

THE EFFECT OF PHOTO-SENSITIZED MERCURY ON
MIXTURES OF ISOBUTANE AND ISOBUTENE

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MIXTURES OF ISOBUTANE AND ISOBUTENE

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CHAPTER I

NATURE OF PROBLEM

Attempts have been made to synthesize isooctane by illuminating mercury-sensitized mixtures of isobutane and isobutene with 2536 Å radiation. There was evidence in the form of drops of a volatile liquid, at room temperature, of alkylation or polymerization. The product smelled very much like isooctane, but the experiments were done on such a small scale that there was not enough of the C₄'s converted to the heavier molecules for identification.

It was thought that if larger volumes of these same gases were illuminated with the 2536 Å radiation enough of the volatile liquid would be obtained to run identification tests. The author undertook the problem of illuminating large volumes of these gases with the hope that the product, when identified, would be isooctane. Since using a larger reaction vessel would necessitate using a larger lamp, it was thought best to devise an apparatus in which the gases could be recirculated through the illuminated zone for prolonged periods.

CHAPTER II

SURVEY OF LITERATURE ON PHOTOCHEMICAL ALKYLATION AND POLYMERIZATION

In comparison with the amount of study that has been done on all types of reactions of hydrocarbon compounds, very little time has been given to the effect that light will produce. The majority of the work that has been done on this phase of hydrocarbon reactions has been in the last fifteen years. It was only in 1935 that the polymerization of cracked gas into gasoline went into commercial use.¹ The work that has already been done has not been spread evenly over the field nor has there been an appreciable degree of uniformity in the types of investigations carried out by different experimenters. Moreover, many compounds have not been touched at all, some have been studied meagerly, and few have been studied exhaustively.² These facts are shown by the reports given below.

Blythe and Hofmann noted that the formation of meta-styrene from styrene required three weeks in the summer sun, and three days in a sealed bulb at 100°C., but only one half hour in sealed tube at 200°C. Although heat and light cause

¹Gustav Egloff, Reactions of Pure Hydrocarbons (American Chemical Society Monograph Series, No. 73), p. 5.

²Ibid.

polymerization, this change was not observed if a sample was kept in a sealed tube at room temperature in the dark.³

Fritzsche exposed anthracene obtained from coal tar to sunlight. The hydrocarbon changed to a white solid having a higher melting point, but reverted to the original compound after melting. The name paranthracene was proposed for the polymer.⁴

Behr and van Dorp observed that acenaphthylene polymerized very readily, for when a benzene solution of the hydrocarbon was kept in the sunlight for a time, some solid separated.⁵ The new compound melted at 226°C., but the heating required for taking the melting point caused a lowering of the melting point.

Isoprene, exposed to light in a sealed tube for an extended period, polymerized to a rubber-like mass according to Wallach.⁶ Some authors have claimed that his isoprene, which was obtained by the dry distillation of rubber, may have contained an impurity, such as a small piece of rubber from the original material. This might have caused the reformation of rubber, since evidence from other investigators indicated that rubber itself catalyzed the polymerization

³Annalen der Chemi⁶, LIII (1845), 311, cited by Egloff, op. cit., p. 580.

⁴Journal fur Praktische Chemie, (1), XXXIII (1867), 101, cited by Egloff, op. cit., p. 602.

⁵Ann., CLXXII (1874), 263, cited by Egloff, op. cit., p. 610.

⁶Ann., CCXXV VIII (1897), 88, cited by Egloff, op. cit., p. 778.

of isoprene to caoutchouc. On the other hand, Harries⁷ showed that pure isoprene can be polymerized, by means of ultraviolet light, to a solid white substance which contains a small proportion of rubber-like material.

Linebarger prepared paranthracene by exposing solutions of anthracene to sunlight.⁸ Benzene, toluene, xylene, ethylbenzene, alcohol, acetic acid, ethyl benzoate, bromobenzene, and chloroform were useful solvents; but ethylene bromide or carbon bisulfide did not yield the white insoluble crystals. As previously found by Fritzsche, paranthracene melted at 243° to 244°C., but if allowed to cool after the first melting, a second melting point determination gave a value equal to that for anthracene. Linebarger noted that if both gamma positions of anthracene were substituted no photopolymerization occurred. He considered the polymerization of anthracene to be the activation or loosening of the bonds of the gamma carbon atoms by the action of sunlight, these loosened bonds uniting to form a double molecule.

