westinghouse Sterilamp like the one described for unit two. Two Westinghouse transformers furnished the current for the lamps through nonex electrodes. A thermometer was attached to each Sterilamp and No. 22 nichrome wire spirals heated the reaction vessels to such a temperature as was necessary to keep the reaction in the gaseous phase.

The inclination of the reaction vessels was such that any condensate formed as a product would flow down through condenser C_2 into trap T_1 . The unreacted charge as well as the product was condensed in this cold spot. As the trap filled, a gravity head forced the two into the boiler where the charge was vaporized and recirculated while the heavy high boiling product was concentrated. The condensers were connected in series. A glycerol-alcohol mix maintained at 0°C . was circulated by a centrifugal pump through the jackets

except when the boiling point of the hydrocarbons allowed the use of tap water.

The nichrome wire spiral heaters were controlled by auto-transformers--one each for the mercury saturator, the reaction vessels, the fractionating column, and the boiler heater. The spiral was wound on the element to be heated in all cases except the boiler. The boiler heater was wound on asbestos paper rather than directly on the boiler. The voltage regulators were adjusted so that flow was established and maintained at a desired rate for the hydrocarbon charged.

A sidearm between the two reaction vessels was connected to an open mercurial manometer capable of measuring a pressure difference of 2000 mm. A sidearm from the manometer tube lead to a ballast made of an inverted 3-liter flask drawn and sealed into the system.

Three isooctane runs were made with an average time of 99 hours per run. Seven 2,3-dimethyl butane runs were made.

When a run had been completed, a gas density was determined by an Edwards balance using oxygen for a standard. Each gas was admitted to the evacuated balance chamber and the pressure adjusted until the rider was balanced. The pressure difference as read from an open mercury manometer was converted to absolute pressure. Using the relationship,

$$\frac{p_{O_2}}{p_{Gas}} = \frac{\text{Mol. Wt. Gas}}{\text{Mol. Wt. } O_2}$$

where p is the absolute pressure in mm. of mercury required

to balance the rider, the average molecular weight of the gas sample may be calculated. The gas sample was taken from a capillary at the top of the first reaction vessel by breaking the capillary into pressure tubing which lead to a freeze-out trap then to the Edwards balance.

The liquid product was removed by breaking the tip from the drawn capillaries on the traps and boiler and draining the liquid into a glass stoppered receiver. The unreacted hydrocarbon was recovered by fractionation to be recharged.

The product was fractionated in a small column under reduced pressure to prevent "cracking." The physical constants were determined in an effort to identify the hydrocarbons in the products and to determine the nature of the reaction.

The combined isooctane yields and a gas sample from run No. 3 were sent to the Texas Company, Beacon, New York Laboratories for analysis and identification.

CHAPTER IV

RESULTS

Results Obtained from the First Unit

A study of the illumination products in the first unit indicate very little in the way of a reaction. The difference in the refractive index of the charged cumene, $n_D^{20} = 1.4892$, and the product, $n_D^{20} = 1.4900$, was within the limits of experimental error. However, it was noted that as the run proceeded a white solid formed on the mercury in the stirrer receptacle and a mercury sol formed in the reaction vessel. The white solid which did not melt was probably a mercury salt because an ignition test gave a black residue and a basic litmus test. At the end of the third run with cumene a white precipitate was observed on the side of the reaction vessel next to the ultraviolet lamp. The crystals were removed from the flask along with some of the mercury salt. There was not enough of either to effect a separation, so the two were transferred to a micro melting point tube. At 200-210° C. yellow oil-like droplets formed in the tube. They were fairly evenly distributed in the mercury salt which, of course, did not melt.

The results of the 2,4-dimethyl pentane also indicated some reaction. The liquid taken off had an ethereal odor and some mercury had plated out on the side of the reaction cell

next to the light source. The liquid was not fractionated, but a difference in the refractive index, $n_D^{20} = 1.3815$ for the product and $n_D^{20} = 1.3794$ for the charge, was noted.

Results Obtained from the Second Unit

The results of the cumene, toluene, and isooctane runs were comparable. In each case, a greenish-yellow color appeared in the liquid in the trap after a few hours of run, a brown residue coated the lamp, and the contents of the boiler were reddish brown.

In Table 1 the data are shown for each of the three hydrocarbons reacted in this unit. The temperature listed is the average temperature maintained in the reaction vessel after flow was established. P_1 was the absolute pressure due to the vapor pressure of the hydrocarbon and was recorded at the time flow was established while P_2 was the absolute pressure recorded just before the run was stopped. The refractive index of the product was the value for the liquid as it was taken from the unit.

