# REACTIONS OF HYDROCARBONS IN ELECTRICAL DISCHARGES[1]

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CONTENTS

## I. INTRODUCTION

The reactions of hydrocarbons in electrical discharges are interesting and important from both the practical and the theoretical points of view. Theoretical studies establish what reactions occur and throw light on the mechanism of activation which causes reactions at room temperature. If the theory of these reactions is known, it is possible to utilize them to the greatest advantage from the practical point of view.

The present study seeks to establish the fundamental chemistry of the hydrocarbon reactions occurring in these discharges and at the same time to present some mechanisms and theory of these reactions. All of the information that would be desirable for such an evaluation is not available, since complete experiments have not been made.

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## II. TYPES OF ELECTRICAL DISCHARGE

Broadly, electrical discharges can be divided into two main classifications: (*A*) non-disruptive or silent discharges and (*B*) disruptive discharges. These may be further subdivided as follows:

A. Non-disruptive or silent discharges:
    1. The ozonizer discharge
    2. The semi-corona discharge
    3. The corona discharge
    4. The glow discharge
    5. The electrodeless discharge
B. Disruptive discharges:
    1. The spark
    2. The arc

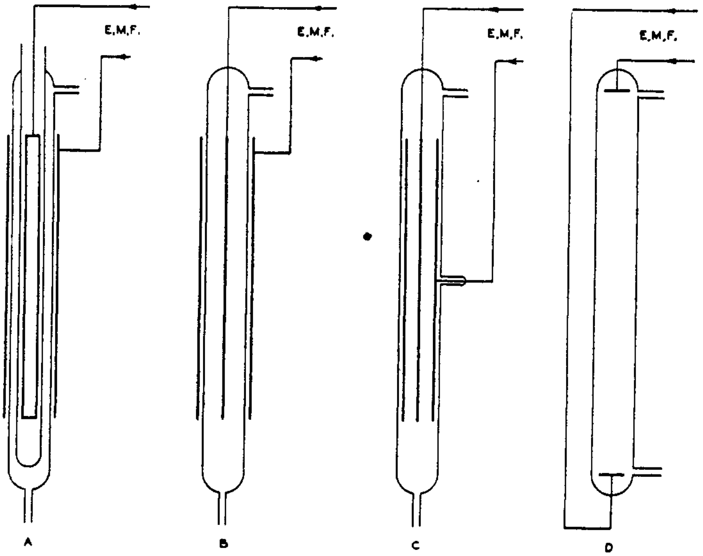


FIG. 1. Types of discharge apparatus. A, ozonizer discharge; B, semi-corona discharge; C, corona discharge; D, glow discharge.

The type of discharge used in studying any particular hydrocarbon reaction often plays a very important rôle in determining the reactions which occur and the products obtained. The disruptive discharges are accompanied by a localized high-temperature zone in and near the discharge, so that the reactions are a combination of the thermal reactions due to this high temperature and the electrical reactions from electrons present and the electrical field. The silent discharges are more diffuse and are not accompanied by such high-temperature zones. The silent discharges therefore cause chemical reactions that are due, almost entirely, to the electric field. For this reason the reactions in the silent discharges will be presented first.

The types of silent discharge may be differentiated by referring to figure 1.

## A. NON-DISRUPTIVE OR SILENT DISCHARGES

### 1. *The ozonizer discharge or the Siemens ozonizer*

As can be seen from A in figure 1, two electrodes, both separated from the reaction space by a glass wall, constitute an ozonizer. Ordinarily it is constructed from tubes, although other forms have been used. It is also possible that dielectrics other than glass could be employed to separate the electrodes from the reaction space.

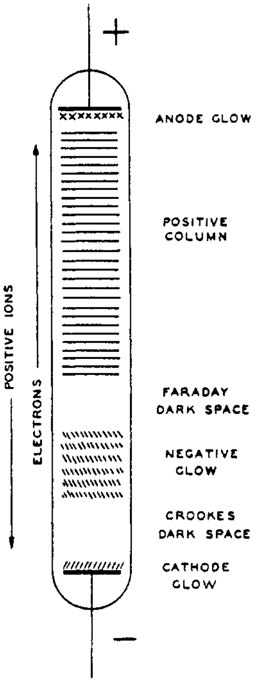


Fig. 2. Details of the glow discharge

Ordinarily, voltages from about 5 to 25 kilovolts are used to operate the ozonizer. Various frequencies have been used; at zero frequency the discharge does not occur, but quite satisfactory discharges occur from about 50 cycles per second on up.

The discharge can be operated at high or low pressures and with liquids or gases.

### *2 and 3. The corona discharges*

"When the electric field around a point or wire becomes sufficiently high for break-down at these regions before a spark can propagate across the gas space a corona discharge around the point or wire occurs." (172, page 485.) The corona discharges can occur at any frequency, including zero, and at voltages that are determined by the physical character of the apparatus and the conditions of pressure and temperature.

### *4. The glow discharge*

When sufficient voltage is applied to two electrodes in a reaction space at a pressure of from 0.01 to 100 mm. (usually about 5 mm.), a glow discharge will occur. When conducted at zero frequency the discharge assumes the form given in figure 2. The voltage required varies from about 100 volts upwards and depends on the pressure and composition of the gas in the discharge.

The physical aspects of this discharge have been studied very extensively, so that most of the characteristics of the discharge are known. These characteristics, so pertinent to the electrical reactions of hydrocarbons, are considered in detail in the section on theory.

### *5. The electrodeless discharge*

A conducting coil (inductance) through which a high-frequency current is flowing can cause a discharge to take place in an adjacent gas if the gas is of the correct pressure and the intensity of the electromagnetic field is great enough. Ordinarily, the inductance is wound around the outside of a glass discharge vessel. The pressure conditions inside the flask must be within the range of 0.01 mm. to 100 mm. for the discharge to occur. In most respects this discharge resembles the glow discharge, except that it will operate only at high frequencies.

## III. Reactions of Pure Hydrocarbons in the Non-disruptive or Silent Discharges

### A. OLEFINS

Of the various types of hydrocarbons, the olefins are among the most reactive chemically. This is also true in the silent discharges. Since these reactions can be made to occur under comparatively mild conditions, the reactions of the olefins offer the best opportunity for obtaining an insight into these electrical reactions. Once the reactions of the olefins are understood, the reactions of other hydrocarbon types can better be approached.