Orndorff and Cameron confirmed Linebarger's observations, but proposed that the solid be called dianthracene in place of paranthracene.⁹

⁷C. Harries, "Comparison of the Product of the Auto-polymerization of B, G-Dimethylbutadiene with That of the Polymerization by Heat," Ann., CCCXCV (1913), 266.

⁸American Chemical Journal, XIV (1892), 602, cited by Egloff, op. cit., 602.

⁹Am. Chem. Jour., XVII (1895), 658, cited by Egloff, op. cit., p. 602.

Lemoine showed that styrene polymerized to the extent of 0.5 per cent in the course of a year when kept in the dark. With an incomplete exclusion of light, and at various temperatures, an equilibrium between styrene and metastyrene was established depending on temperature and pressure. He used the sun as a source of light in his radiation experiments. Lemoine makes the following statement concerning the light reaction: "The principal purpose of the light is to accelerate an exothermic transformation which would be produced in the dark at the same temperature but much more slowly."¹⁰

Pure acetylene was exposed to bright sunlight in glass bulbs for two or three days by Bone and Wilson.¹¹ A faint brown deposit which increased in thickness and became darker as the exposure was prolonged was produced. No deposit formed in a portion of the tube which was protected from the light. Besides unchanged acetylene, the residual gas contained about two per cent of a "fairly dense hydrocarbon" (not saturated) possibly mixed with a small quantity of hydrogen.

Orndorff and Negraw used B-methylanthracene in benzene solution to prepare dimethyldianthracene.¹² The white solid precipitated by the action of sunlight had double the molecular weight of the starting material but the same elementary

¹⁰ Chemisches Zentralblatt, II (1897), 1024, cited by Egloff, op. cit., p. 580.

¹¹ Proceedings of Chemical Society, London, XIV (1896), 158, cited by Egloff, op. cit., p. 452.

¹² Am. Chem. Journ., XXII (1899), 152, cited by Egloff, op. cit., p. 603.

analysis. The solid product melted at 225° to 230°C. but if allowed to cool it melted at 200°C., the melting point of methylanthracene.

Ciamician and Silber allowed a benzene solution of stilbene to stand in the sunlight for slightly more than two years.¹³ A solid product was obtained which melted at 163°C.

Weger and Billmann exposed indene to the light and obtained a tetramolecular indene which they called "para-indene."¹⁴

Gomberg and Cone observed that triphenylmethyl when kept in direct sunlight formed triphenylmethane and an oil besides two difficultly separable substances melting at 237° and 194°C.¹⁵ Since triphenylmethyl gave no triphenylmethane on radiation in a carbon tetrachloride solution, these authors thought the benzene solvent acted as a reducing agent in the light reaction.

Berthelot and Gaudechon observed that exposure of acetylene to ultraviolet light from a mercury vapor lamp for several seconds caused precipitation of a yellowish

¹³Berichte der Deutschen Chemischen Gesellschaft, XXXV (1902), 3538, cited by Egloff, op. cit., p. 634.

¹⁴Ber., XXXVI (1903), 640, cited by Egloff, op. cit., p. 652.

¹⁵Ber., XXIVII (1904), 3538, cited by Egloff, op. cit., p. 620.

brown, waxy solid.¹⁶ The polymerization of acetylene was not accompanied by decomposition nor by formation of benzene.

In other experiments by Berthelot and Gaudechon, ethylene was exposed to ultraviolet light and polymerized to a waxy, rancid-odored liquid which boiled at about 100°C. and resembled octene.¹⁷

Similar results were obtained by Landau, with light from a mercury lamp.¹⁸ Ethylene was changed to the extent of 85 per cent in 134 hours with a 100-volt lamp. While long exposure to a 500-volt mercury lamp caused full conversion into higher boiling products.

A 15 to 20 per cent benzene solution of acenaphthylene was exposed for five days during the summer by Dziewonski, Rapalski, and Leyko.¹⁹ A 15 per cent yield of a solid crystalline, colorless polymerization product together with another polymer, melting at 234°C., a member of the $(C_{12}H_8)_n$ series.

Stobbe and Reuss studied the polymerization effect of sunlight on phenylbutadiene, using the change of refractive

¹⁶D. Berthelot and H. Gaudechon, "Chemical Effects of Ultraviolet Rays on Gases," Comptes Rendus Hebdomadaires des Seances de L'Academie des Sciences, CL (1910), 1189.