TABLE 1
DATA FOR THE RUNS

Compound	P_1 mm	P_2 mm	$T^\circ \text{C.}$	n_D^{20}		Run time hours
				Product	Charge	
Cumene	3.45	4.01	111	1.4892	1.4889	80
Toluene	5.30	14.97	158	1.4928	1.4928	118
Isooctane	8.44	37.78	159	1.4925	1.3895	34

A spiral of the reaction vessel heater burned out at the end of 34 hours on the isooctane run and shorted the heater to the frame. The intense heat cracked the unit so that this run was stopped prematurely. However, the increase in refractive index and pressure suggested a more extensive reaction in this run than in either of the other two.

Results Obtained from the Third Unit

The general characteristics of the runs were in accordance with those obtained by previous investigations. That is, the pressure was low at the beginning but steadily rose to a maximum a few hours before the run was stopped. The absolute pressures in mm. at the initial part of the three runs were 1378, 1433, and 1415 while the corresponding final pressures were 2690, 2681, and 2695. As long as the liquid was flowing and the pressure was not dropping the run was continued. The average run time was 94 hours. The temperature in the first reaction tube averaged 69° C. but was increased to about 78° C. during the last run. The second reaction tube was operated at an average of 75° C. but was increased to 84° C. in the last run.

Of the 175 ml. of isooctane charged per run an average of 100 ml. were recovered by fractionation and recharged to the unit.

The bottoms from the above-mentioned fractionation were

then vacuum distilled into fractions. A pump capable of producing a 3 mm pressure was used but stopcocks in the unit were controlled so that the distillation was not carried out in such a high vacuum. In Table 2 the results of this separation are given. The specific gravity was determined by use of a pycnometer. The boiling ranges were found on micro equipment. One point of interest was that 87% of the product had a boiling range above 220° C. at atmospheric pressure.

TABLE 2
PHYSICAL CONSTANTS OF THE FRACTIONS

Fraction	B.R. °C. at 10 mm	n_D^{20}	Sp. Gr. $\frac{20}{20}$	% of total volume
1	104-105	1.3911	0.691	2
2	109-110	1.3915	trace
3	169-172	1.4147	1
4	182-195	1.4318	0.765	4
5	198-210	1.4332	0.770	6
6	above 220	1.4500	0.809	87

Determination of gas density showed an average of 14.47 for the gas samples from these C-8 runs. This suggests that the gaseous products have low molecular weights.

An analysis of the entire product by the Beacon Laboratories of The Texas Company gave the analysis shown in Table 3. A 50-theoretical plate Podbielniak column operated at 2% take-off was used to fractionate the sample at reduced pressure. The densities and refractive indices were determined for each cut and plotted as shown in the distillation curve in Figure 3.