Most of the study on the reactions in the electric discharges has been qualitative in nature rather than quantitative. The reason for this is that the variables involved are not easily measured or controlled. Probably the most important variables are (*1*) effective discharge intensity and (*2*) effective residence time in the discharge. The effective discharge intensity may be likened to temperature in thermal work and the residence time to contact time. The discharge intensity is a function of the voltage, frequency, current, and structural characteristics of the apparatus, as well as the pressure in the discharge space.

The limitations of analytical methods for determining the nature of the product also restrict the results to qualitative rather than quantitative interpretation. The gases can be analyzed with considerable accuracy, but the methods for the liquid products are inadequate. It seems quite likely that many, if not most, of the liquid products are complex mixtures that would have to be analyzed by proximate methods to give the type of hydrocarbons present, e.g., acetylenes, olefins, aromatics, naphthenes, and paraffins. Even this has not been done in most cases.

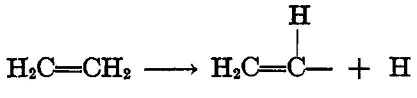
### *1. Ethylene*

Considerable qualitative and exploratory work on ethylene has been done. The products most frequently identified have been hydrogen, acetylene, and a liquid. This liquid varies in nature from a thin, mobile, colorless product, which is probably a mixture of simple polymers, to high-boiling oils and solids. A summary of these studies is given in table 1, where the type of discharge and the reaction products are given.

The results given in table 1 indicate the complexity of the reactions taking place in the silent discharges. It is obvious that (*1*) the primary reaction products are subjected to secondary reactions; (*2*) more than one primary reaction occurs; or (*3*) both 1 and 2 may take place. It seems worth while to try to establish which occurs.

In the glow discharge radicals are formed that are capable of removing antimony or lead mirrors, but not zinc or cadmium mirrors. The radicals from ethylene have not been identified. This is quite an interesting observation, for ethylene does not give radicals that remove such mirrors when treated thermally under conditions that give such radicals from saturated hydrocarbons (213).

The present writers suggest that these radicals from ethylene in the discharge are vinyl radicals and that they are produced by breaking a carbon–hydrogen bond:



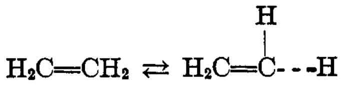
$$H_2C{=}CH_2 \longrightarrow H_2C{=}\overset{\displaystyle H}{\overset{|}{C}}{-} + H$$

A rapid formation of acetylene in the ozonizer discharge has been observed as an initial reaction (241). The vinyl radical could give this acetylene. On the other hand, when high flow rates were used and the products immediately cooled to −60°C., 1-butene and 1-hexene were found in 90 to 95 per cent yields (188). These compounds are simple polymers of ethylene. They could be built up by adding the vinyl radical to other ethylene molecules with later saturation. Alternatively, it seems quite possible that the carbon–hydrogen bond that is broken to give vinyl radicals is broken only in extreme cases and is activated in other cases. This can be represented as follows:

TABLE 1

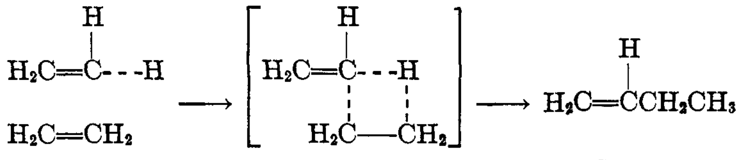
*Ethylene in the ozonizer-type discharge*

| REACTION PRODUCTS | REFERENCES |
|---|---|
| Colorless liquid product | (251) |
| $H_2$, $C_2H_2$, and a liquid product | (34, 38) |
| $H_2$, $C_2H_2$, $C_2H_6$, liquid $(C_8H_{14})_n$, and resins | (42) |
| At −20°C., $H_2$, liquid mixture (b.p. 100–250°C.), and a rubber-like solid analyzing close to $(C_5H_8)_n$ | (54) |
| Yellow oil, b.p. > 200°C. | (181) |
| Yellow oil $(C_{12}H_{22})$, b.p. > 260°C. | (174) |
| Liquid, $C_{14}H_{26}$, b.p. 100–110°C. at 14 mm. | (179) |
| Solid $(C_{16}H_{26})_9$, m.p. 105°C. | (179) |
| Solid $(C_{16}H_{26})_n$, m.p. 110°C. | (179) |
| Liquid, $C_{30}H_{54}$ | (133) |
| Liquid containing oxygen (probably absorbed oxygen from the air) | (135) |
| At −60°C., 1-butene and 1-hexene | (188) |
| Liquids: $C_{16}H_{30}$ and $C_{26}H_{44}$ before exposure to air; $C_{16}H_{30}O$ and $C_{26}H_{44}O_2$ after exposure to air | (177) |
| $H_2$, $C_2H_2$, $C_2H_6$, 1-$C_4H_8$, $C_4H_{10}$, liquid, and a resin | (222) |
| Polymers $(C_2H_4)_3$ to $(C_2H_4)_6$; a small amount of paraffins found in product, b.p. 90–210°C. | (63) |
| $H_2$, $CH_4$, $C_2H_2$, $C_2H_6$, $C_3H_8$, $C_4H_{10}$, and an unsaturated liquid, $C_nH_{1.6n}$ | (164) |
| $H_2$, $C_2H_2$, $C_4H_6$, $C_4H_8$, and $C_4H_{10}$ plus $C_6$-paraffins and $C_6$-olefins | (247) |
| $H_2$, $C_2H_2$, saturated and unsaturated condensation products | (241, 263) |
| $C_2H_2$ | (204) |
| Polymers | (269) |



$$H_2C{=}CH_2 \rightleftarrows H_2C{=}\overset{\displaystyle H}{\overset{|}{C}}{-}{-}{-}H$$

where C- - -H indicates an activated carbon–hydrogen bond. This molecule containing an activated bond can then react with another ethylene molecule:



Postulated intermediate

1-Butene

From this discussion it seems certain that there are two primary reactions of ethylene in the silent discharge: (*1*) dehydrogenation to acetylene, and (*2*) polymerization.

The primary reactions having been established, it is worth while to examine the reaction products in more detail. The liquid product in some cases is known (133, 134) to absorb oxygen from the air quite readily. Ethylene polymers (i.e., monoölefins) do not absorb oxygen so readily, while the acetylene polymers are quite noted for this property. This suggests that one of the secondary reactions is the polymerization of acetylene.