¹⁷Ibid.

¹⁸M. Landau, "Application of Light Energy to the Study of Some Questions of Chemical Analysis," Compt. Rend., CLV (1912), 403.

¹⁹K. Dziewonski, J. Rapalski, and Z. Leyko, "Photochemical Transformation of Acenaphthylene," Ber., LIV (1912), 2491.

index as a criterion for polymerization.²⁰ Samples that had not been irradiated showed only 12 to 13 per cent change, whereas radiated samples, over the same period of two and one half months, polymerized 75 to 76 per cent. Although phenylbutadiene polymerized slowly in the dark, it was evident that radiation greatly accelerated the process. This same phenomenon was observed with styrene and pure metastyrene, and was considered by Stobbe and Reuss to be indicative of the relation of physiological action to saturation of organic bonds.

Methylacetylene was polymerized under the influence of light to a white solid by Berthelot.²¹

Taylor and Lewis showed that the photopolymerization of anthracene to dianthracene was effected by the blue-violet light.²²

Stobbe and Farber exposed indene to the light of the sun for almost a year in a tube sealed in an atmosphere of nitrogen and obtained about 8 per cent of a polymer.²³ The

²⁰H. Stobbe and E. Farber, "Influence of Light on Polymerization Velocity of Phenylbutadiene," Ber., XLV (1912), 3496.

²¹D. Berthelot, "Role of Ultraviolet Light in Chemical Reactions," Notice Sur les Francais Scientifiques, p. 130, cited by N. H. Dhar, The Chemical Action of Light, p. 303.

²²J. A. Taylor and W. C. Lewis, "Chemical Reactivity," Journal of American Society, XLVI (1924), 1606.

²³H. Stobbe and E. Farber, "Polymers of Indene," Ber., LVII (1924), 1834.

granular product sintered at 145°C . and melted at about 160°C ., but when it was recrystallized from ethyl acetate, these points rose to 200° and 220°C . Molecular weight values indicated $(\text{C}_9\text{H}_8)_{16}$, while the solid precipitated from the ester by alcohol was the $(\text{C}_9\text{H}_8)_8$ polymer.

Bates and Taylor found that ethylene could be polymerized by the use of excited mercury atoms, but was not changed by ultraviolet light alone.²⁴

Olson and Meyers exposed ethylene in presence of mercury vapor in a quartz vessel at low pressures and moderate temperatures to radiation from a mercury lamp.²⁵ Pressure readings showed that the ethylene at first decomposed slightly, and then the remainder polymerized.

The yellow solid "cuprene" was formed by Bates and Taylor from polymerization of acetylene both by ultraviolet light and by excited mercury atoms.²⁶ When a hydrogen-acetylene-mercury mixture was illuminated by a cooled arc, "cuprene" was deposited on all portions of the reaction vessel except that adjacent to the arc which became coated with a colorless oil. The cuprene which condensed in this region seemed to have been acted upon by hydrogen atoms.

²⁴J. R. Bates and J. S. Taylor, "Studies In Photosensitization," Proceedings of National Academy of Science, XII (1926), 714.

²⁵A. R. Olson and C. H. Meyers, "Polymerization and Hydrogenation of Ethylene by Means of Excited Mercury Atoms," Journal of American Chemical Society, XLVIII (1926), 389.

²⁶Bates and Taylor, Ibid., XLIX (1927), 2438.

Benzene was decomposed by Bates and Taylor by means of excited mercury atoms.²⁷ The pressure following the action was very low, hence, little hydrogen could have formed for the gas would have raised the pressure. A heavy, tarry residue was deposited on the reaction vessel and a strong odor of diphenyl was noted.

Everest found that two dimers were formed when acenaphthylene was exposed to sunlight and that these dimers could be pyrolyzed to yield decacyclene and leucacene which contained 3 and 5 acenaphthene residues, respectively.²⁸

Ethylene, in the presence of cadmium vapor at 225-260°C., was polymerized, according to Bates and Taylor, by exposure to radiation from a cadmium lamp.²⁹

Reinicke noted that acetylene was polymerized in absence of air or moisture when illuminated by a quartz mercury arc at pressures of one to ten atmospheres. The product was a yellow amorphous solid insoluble in most solvents.³⁰

Activated mercury atoms produced by the absorption of light of wave length of $2536 \overset{\circ}{\text{A}}$ were used by Frankenburger and Zell to decompose n-pentane. Air, nitrogen, and carbon

²⁷ Ibid., p. 3142.