FIGURE 3

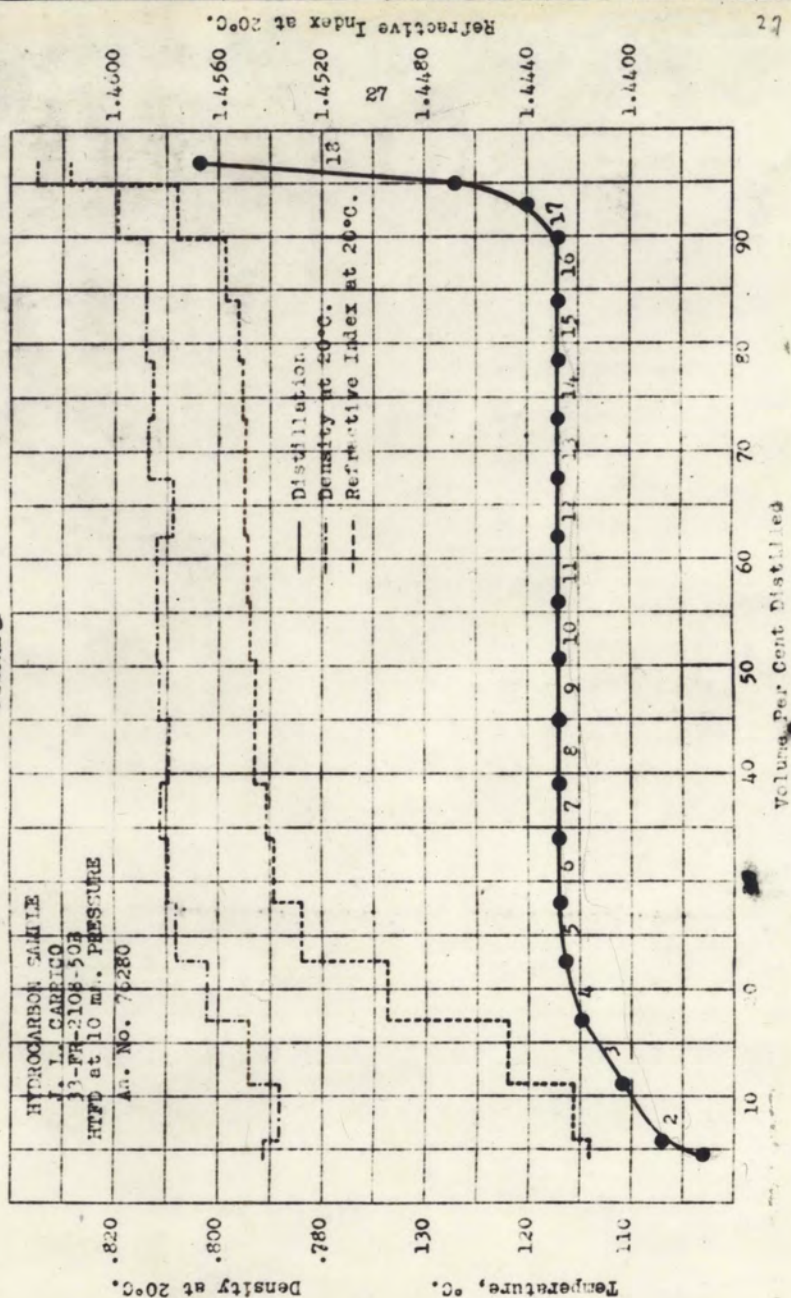


TABLE 3
ANALYSIS FROM DISTILLATION CURVE

Cut	Product	B. R. °C at 10 mm	Volume %
1-5	Forerun	67-117	28
6-16	Eicosane	117-117	62 ✓
17-18	residue	117-175	10

Cut No. 13 was analyzed for carbon and hydrogen by the combustion method and a molecular weight determination made. The results shown in Table 4 indicate that the main portion of the sample was not the predicted $C_{16}H_{34}$ but a $C_{20}H_{42}$ paraffin. Lack of literature on the large number of possibilities made an estimate of the structure impossible. However, constants of the product roughly followed those of the hydrogenated butylene pentamers.

TABLE 4
DATA FOR EICOSANE AND ISOBUTYLENE PENTAMER

Compound	n_D^{20}	d_4^{20}	b.p. °C. at 10 mm	Mol. Wt.	%C	%H
Eicosane (Product)	1.4550	0.8136	117	277, 272,	84.31	14.77
(Literature)	260 282	85.11	14.89
Isobutylene pentamer (hydrogenated)	1.4524	0.8087	150	283	84.82	15.18

The composition of the gas was determined by the mass spectrograph. The gas was 65.6% hydrogen. Smaller amounts

of oxygen, 6.6%, and nitrogen, 27.8%, were present. The latter two were roughly in the proportion as in air. Probably their presence was due to leakage of the sample tube.

The seven dimethyl butane runs were made with the temperature of the reaction vessels maintained at 80° C. The average absolute pressure at the initial part of the run was 1049 mm, while 2684 mm was the average final pressure. The final pressure was reached about 125 hours after flow was established.

A 14% yield of higher boiling product was obtained from the 175 ml. of hydrocarbon charged per run. The charge was removed by fractionation. The bottoms from all the runs were mixed and sent to the Texas Company Laboratories for complete analysis.

Examination of the composite mixture showed a refractive index (24.8° C.) of 1.4509 as compared to 1.3734 for the charge at the same temperature. Calculation of the refractivity intercept for the mixture was 1.0461 which was in agreement with that for paraffins.

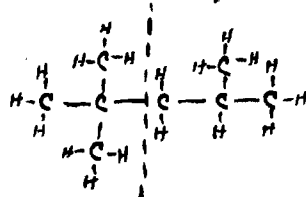
On fractionation, slightly more than 90 volume per cent had a boiling range above 170° C. at atmospheric pressure. However, about 1.5% distilled at 110-120° C. The refractive index (24.8° C.) for this cut was 1.4277.

The gas density recorded for runs 6 and 7 were 6.41 and 6.60 respectively.

CHAPTER V

THE CONCLUSION

From the analysis of the product obtained by the illumination of mercury-sensitized isooctane by 2536 Å radiation, one reaches the conclusion that the reaction was not one of simple alkylation as was expected. The C-C bond rupturing seems to have been the extensive effect. Splitting between the second and third carbons, as shown, would produce C-4



fragments. Combination of these fragments could account for the formation of the C₂₀H₄₂ paraffin. An analysis of the liquid recovered as unreacted isooctane would be helpful since the isolation and identification of any low boiling fragments, or building blocks, would be useful in determining the nature of the reaction.

Studies should be made concerning the effect of heat on the nature of the product. Further investigations should be made with the other hydrocarbons considered herein.

Cumene, toluene, and 2,4-dimethyl pentane should be reacted in a large unit and the products that are obtained analyzed. Such an analysis would probably indicate whether the reaction

was one involving the removal of the t-hydrogen or whether there was extensive C-C bond splitting. A number of runs made at different temperatures, rates of flow, and lengths of run time probably would show the effect of each of these variables on the nature of the product and consequently suggest a means of controlling these ruptures to produce the desired product.

An analysis of the product obtained from the 2,3-dimethyl butane runs would be useful for the same reasons. Possibly, the conditions necessary to produce cyclization could be determined.

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