Still another series of experiments throw light on the secondary reactions of ethylene. These experiments were made in an ozonizer using a high-frequency power source and the products were condensed by cooling to −70°C. The following products were obtained:

| PRODUCT | PER CENT |
|---|---|
| Uncondensed ($H_2$, $C_2H_2$, $C_2H_6$) | 13 |
| Butane | 45 |
| 1-Butene | 15 |
| Fraction boiling 35–45°C | 4 |
| $C_6$-fraction | 15 |
| Higher hydrocarbons | 8 |

The $C_6$-fraction contained 1-hexene and paraffin hydrocarbons, presumably hexanes (222).

The saturated hydrocarbons are the interesting ones in this experiment. Are they formed by simple hydrogenation of the corresponding olefin? This is entirely possible. On the other hand, it is conceivable that the butane is formed by the alkylation of ethane with ethylene. There is nothing that will permit a selection, except that the low concentration (<13 per cent) of ethane might tend to favor the postulate of direct hydrogenation.

By using high-frequency current to energize the ozonizer, it was found that the nature of the reaction products could be controlled by the experimental conditions. In one case the major product was butene, in another acetylene, and in still another butadiene. The energy consumption was 20 kw.-hr. per kilogram of ethylene reacted (247).

Low-boiling olefinic polymers were obtained by other workers (140) when an ozonizer excited by high-frequency current was used to treat ethylene. The exit gas analyzed as follows: 91 per cent $H_2$ and paraffins; 6 per cent $C_2H_4$; 3 per cent $C_3H_6$ and $C_4H_8$. One gram-mole of ethylene reacted for each 2.3 kw.-hr. consumed.

The kinetics of the reaction of ethylene in the ozonizer discharge have been studied (163, 164, 165). There seems a little doubt that there is a definite induction period. The reaction resembles the reaction caused by alpha-particles (158).

In the high-frequency corona discharge, static ethylene reacted completely in 10 hr. The gaseous product contained 67 per cent of hydrogen and 20 per cent of saturated hydrocarbons. The liquid fraction was a dark oil with a molecular weight of about 500. An induction period of about 2 hr. was found, and it was noted that admixing hydrogen in the charge shortened the induction period and increased the reaction velocity. In a dynamic system, butadiene was found in the products condensed at −85°C. The yield of butadiene was a maximum of 30 per cent of the ethylene reacted when the initial gas contained 23 per cent of hydrogen. Since the reaction had an induction period and was sensitive to an added gas (hydrogen), it was concluded that reaction occurred through a chain mechanism (13; *cf.* also 69).

In the semi-corona discharge, ethylene gave liquid products with densities from 0.78 to 0.82, molecular weights from 130 to 160, and $n_D^{20°}$ from 1.45 to 1.46. The yield was 0.204 g. of liquid per kilowatt-hour (161).

The electrodeless discharge in ethylene also gives hydrogen and condensation products (117).

### *2. Higher olefins*

In the ozonizer propene is known to polymerize to a liquid product and the gas contains hydrogen and methane (30, 208). In one case the liquid had the following properties: d = 0.824, refractive index = 1.4578; average molecular weight = 233.

Complete analysis of the gases produced during the polymerization of propene in the ozonizer tells very little about the actual reactions taking place, for it can not be told whether the gas comes directly from the propene or from secondary reactions of the propene polymer. Since 85 to 90 per cent of the reacting propene is polymerized, the other reactions are of minor importance. Table 2 gives the moles of product per 100 moles of propene reacted (166).

2-Butene in the ozonizer gave an oil having an average molecular weight of 202, a density of 0.831, and an iodine number of 156 (208). No gaseous products were reported.

In the high-frequency ozonizer propene polymerized, 2.3 kw.-hr. causing 1 gram-mole of propene to react. The liquid formed was mostly dimers and trimers. The exit gas analyzed as follows: 12 per cent $C_2H_4$; 50 per cent $C_3H_6$ and $C_4H_8$; 38 per cent $H_2$ and paraffins (140).

Isobutene polymerizes in the ozonizer to give a mobile yellow-brown liquid (63). A detailed investigation (208) revealed that the liquid had the following average properties: $d_{4°}^{20°} = 0.831$; $n_D^{20°} = 1.4483$; molecular weight, 202; iodine number (Wijs), 156; C = 84.46 per cent; H = 14.60 per cent. Upon fractionation it was found that the largest fractions correspond to di- and tri-isobutene, although some of the evidence indicated that 2,3-dimethylbutane and 2,3-dimethyl-2-butene might be in the 32–52°C. fraction, and that 2,2-dimethylpentane, 2,4-dimethylpentane, 2,2,3-trimethylbutane, and the related olefins might be in the 75–85°C. fraction. The higher fractions are richer in olefins than the lower boiling fractions; these higher fractions also contain naphthenes, but apparently no aromatics.

TABLE 2

*Gaseous products from propene in the ozonizer discharge*

| | | | |
|---|---|---|---|
| Time, minutes | 24.5 | 73.5 | 73.5 |
| Products, moles per 100 moles reacted: | | | |
| $H_2$ | 10.7 | 16.9 | 16.4 |
| $CH_4$ | 3.7 | 6.1 | 6.8 |
| $C_2H_2$ | 18.3 | 2.5 | 1.7 |
| $C_2H_4$ | 11.1 | 1.4 | 1.4 |
| $C_2H_6$ | | 1.8 | 2.5 |
| $C_3H_8$ | 13.0 | 5.7 | 7.1 |
| $C_4H_8$ | 13.9 | | |
| $C_4H_{10}$ | | | |
| $C_5H_{12}$ | 2.2 | 1.8 | 0.8 |
| Per cent $C_3H_6$ reacted | 48.2 | 94.2 | 95.1 |
| Per cent of original $C_3H_6$ to liquid | 20.4 | 74.6 | 77.3 |

To workers studying fuels for internal-combustion engines, it would be interesting to have data on the antiknock properties of the products produced by the electrical polymerization of isobutene. Similar data on the completely hydrogenated product would be interesting, as it is a potential aviation fuel. From the data given above, it seems that isobutene polymerizes as easily electrically as it does catalytically, so that it should not be too difficult to obtain sufficient product for these tests and, if the product has useful properties that are not easily obtainable catalytically, it should not be difficult to produce such products on a large scale.

"Amylene" from fermentation amyl alcohol has been studied both in the ozonizer discharge and in the semi-corona discharge. A summary of the results is given in table 3 (185).