²⁸ A. E. Everest, The Higher Coal-Tar Hydrocarbons, p. 49.

²⁹ Bates and Taylor, "Studies in Photosensitization," J. Am. Chem. Soc., L (1928), 771.

³⁰ R. Reinicke, Zeitschrift für Angewandte Chemie, XLI (1928), 1144.

monoxide were used as carriers by passing streams of those gases through liquid pentane at 0°C., and then through mercury at 40-50°C. After exposure to a mercury arc, the products were condensed by means of a CH₂Cl₂-solid CO₂ mixture. The extent of the reaction was small. The products differed, depending upon the nature of the carrier gas used. With nitrogen, hydrocarbons of six to ten carbons were formed. When carbon monoxide was used as the carrier, aldehydes were found to be present besides the higher boiling hydrocarbons. With air, a liquid and solid mixture of an ester-like odor resulted. This mixture gave a positive aldehyde, hydrogen peroxide and iodoform test. It is assumed that the primary reaction was scission of C-C and C-H bonds and that the high boiling products were the result of reactions of the radicals so produced. Hydrogen peroxide and the aldehydes were supposed to result from the reactions of atomic hydrogen as well as of resulting radicals with the carrier gas.³¹

Klemenc and Patat observed that acetylene and a volatile liquid product of petroleum-like odor were formed when ethylene was exposed to ultraviolet light.³² The ethylene was thought to be decomposed to hydrogen and acetylene, and the latter to polymerize to the volatile liquid. It is possible that the ethylene itself polymerized.

³¹W. Frankenburger and R. Zell, "Action of Optically Excited Mercury Atoms on Hydrocarbon Molecules," Zeitschrift für Physikalische Chemie, B2 (1929), 395.

³²A. Klemenc and F. Patat, "Reactions of Photochemically Excited Oxygen," Z. Phys. Chem., Abt. B, III (1929), 289.

Klemenc and Patat found that when n-pentane is irradiated with ultraviolet light, decomposition and polymerization occur whether or not mercury is present in the gas.³³ The presence of mercury had a marked catalytic influence on the production of hydrogen from n-pentane.

Kato obtained spectroscopic evidence of the formation of benzene by the photochemical reaction of acetylene at 0°C., and also above 270°C., contrary to the results of others who obtained only cuprene.³⁴ He claimed that the formation of benzene was favored by the elevated temperature and by light of short wave length.

Taylor and Vernon investigated the effect of light on a 46 per cent solution of styrene in ethylbenzene under oxygen-free conditions and in contact with oxygen.³⁵ The experimenters concluded that both light and oxygen have a polymerizing effect on styrene, each increasing the effect of the other.

Lind and Livingston reported that ultraviolet light converted allene to complex polymers at room temperature. The similarity between the curves representing reaction rate

³³Klemenc and Patat, "Behavior of Atomic Hydrogen," Z. Phys. Chem., A149 (1930), 449.

³⁴Y. Kato, Institute of Physical and Chemical Research (Toyko), X (1931), 343, cited by Egloff, Reactions of Pure Hydrocarbons, p. 455.

³⁵J. S. Taylor and A. A. Vernon, "Photopolymerization of Styrene and Vinyl Acetate," J. Am. Chem. Soc., LIII (1931), 2527.

and light absorption as functions of pressure led to the conclusion that the effect of changing the pressure is to change the percentage absorption, and that the rate of reaction is directly proportional to the intensity of the light absorbed.³⁶

The formation of a solid product on the walls of the container was observed by Kemula and Mrazek when acetylene was exposed to illumination by a quartz mercury vapor lamp.³⁷ Its formation in the gas phase was noted during the first minute of the reaction by the appearance of a pronounced Tyndall effect which slowly disappeared. Due to absorption of the light by the solid material the rate of the reaction soon decreased. Absorption spectra indicated the presence among the products of vinylacetylene, benzene, naphthalene, and "other reaction products."

Lind and Livingston studied the photopolymerization of methylacetylene under the influence of a hot mercury arc.³⁸ No methane or hydrogen was formed, but polymerization occurred, with the formation of a white substance which appeared to be a solid. The only effect of pressure was to change the percentage absorption of the light. The rate of polymerization

³⁶S. C. Lind and R. Livingston, "Photochemical Polymerization of Methylacetylene and Allene," J. Am. Chem. Soc., LV (1933), 1036.