In the presence of hydrogen the three isomeric pentanes, various pentenes, isopropylacetylene, and other products were observed. (So far as the writers know, this is the only case in which neopentane has been reported as a product of electrical action on a hydrocarbon. In this case the evidence is the boiling point of a few drops of material, without other supporting data.) The acetylene in the gas included not only acetylene, but also propyne, vinylacetylene, and diacetylene. Thus the reactions taking place probably include polymerization, isomerization, cracking, dehydrogenation, and, especially in the presence of hydrogen, hydrogenation (185).

TABLE 3

*Products obtained by the electrical treatment of "amylene"*

| TYPE OF DISCHARGE | CARRIER GAS | AMYLENE CHARGED IN PRODUCT |  | PRODUCTS IN GAS |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  | Liquid | Gaseous | Saturated hydrocarbons | Olefins | Acetylene | Hydrogen |
|  |  | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* |
| Ozonizer...... | $H_2$ | 79.1 | 2.5 | 63.5 | 9.5 | 27.0 |  |
| Semi-corona... | $H_2$ | 14.8 | 15.6 | 46.7 | 20.0 | 33.3 |  |
| Ozonizer...... | None | 57.4 | 7.1 | 65.0 | 4.1 | 24.4 | 6.5 |
| Ozonizer...... | $H_2$ | 81.7 | 5.0 | 38.2 | 8.8 | 23.6 | 29.4 |

TABLE 4

*Olefins in the glow discharge*

| OLEFINS | ANALYSIS OF GAS IN VOLUME PER CENT |  |  |  | dp/dt | W |
|---|---|---|---|---|---|---|
|  | Hydrogen | Acetylenes | Olefins | Paraffins |  |  |
|  | *per cent* | *per cent* | *per cent* | *per cent* |  |  |
| 1-Heptene.............. | 36.3 | 24.1 | 25.4 | 12.3 | 115 | 0.77 |
| 2,2,3-Trimethylbutene.. | 37.9 | 7.9 | 26.9 | 27.3 | 97 | 0.58 |
| (?)-Octene.............. | 38.7 | 14.0 | 36.4 | 10.9 | 105 | 0.80 |
| Diisobutene............ | 57.3 | 11.0 | 13.8 | 17.9 | 139 | 1.19 |

$dp/dt$ = rate of gas formation, in cubic centimeters per milliampere per second $\times 10^4$.
$W$ = rate of solid formation, in grams per milliampere per second $\times 10^6$.

Two main differences were noted between the reactions in the ozonizer discharge and in the semi-corona discharge: (*1*) For a given energy input the amount of reaction taking place in the semi-corona was much more than the amount in the ozonizer, and (*2*) the changes in the semi-corona were more deep seated with more gas formation and carbon deposition on the wire electrode (185).

A few of the liquid olefins have been studied in the glow discharge, the low pressure in this type of discharge permitting the study of the vapor at room temperature. In this study only the gaseous products were analyzed. As can be seen from table 4, dehydrogenation is the chief reaction, the reduced pressure in the reaction zone, the high molecular weight of the olefin, or both operating to reduce the polymerization and condensation reactions observed with the lower olefins (170).

### *3. Butadiene*

In the glow discharge at $10^{-3}$ to $10^{-1}$ mm. butadiene decomposes without evidence of polymerization. Above $10^{-1}$ mm. polymerization predominates. The constitution of the polymer is not known. When butadiene is reacted in the presence of hydrogen, polymerization also occurs. An induction period of 3 to 7 min. and the acceleration of the reaction rate by oxygen and argon and by increasing the size of the vessel were considered sufficient evidence for a chain mechanism (221).

The treatment of butadiene in the high-frequency ozonizer gave a liquid product that was thought to contain cycloölefins. The exit gas from the ozonizer analyzed as follows: 46.67 per cent ethylene; 25.4 per cent $C_3H_6$ and $C_4H_8$; 28 per cent hydrogen and paraffin hydrocarbons (140).

## B. ACETYLENES

As might be expected from the work on olefins just discussed, acetylene has a strong tendency to polymerize when subjected to the silent discharges. Table 5 gives a summary of the available work on acetylene. The liquid and solid products obtained from acetylene by electrical treatment have a powerful tendency to absorb oxygen from the air (134, 135, 180). This makes the study of these products rather tedious, if it is desired to study the unchanged products. Considerable confusion has resulted in the past, because oxygen would be absorbed unsuspected by the worker, and when carbon and hydrogen were determined by combustion the total would not equal 100 per cent. A special analytical technique has been evolved to cope with this situation (97).

When acetylene reacted in a high-frequency ozonizer discharge and the reaction products were cooled to $-60°C.$ before recycling, a 70 per cent yield of a colorless liquid was obtained (187, 188, 222). This liquid had the molecular weight of the trimer and from the reactions of the liquid it was concluded that it contained 1,5-hexadiyne, methylpentadiyne, and 1,5,3-hexadienyne. The liquid had a boiling point of −10°C. at 23 mm., $n_D^{9.15^\circ} = 1.4446$, and $d_{4^\circ}^{19.5^\circ} = 0.752$; it polymerized further on standing at room temperature, oxidized at room temperature when in contact with the air, and exploded on heating. These products are all isomeric with benzene, but no benzene was found. Both the density and the refractive index of the product argue against the presence of appreciable amounts of benzene.

TABLE 5

*Acetylene in the ozonizer-type discharge*

| REACTION PRODUCTS | REFERENCES |
|---|---|
| Yellow oily liquid | (269) |
| Liquid and solid | (252) |
| Thick brown liquid, a brown solid, and a little gas consisting of 92% $H_2$, 4% $C_2H_4$, and 4% $C_2H_6$ | (29, 31, 32) |
| Resinous solid containing oxygen | (229) |
| Brown "semi-solid" that absorbed oxygen | (127) |
| Thick brown liquid that later solidified | (174) |
| Insoluble solid | (133) |
| Hydrogen, carbon, a liquid that explodes when heated above 100°C., and a yellow-brown solid | (179) |
| "Warm" apparatus: a liquid and a solid | (137) |
| "Cold" apparatus: only a liquid, $(C_2H_2)_n$ | (137) |
| In the presence of hydrogen (optimum $1C_2H_2:4H_2$), acetylenes to $C_{10}$ and paraffins to $C_8$ | (266) |
| Brown condensation product in the presence of hydrogen; hydrogen absorbed | (164, 165) |
| At −60°C., 70% to trimers: 1,5-hexadiyne, methylpentadiyne, and 1,5,3-hexadienyne | (187, 188, 222) |
| Solid that absorbs oxygen | (138) |
| Condensation products | (83) |

It has been found that only liquid products are obtained if the reaction vessel is kept "cold," while both liquid and solid products are found if the vessel is kept "warm." The reactions of both liquid and solid indicated the presence of benzene derivatives in which unsaturated side chains were probably attached to the benzene ring (137). This type of product could be formed by the cyclization of the higher acetylene polymers.

While the products from acetylene are absorbing oxygen from the air, it has been found that a photographic plate becomes exposed and the iodine is liberated from a solution of potassium iodide (137, 175). Both of these actions stop as soon as the absorption of oxygen ceases.

From this work it seems that the primary action of the silent discharge on acetylene is to form polymers. If the reaction products are quickly removed from the system, relatively simple polymers are formed. Further reaction may result in the formation of long-chain, highly unsaturated aliphatic compounds, or cyclization may take place with the formation of aromatic hydrocarbons with unsaturated side chains.

In the presence of hydrogen, acetylene reacts faster than acetylene alone. After the reaction has proceeded for a while, the effect decreases and the reaction finally proceeds at the normal rate. In the presence of inert gases, the rate of reaction is proportional to the acetylene concentration. The reaction products were not given (242).

In another study, in the presence of hydrogen, a complex mixture of liquid products was obtained. This was said to contain acetylenic hydrocarbons up to $C_{10}$ and saturated hydrocarbons to $C_8$. At reduced pressures less polymerization and more hydrogenation took place (266).

In the presence of benzene, acetylene reacted only slightly differently from acetylene alone. There is no evidence that benzene took part in the reaction (176). It has been claimed that methane and acetylene interact in the silent electric discharge to give as high as 70 per cent yields of propene (109).

It has been found that increasing the wave length from 20 to 48 meters increases the amount and rate of the reaction of acetylene (65).

When compared in ozonizer apparatus of the same type and under identical conditions, it was found that the relative rates of reaction were as follows: acetylene, 20; ethylene, 10; methane, 2 (165).

In the electrodeless discharge acetylene gives a solid product, which has been variously reported as a yellow-white powder (191), an insoluble red-brown solid (105, 106), and polymers (and hydrogen) (117); no mention is made of the solid in one case (11).

One of the noticeable features of various electrical discharges in gases is that light is emitted. Quite often very beautiful color effects are present. A spectrometric examination of the light produced when acetylene is in the discharge indicates the presence of $C^+$ ions, carbon atoms, and hydrogen atoms (105, 106, 141). We do not know the chemical reactions of such fragments as $C^+$ ions and carbon atoms; hence the difficulty of proposing a complete reaction mechanism which is related to the actual processes occurring.

From the foregoing discussion, one may judge that acetylene is quite reactive in the electrical discharges. This is of special significance if acetylene is to be made by treating petroleum hydrocarbons in the electric discharge, for it means that the acetylene should be removed from the reaction zone as soon as formed, otherwise the yield will be reduced by secondary reactions. These secondary reactions may be minimized by using the electric discharge at subatmospheric pressure and limiting the amount of reaction during the passage through the discharge.

### *Higher acetylenes*

So far only results on the ozonizer treatment of 1-heptyne and 1-octyne have been reported. 1-Heptyne is said to give "diheptyne" (a colorless mobile liquid), "triheptyne" (a thick odorous oil), and "undecaheptyne" (a dark red mass insoluble in ether or benzene) (179).

1-Octyne produced "dioctyne" (a colorless liquid) and "nonaoctyne" (a dark red soft mass soluble in ether and benzene but insoluble in alcohol) (179).

The heavy viscous polymers obtained are apparently complex mixtures having an average molecular weight corresponding to undecaheptyne and nonaoctyne, respectively.

No gaseous products have been reported as the result of the action of the silent electric discharge on the higher acetylenes.

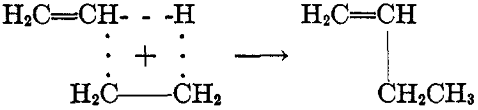
## C. AROMATIC HYDROCARBONS

### *1. Benzene*

Diphenyl is the most common identifiable reaction product reported to result from the action of electrical discharges on benzene (12, 62, 117). More complex products of a resinous nature are also formed, which have a composition closely approaching $(CH)_x$. Such products readily absorb oxygen from the air, and in some cases apparently combination with water vapor seems to occur. Such action brings to mind the reactions of the products from acetylene. Since acetylene is formed in the discharge and may itself react, the finding of such products is to be expected (12, 105, 106, 169, 176).

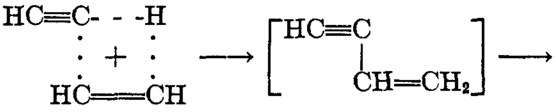
Hydrogen and acetylene are the most common gaseous reaction products. Table 6 gives a summary of the reactions of benzene.

When benzene is treated in the ozonizer under mild conditions, diphenyl is produced, along with a liquid fraction boiling in the same range as diphenyl. This liquid can be separated from the diphenyl by cooling to about −30°C., when the diphenyl crystallizes. Upon analysis it was found that the liquid contains more hydrogen than corresponds to diphenyl. From the data available, it was concluded that this liquid product was probably a mixture of dihydrodiphenyls. Although this product might appear a little unusual at first, it can be formed by reactions which are analogous to those already observed in the case of ethylene and acetylene.

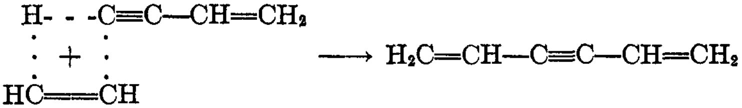


$$H_2C{=}CH\cdots H + H_2C{-}CH_2 \longrightarrow H_2C{=}CH{-}CH_2CH_3$$

1-Butene

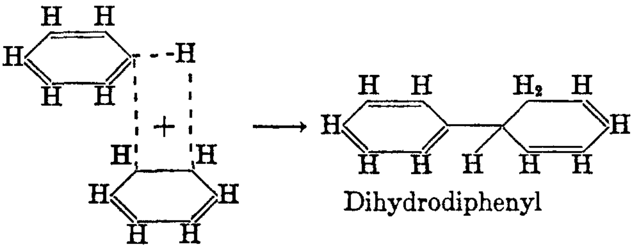


$$HC{\equiv}C\cdots H + HC{=}CH \longrightarrow \left[HC{\equiv}C{-}CH{=}CH_2\right] \longrightarrow$$



$$H\cdots C{\equiv}C{-}CH{=}CH_2 + HC{=}CH \longrightarrow H_2C{=}CH{-}C{\equiv}C{-}CH{=}CH_2$$

Divinylacetylene



Dihydrodiphenyl

In view of this analogy, the reaction seems reasonable enough. It is to be regretted that the original workers (222) did not obtain additional evidence for the dihydrodiphenyl. For example, the dihydro ring contains a conjugated diene structure that should react readily with maleic anhydride to give a solid derivative. The dihydrodiphenyl was postulated as the intermediate between benzene and diphenyl in the discharge. From this, it seems that the action of the discharge was one of polymerization followed by dehydrogenation. A continuation of this process would account for the resinous substances formed in the discharge.