³⁷W. Kemula and S. Mrazek, "Action of Ultraviolet Light on Acetylene," Z. Physik. Chem., B XXIII (1933), 358.

³⁸Lind and Livingston, op. cit.

was directly proportional to the intensity of the absorbed light.

Toul found that pure acetylene does not polymerize in sunlight alone or with nitrogen or mercury.³⁹ However, slow polymerization takes place in ultraviolet light and is catalyzed by mercury vapor.

Staudinger and Heuer report that styrene, in the presence of ultraviolet light, forms a soluble polymer and also an insoluble non-swelling polymer.⁴⁰ The latter was believed to be composed of three-dimensional molecules formed by the loss of hydrogen between thread molecules of polystyrene.

Melville studied the mercury-photosensitized polymerization of acetylene at pressures of 0.05 to 10 mm. and temperatures of 20-500°C.⁴¹ He believed that excited mercury atoms formed complexes with acetylene molecules, that the complexes reacted further with acetylene molecules to produce polymer molecules by a chain mechanism, and that the cessation of polymer growth was caused by collision with acetylene molecules different from the collisions responsible for chain growth. Melville found that the chain length (the number of

³⁹F. Toul, "Catalysis of Acetylene Polymerization in Ultraviolet Light by Mercury Vapor," Collection of Czechoslovakian Chemical Communications, VI (1934), 162.

⁴⁰J. Staudinger and W. Heuer, "Highly Polymerized Compounds," Ber., LXVII (1934), 1164.

⁴¹J. W. Melville, "Mercury-Photosensitized Polymerization of Acetylene," Transactions of Faraday Society, XXXII (1936), 258.

acetylene molecules polymerized by one excited mercury atom) was independent of the acetylene pressure, of the rate at which the chains were started, and of the surface area of the silica reaction vessel. The chain length varied with temperature, however, ranging from 10 at 20°C. to 100 at 250°C. and then decreasing with further temperature rise.

Fries and Bestian showed that *o*-divinylbenzene polymerized in direct sunlight to a colorless, rubber-like mass.⁴²

Lauer and Oda found that the solvent had a great deal to do with the change of anthracene into dianthracene by means of radiation from a mercury-vapor lamp at 69°C.⁴³ The reaction velocity was much higher in benzene than in hexane, cyclohexane, and absolute alcohol.

Nikiforou and Puntzo could polymerize pure divinyl in the gas state by the action of light from a quartz mercury-vapor lamp.⁴⁴ Technical divinyl (70 per cent divinyl, remainder chiefly pseudo-butylene) after 80 hours gave a white solid insoluble in alcohol, ether, and benzene.

Phenylacetaldehyde was exposed in both brown and ordinary glass bottles to both diffuse and direct sunlight by Muller.

⁴²K. Fries and J. Bestian, "*o*-Divinylbenzene and Naphthalene," Ber., LXIXB (1936), 718.

⁴³Karl Lauer and Ryohei Oda, "Effect of Solvents on Photochemical Reactions," Ber. LXIXB (1936), 137.

⁴⁴V. K. Nikiforou and P. M. Runtzo, "The Photochemical Polymerization of Divinyl," Chemical Abstracts, LIX (1936), 2493.

Polymerization went on more rapidly in the brown bottles when exposed to sunlight, while it was more rapid in the ordinary bottles when the exposure was to diffuse light.⁴⁵ The polymerization of phenylacetaldehyde seems to be susceptible to the influence of light of short wave length.

Gary reported that a 3.2:1 isobutane-isobutene mixture saturated with mercury vapor at room temperature gave nothing heavier than C_4 when illuminated with 2536 Å, a mercury resonance line, using a flow method. It was found that when a static method was used, 3.2:1 isobutane-isobutene mixtures illuminated with 2536 Å at temperatures ranging from 27°C. to 200°C. gave pressure drop rates of some 8-35 mm. per hour over periods of 2 to 12 hours. A volatile liquid condensed in the manometer and in vessel after illumination and cooling to room temperature.⁴⁶

⁴⁵Arno Muller, "The Polymerization of Phenylacetaldehyde," Chemical Abstracts, XXX (1936), 7357.