When the intensity of the discharge was increased, it was not possible to isolate the dihydrodiphenyl but only the diphenyl, indicating that the dehydrogenation to diphenyl with the formation of an aromatic ring takes place readily (222). It seems quite possible that this same mechanism for the formation of diphenyl could also apply to the thermal reactions of benzene in some cases.

Acetylene was also formed in the discharge, indicating that a depolymerization of benzene was also taking place.

$$C_6H_6 \leftrightarrows 3C_2H_2$$

From the ratio of the products the ratio of the two reactions has been calculated.

$$C_6H_6 \begin{array}{l} \nearrow \text{Polymerization + dehydrogenation, 60 per cent} \\ \searrow \text{Depolymerization, 40 per cent} \end{array}$$

TABLE 6

*Benzene in the ozonizer-type discharge*

| REACTION PRODUCTS | REFERENCES |
|---|---|
| Gummy condensation product | (181) |
| Gummy, wax-like material | (110, 111) |
| $H_2$, $C_2H_2$, and hydrocarbon gases | (110, 111) |
| An oil and a solid, both $C_{24}H_{25}$ and both absorbing oxygen from the air | (176) |
| An oil, $(C_6H_6)_n$, and a solid, $C_{24}H_{26}$ | (177) |
| Diphenyl and a solid condensation product | (12) |
| Diphenyl, *p*-diphenylbenzene, a resin $(C_6H_4)_x$, and a gas consisting of 52.6% $H_2$, 29% $C_2H_2$, 12.1% $C_2H_4$, and 6.3% paraffins | (62) |
| Diphenyl (solid), dihydrodiphenyl (liquid), a solid brown resin, and a gas consisting of 52% $H_2$, 32.8% $C_2H_2$, 7.2% $C_2H_4$, and 0.8% higher olefins | (222) |
| Hydrogen plus benzene gives a product which absorbs oxygen. By steam distillation the product can be separated into an oil, $C_{12}H_{14}$, and a solid, $C_{28}H_{34}$ | (176, 177) |
| Methane plus benzene gives a yellow-red oil, $C_{28}H_{36}$ | (176) |
| Ethylene plus benzene gives a brown-red liquid, $C_{28}H_{34}$ | (176) |
| Acetylene plus benzene gives a yellow-brown solid, $C_{48}H_{46}$ | (176) |

A spectrometric study of the light emitted by benzene in the electrodeless discharge indicates that $C^+$ ions, carbon and hydrogen atoms, and $C_2$ and CH molecules are present (105, 106, 117). The reaction product is a brown, insoluble product, $(CH)_x$. Just how much of the material goes through these stages and just how much effect these active particles have in determining the reaction products is not known. From the fluorescence spectra it has been calculated that a considerable portion of the benzene molecules having vibrational energy greater than $5 \times 10^{-3}$ ergs decompose (1). In the glow discharge, CH, $C_2$, C, H, and $H_2$ (no $C^+$) were found by a spectroscopic study (107).

### *2. Benzene with other substances in the ozonizer*

*Methane.* A yellow-red oil, the nature of which is unknown, was produced (176). Both methane and benzene reacted.

*Acetylene.* A solid and a liquid product was formed. So far as could be told, the solid was identical with that produced from acetylene alone. The liquid was different, and apparently also different from that obtained from benzene alone (176).

*Ethylene.* A brown-red liquid soluble in benzene and ether was produced. Apparently both ethylene and benzene react, although the ratio was not determined (176).

*Hydrogen.* This product was different from that produced by benzene alone, but the presence of the hydrogen did not destroy the ability of the product to absorb oxygen from the air (176). The product could be separated by steam distillation into a liquid and a solid. The liquid was colorless (b.p. 241–243°C.), while the solid was a clear red mass (177).

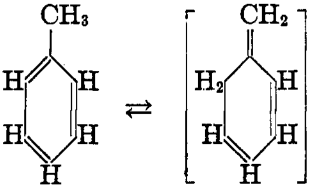
### *3. Toluene*

The reactions of toluene in the discharge resemble those of benzene qualitatively, with the exception that dibenzyl has been identified as one of the products.

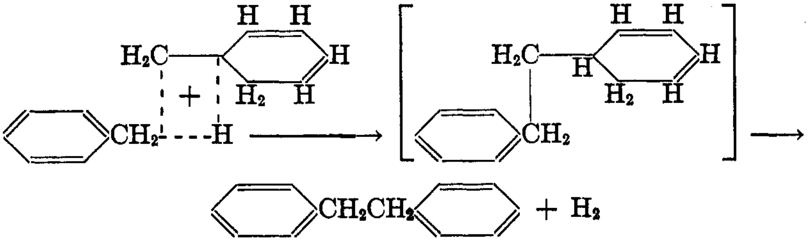
In the ozonizer the products were a thick yellow liquid, boiling at 140–150°C. at 14 mm. and having the composition of a toluene dimer, together with a resin melting at 150°C. (179). In the semi-corona discharge toluene gave a shellac-like deposit having a density of 0.95, a carbon content of 79.16 per cent, and a hydrogen content of 5.9 per cent. The rest of the composition was assumed to be oxygen. In other experiments dibenzyl, 2,2′-dimethyldiphenyl (m.p. 17°C.), and a liquid which boiled $>$200°C. and did not freeze at 0°C. were found. This last product was thought to be a mixture of isomers of dimethyldiphenyl (12).

Under similar conditions in the ozonizer the composition of the gas from toluene was determined; this was hydrogen, 58 per cent; acetylene and homologs, 10 per cent; ethylene, 8 per cent; higher olefins, 3 per cent; ethane, 4 per cent; and methane, 14 per cent. Under identical conditions the rate of gas evolution was twice that observed with benzene. Besides the gas, a liquid boiling at 110–145°C. at 18 mm. and a brown resinous powder were formed. The liquid was separated into dibenzyl plus a residual liquid, boiling at 130–136°C. at 17 mm. and having the composition of a polymer of toluene (222).