⁴⁶Felice Gary, "Mercury-Sensitized Photochemical Action on a Mixture of Isobutane and Isobutene," (Unpublished M. S. thesis, Department of Chemistry, North Texas State Teachers College, 1939).

CHAPTER III

APPARATUS AND PROCEDURE

The apparatus as shown in Figure 1 was built. A quartz reaction vessel, D, 2.54 cm. internal diameter and 20 cm. in length with quartz to pyrex graded seals at each end was built into a system containing a cooling waterjacket, C, a differential manometer, C, and a condenser for C_4 's, A. A variable resistance, E, permitted temperature control of section H and the reaction vessel, D, over a range of 25°C. to 200°C. A thermometer was inserted in the thermometer well, K, built in and coaxial with the quartz reaction vessel, D, for the measurements of temperatures of gas mixtures.

The source of 2536 Å⁰ radiation was a Braun Fluoro mercury-vapor lamp, F, purchased from Ultra Violet Products Corporation. Ninety per cent of the radiation of this lamp is 2536 Å⁰ radiation, so the lamp was used without color filters.

Hydrocarbons flowed from a "mixing bomb", J, a small steel cylinder fitted with needle valves. During delivery the bombs were kept inverted to insure that the composition of the hydrocarbons delivered would be the same as the liquid in the bomb.

The isobutane:isobutene mixtures of known composition were prepared from isobutane purchased from the Ohio Chemical Company and from "Alky Gas", a 1.2:1 isobutane:isobutene

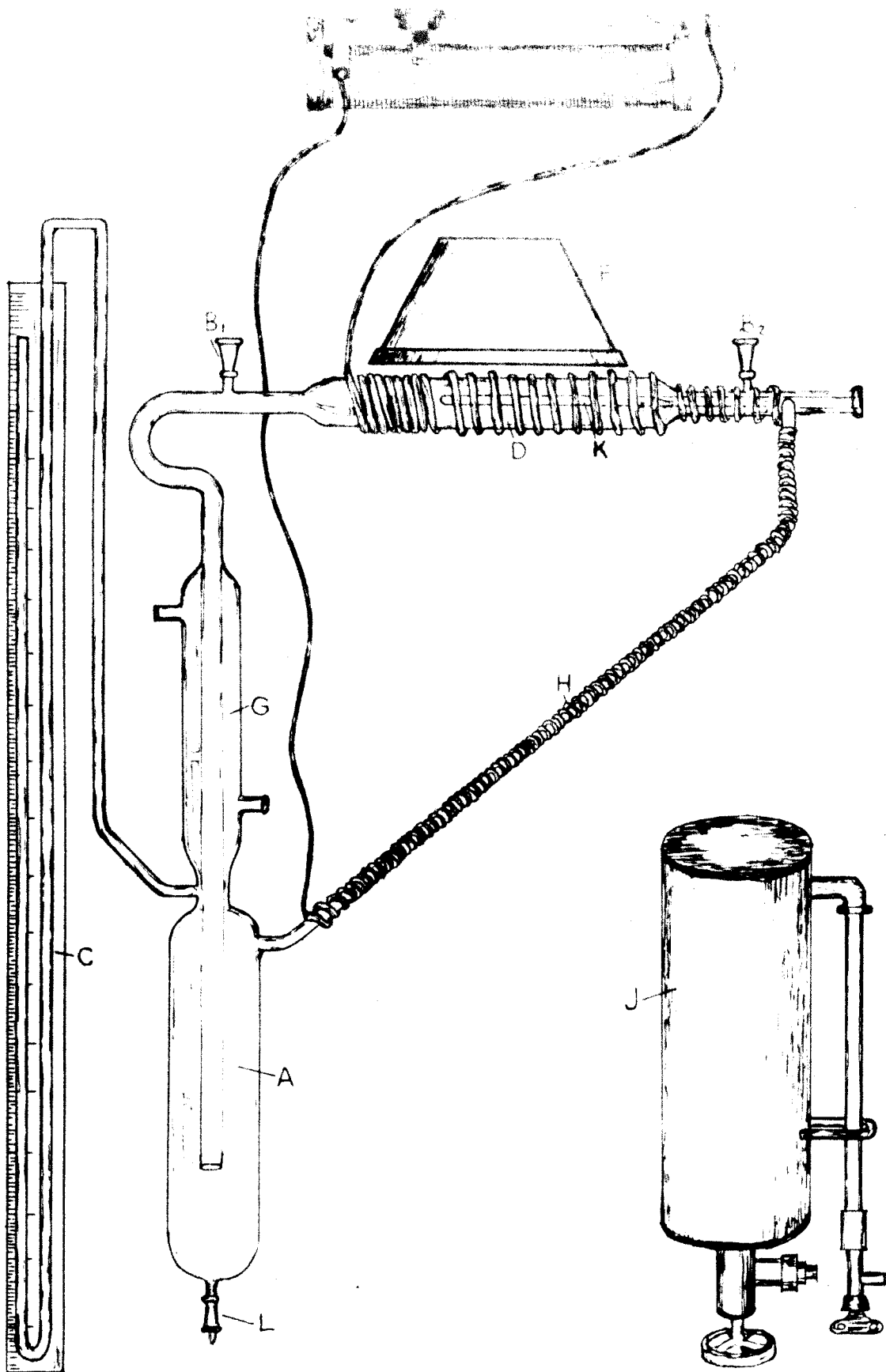


Fig. 1. - apparatus

mixture by weight, furnished by The Texas Company. The isobutane was chemically pure.

Mercury was admitted through a ground-glass joint, B₁, and allowed to flow into the quartz reaction vessel. B₁ was then connected with the "mixing bomb", J, containing a 2.6:1 isobutane:isobutene mixture. With ground-glass joints B₂ and L open the whole system was flushed with the C₄ mixture to sweep out all air. Then the ground-glass joints were closed and an ice-salt bath was placed around the condenser until approximately 100 c.c. of the 2.6:1 isobutane:isobutene mixture condensed in A. The temperature of the reaction vessel was raised to 200°C., and the lamp was turned on. The differences in temperature in heated section H and D and in the water-cooled section G should produce differences in gas densities that would cause a counterclockwise circulation of gases in the system which would enable the gases present to recirculate for repeated periods of illumination with 2536 Å⁰ radiation from the mercury-vapor lamp.

The mixture was illuminated for 12 days and 16 hours (304 hours). There was no pressure drop in the system as would be expected if either polymerization or alkylation of the C₄'s had occurred. As Gary had gotten a pressure drop in the illumination experiments ~~we~~ made on mixtures of these same gases, it was anticipated that the pressure in this system would make a distinct drop. Furthermore, there was a counterclockwise circulation of gas in the system as evidenced by the condensation and collection of

TABLE 1
 VARIATION OF TEMPERATURE AND PRESSURE AT 200°C.

Date	Pressure Prior to Packing cm.	Time	Temp. Prior to Packing °C.	Pressure Drop on Packing cm.	Average Temp. on Packing °C.
4/1/40	6.0	5:00 P.M.	-10.0	0.0	-14
4/2/40	17.0	11:00 P.M.	-8.0	3.0	-14
	23.0	8:00 A.M.	-6.5	7.0	-14
	17.0	3:00 P.M.	-8.5	4.0	-14
4/3/40	16.0	11:00 P.M.	-8.0	4.0	-14
	18.6	8:00 A.M.	-6.5	6.2	-14
	7.5	6:00 P.M.	-12.0	14.0	-15
4/4/40	15.0	11:30 P.M.	-9.5	7.5	-15
	17.0	8:15 A.M.	-9.0	4.0	-15
	11.5	4:45 P.M.	-11.0	5.0	-15
4/5/40	12.0	11:15 P.M.	-11.0	5.5	-15
	17.5	7:15 A.M.	-9.0	2.0	-14
	15.3	4:15 P.M.	-9.5	7.5	-15
4/6/40	13.0	11:45 P.M.	-9.0	7.5	-15
	7.0	9:30 A.M.	-11.0	16.0	-15
	5.5	4:45 P.M.	-11.0	16.0	-15
4/7/40	13.0	10:30 P.M.	-9.5	7.5	-16
	9.0	9:30 A.M.	-10.0	7.5	-16
	9.5	4:00 P.M.	-9.0	17.5	-17
4/8/40	7.0	10:30 P.M.	-11.0	13.5	-17
	13.0	7:00 A.M.	-9.0	5.5	-17
	9.5	4:15 P.M.	-9.5	15.0	-17
4/9/40	13.5	10:30 P.M.	-9.0	16.5	-17
	9.5	8:00 A.M.	-10.0	14.5	-17
	11.5	3:15 P.M.	-10.0	7.5	-16
4/10/40	16.0	10:45 P.M.	-7.5	8.0	-15
	13.0	8:15 A.M.	-9.5	7.5	-16
	7.0	5:45 P.M.	-10.5	14.5	-17
4/11/40	12.0	11:30 P.M.	-9.0	11.5	-16
	9.0	8:45 P.M.	-10.0	10.5	-16
4/12/40	8.0	7:15 A.M.	-10.5	12.5	-16
	17.5	8:15 P.M.	-8.0	11.5	-16
4/13/40	15.0	8:45 A.M.	-8.0	12.0	-