Toluene can be depolymerized to acetylenes and also polymerized. The polymerized product may be dehydrogenated in the discharge to give dimethyldiphenyls. In these respects toluene resembles benzene in its reactions. In addition to the reaction products analogous to those from benzene, dibenzyl has been found. By making a simple assumption, it is possible to write an equation explaining the formation of dibenzyl by means of reactions entirely analogous to those already presented. The assumption is that toluene is capable of the *allylic rearrangement* under the influence of the discharge. Structurally this change is represented as follows:



The addition of an activated toluene molecule to the methylene double bond, followed by dehydrogenation, gives dibenzyl.



The allylic rearrangement is thought to be ionic in nature, so that there seems to be no objection to its occurrence in an electric discharge. More evidence is needed before the assumption can have validity. For the time being, the mechanism can be justified only by known analogies and because it explains the product.

### *4. Higher aromatic hydrocarbons*

A whole series of substituted benzenes have been studied in a glow discharge at reduced pressure. The rate of gas evolution and the composition of the gas were determined (170). A summary of these results is given in table 7. The original workers made the following observations in regard to the results: (*1*) For any given series the amount of gas produced increases with increasing molecular size. (*2*) Increasing centralization of the molecule results in decreasing amounts of gas produced. Example: the butyl-substituted benzenes. (*3*) Increasing proximity of substituted groups in the benzene ring decreases the amount of gas produced. Example: the *o*-, *m*-, and *p*-xylenes.

Although the picture is somewhat complicated by secondary reactions, the principal primary ones seem to be as follows: (*1*) Polymerization of the hydrocarbon followed by dehydrogenation. The products are dehydropolymers (resins) and hydrogen. (*2*) Depolymerization to give acetylenes. (*3*) Dealkylations to give olefins and a simpler aromatic hydrocarbon. (*4*) Hydrogenation of a portion of the acetylenes to produce olefins, and hydrogenation of a portion of the olefins to give paraffins.

TABLE 7

*Benzene and benzene derivatives in the glow discharge*

| AROMATIC HYDROCARBONS | ANALYSIS OF GAS IN VOLUME PER CENT | | | | d$p$/d$t$ | $W$ |
|---|---|---|---|---|---|---|
| | Hydrogen | Acetylenes | Olefins | Paraffins | | |
| | *per cent* | *per cent* | *per cent* | *per cent* | | |
| Benzene | 46.0 | 40.5 | 4.4 | 9.2 | 25 | |
| Toluene | 54.8 | 29.0 | 3.0 | 13.7 | 52 | 4.39 |
| *o*-Xylene | 60.2 | 16.0 | 7.8 | 16.0 | 35 | 1.69 |
| *m*-Xylene | 52.5 | 25.1 | 6.8 | 15.8 | 47 | |
| *p*-Xylene | 73.0 | 11.6 | 6.3 | 9.1 | 63 | 1.37 |
| Mesitylene | 55.1 | 18.9 | 7.4 | 18.7 | 71 | 2.43 |
| Hexamethylbenzene | 54.7 | 11.4 | 13.1 | 20.9 | 79 | 2.76 |
| Ethylbenzene | 50.7 | 19.6 | 12.4 | 17.3 | 64 | 2.82 |
| *m*-Diethylbenzene | 49.8 | 14.1 | 16.9 | 19.2 | 71 | 2.94 |
| *p*-Diethylbenzene | 36.0 | 11.4 | 25.7 | 27.0 | 69 | 1.77 |
| Hexaethylbenzene | 37.8 | 20.6 | 17.8 | 23.8 | 83 | 1.29 |
| *n*-Propylbenzene | 43.0 | 12.8 | 27.0 | 17.2 | 71 | 2.90 |
| Isopropylbenzene | 51.8 | 14.4 | 12.1 | 21.6 | 58 | 1.53 |
| *p*-Cymene | 46.2 | 12.0 | 16.6 | 25.2 | 66 | 2.09 |
| *n*-Butylbenzene | 56.4 | 9.6 | 18.0 | 16.1 | 81 | 2.91 |
| *sec*-Butylbenzene | 50.6 | 16.8 | 16.6 | 16.2 | 80 | 2.13 |
| *tert*-Butylbenzene | 45.5 | 18.8 | 11.9 | 23.8 | 66 | 2.73 |
| Styrene | 45.7 | 18.8 | 30.7 | 4.7 | 45 | 4.32 |

d$p$/d$t$ = rate of gas formation, in cubic centimeters per milliampere per second $\times 10^4$.
$W$ = rate of solid formation, in grams per milliampere per second $\times 10^6$.

Besides the above work, a few of the aromatic hydrocarbons have been studied under different conditions.

*Xylenes.* In the ozonizer discharge the xylenes give "dixylenes" as thick yellow liquids, together with more complex products. The "dixylene" from *o*- and *p*-xylene boils at 160–170°C. at 14 mm., while that from *m*-xylene boils at 160–165°C. at 14 mm. (179).

Similarly treated, *p*-xylene gave a shellac-like product which, when analyzed, was found to contain oxygen; it had a density of 0.97. In addition, di-*p*-tolylethane (m.p. 81°C.) was isolated, along with a high-boiling liquid thought to be made up of isomers of di-*p*-tolylethane (12). The formation of ditolylethanes from xylenes is analogous to the formation of dibenzyl from toluene.

The light from the electrodeless discharge in xylene was investigated spectrometrically. Evidence was obtained for the presence of CH, $C_2$, $C^+$, and H in the discharge (107).

*Mesitylene.* The products from the ozonizer treatment at reduced pressure are a thick yellowish liquid, boiling at 195–200°C. at 14 mm., and said to be "dimesitylene", and a resin which analyzed correctly for $(C_9H_{12})_{12}$ as the average composition (179).

A spectrometric investigation of the light from mesitylene in the electrodeless discharge indicates the presence of CH, $C_2$, $C^+$, and H in the discharge (107).

*Cumene.* In a discharge of the ozonizer type, cumene gave dicumyl as a thick yellowish liquid, b.p. 162–165°C. at 14 mm., and a resin, m.p. 95°C., said to be "hexacumyl" (179).

*p-Cymene.* Under the same conditions *p*-cymene gave "dicymene" as a thick yellow oil, boiling at 185–190°C. at 14 mm., and a resin said to be "pentacymene", m.p. 80°C. (179).