mercury droplets in G and A. The pressure in the system measured by the differential manometer A varied from 17.5 cm. below atmospheric to 23 cm. above atmospheric, depending on the temperature, -17°C . to -6.5°C . of the ice-salt bath around the condenser, A. The variations of temperature and pressure are recorded in Table 1.

After illumination the hydrocarbons in A were removed through L to a receiver and fractionated with a low temperature Davis Column purchased from E. Matchlett and Sons. The over head temperature of the column was held at -8°C . to -10°C . by ice-salt mixture during the fractionation. The residual bottoms were just a few tiny droplets of hydrocarbons.

A similar experiment was made at 100°C . The new sample of the 2.6:1 isobutane:isobutene mixture was illuminated for 6 days and 11 hours (155 hours). The pressure and temperature readings taken during this period are recorded in Table 2. Again there was no pressure drop in the system as would be expected if either polymerization or alkylation of the C_4 's had occurred. There were no Davis Column bottoms except a few tiny droplets on fractionation of the hydrocarbons after illumination. The odor was not that of isooctane.

TABLE 2

VARIATION OF TEMPERATURE AND PRESSURE AT 100°C.

Date	Pressure Prior to Packing cm.	Time	Temp. Prior to Packing °C.	Pressure Drop on packing cm.	Average Temp. on packing °C.
4/22/40		6:00 P.M.		-19.0	-17.0
4/23/40	17.0	8:00 A.M.	-7.0	- 7.5	-15.5
	15.0	6:00 P.M.	-7.0	-17.0	-16.0
4/24/40	21.0	8:00 A.M.	-6.0	-17.5	-15.5
	15.5	7:00 P.M.	-8.0	-15.5	-15.5
4/25/40	17.0	8:00 A.M.	-8.0	- 7.0	-15.0
	15.0	6:45 P.M.	-8.5	-13.5	-15.0
4/26/40	16.0	7:15 A.M.	-8.0	-14.5	-16.0
	20.0	6:00 P.M.	-7.5	-12.0	-15.5
4/27/40	22.0	8:30 A.M.	-6.6	-16.0	-16.0
4/28/40	21.0	7:00 A.M.	-6.0	-17.0	-17.0
	20.0	7:00 P.M.	-7.0	-15.5	-17.0

CHAPTER IV

SUMMARY OF RESULTS

A 2.6:1 isobutane:isobutene mixture saturated with mercury vapor at 200°C. and illuminated with recirculation for 304 hours with 2536 Å radiation did not give more than tiny droplets of liquid heavier than C₄. The same was true of the mixture illuminated at 100°C. with recirculation for 155 hours with 2536 Å.

CHAPTER V

SUGGESTED FUTURE WORK

Because of the failure of mercury-sensitized illumination of 2.6:1 isobutane:isobutene mixtures to yield a hydrocarbon heavier than C_4 , it is suggested that a 3:1 isobutane:isobutene mixture be illuminated with the $2536 \overset{\circ}{\text{A}}$ radiation at 25°C . for a period of about 6 days.

In the event that no hydrocarbons heavier than C_4 are produced, the same apparatus could be used in an attempt to bring about the mercury-sensitized alkylation of di-isobutylene with isobutane at 30°C . by $2536 \overset{\circ}{\text{A}}$ radiation.

Another experiment that could be done, but with much more difficulty than with the two mentioned above, is the illumination of the liquid phase of C_4 mixtures at various temperatures with $2536 \overset{\circ}{\text{A}}$ radiation. The main difficulty would be in maintaining the C_4 in liquid phase in quartz at temperatures high enough to give mercury vapor pressures sufficiently high to give adequate absorption of the mercury resonance radiation.

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