*Styrene.* The application of an alternating current field to polymerizing styrene has no effect on the rate of polymerization until a critical potential gradient is reached. At 80°C. this is 43.5 kilovolts per millimeter. The polymerization rate is increased suddenly at this potential gradient, but the rate decreases if the gradient is increased further. A short preliminary treatment of the styrene at the critical gradient increases the thermal rate of polymerization and reapplying the field decreases the rate (157).

*Naphthalene.* Under the conditions used for cumene, naphthalene gave a brown, glistening, insoluble, infusible polymerization product (179).

In the electrodeless discharge naphthalene gave the same spectra observed with benzene. The lines were not equally intense when the same time of exposure of the photographic plate was used (105, 106, 107). This may have been due to a lower concentration of naphthalene in the discharge with the same conversion to light-emitting fragments or may have been due to a greater stability of naphthalene.

Polynuclear hydrocarbons have been studied at low pressures in the glow discharge. Under these conditions dehydrogenation and depolymerization to acetylenes takes place. The olefins formed probably result from the hydrogenation of acetylenes. Polymerization or condensation to give solid products also occurs. A summary of the results is given in table 8 (170).

It will be recalled that in the thermal cracking of petroleum oils there can be produced a cracked gas oil of high density which is very refractory to further cracking. This product is said to be aromatic in character. It seems quite likely that refractory gas oil in a suitable electric discharge could be made to give commercial yields of acetylene. This is merely a conjecture based on the experimental data given above on the aromatic hydrocarbons. Nevertheless, the possibility is one of interest to the petroleum industry.

TABLE 8

*Polynuclear aromatic hydrocarbons in the glow discharge*

| HYDROCARBONS | ANALYSIS OF GAS IN VOLUME PER CENT | | | | dp/dt | W |
|---|---|---|---|---|---|---|
| | Hydrogen | Acetylenes | Olefins | Paraffins | | |
| | *per cent* | *per cent* | *per cent* | *per cent* | | |
| Diphenyl | 43.2 | 37.4 | 17.3 | 2.1 | 43 | 5.65 |
| Naphthalene | 42.8 | 32.2 | 23.3 | 1.7 | 39 | 7.51 |
| Stilbene | 46.8 | 44.8 | 6.8 | 1.6 | 57 | 7.24 |
| Anthracene | 44.9 | 36.2 | 18.2 | 0.7 | 35 | 9.70 |
| Phenanthrene | 45.8 | 21.9 | 28.0 | 4.3 | 37 | 8.82 |
| Acenaphthene | 60.8 | 25.4 | 13.3 | 1.4 | 50 | 6.39 |
| Triphenylmethane | 50.1 | 27.3 | 21.8 | 0.8 | 42 | 6.91 |
| Retene | 39.8 | 21.1 | 15.0 | 24.1 | 56 | 5.08 |

$dp/dt$ = rate of gas formation, in cubic centimeters per milliampere per second × $10^4$.
$W$ = rate of solid formation, in grams per milliampere per second × $10^6$.

### D. CYCLOPARAFFINS AND CYCLOÖLEFINS

These types of hydrocarbons have not been studied under sufficiently mild conditions to indicate simple products which could be regarded as primary products. The more drastic conditions give products which are not characteristic of the original hydrocarbon.

### 1. *Cyclopropane*

This hydrocarbon reacts one-half as fast in the ozonizer discharge as propene under comparable conditions (208). The main reaction is condensation to give a liquid product of the empirical formula $C_{15}H_{26}$. This product was thought to be identical or isomeric with the product obtained from propene. For each 100 volumes of cyclopropane charged, 37.3 volumes of hydrogen and 1.5 volumes of methane were formed (30).

### *2. Cyclohexane*

Cyclohexane has been studied in the glow discharge (170) and the gaseous products partially analyzed (table 9). Some work has also been done in the electrodeless discharge (11, 12), but no definite product has been reported. The solid, brown, resin-like deposit usually formed in the electrodeless discharge in hydrocarbons was almost absent when cyclohexane was used.

TABLE 9

*Cycloparaffins and cycloölefins in the glow discharge*

| CYCLOPARAFFINS AND CYCLOÖLEFINS | GAS ANALYSIS, VOLUME PER CENT | | | | dp/dt | W |
|---|---|---|---|---|---|---|
| | Hydrogen | Acetylenes | Olefins | Paraffins | | |
| | *per cent* | *per cent* | *per cent* | *per cent* | | |
| Cyclohexane | 46.0 | 13.2 | 32.1 | 8.7 | 86 | 0.51 |
| Methylcyclohexane | 47.0 | 12.6 | 26.6 | 13.8 | 93 | 0.19 |
| *p*-Menthane | 52.5 | 1.4 | 28.1 | 18.0 | 71 | 0.90 |
| Decalin | 52.5 | 12.8 | 30.0 | 4.7 | 103 | 1.52 |
| Cyclohexene | 48.7 | 16.5 | 30.0 | 4.8 | 105 | 1.06 |
| Isobutylcyclohexene | 40.8 | 12.6 | 31.1 | 15.5 | 105 | 1.36 |
| Dipentene | 48.4 | 11.5 | 27.0 | 13.1 | 114 | 1.66 |
| Pinene | 53.7 | 16.2 | 18.2 | 12.0 | 101 | 1.88 |
| Limonene | 58.4 | 14.9 | 18.0 | 8.7 | 112 | 1.62 |
| Dihydronaphthalene | 54.8 | 23.4 | 19.7 | 2.1 | 72 | 5.40 |
| Tetralin | 57.0 | 17.0 | 20.0 | 6.0 | 71 | |

$dp/dt$ = rate of gas formation, in cubic centimeters per milliampere per second × $10^4$.

$W$ = rate of solid formation, in grams per milliampere per second × $10^6$.

### *3. Pinene*

The ozonizer discharge produces a small amount of diterpene (polymer) but no gas. The polymerization, although slow, was especially clean cut in a carrier gas (hydrogen or nitrogen) (30). Another worker (179) obtained a dimer and a heptamer by treating pinene in the ozonizer.

### *4. Camphene*

In the ozonizer, camphene gave a dimer and an octamer (179).

### *5. Limonene*

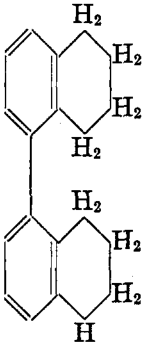
Limonene and the ozonizer gave a liquid dimer, a solid hexamer, and an insoluble solid (179).

### *6. Menthene*

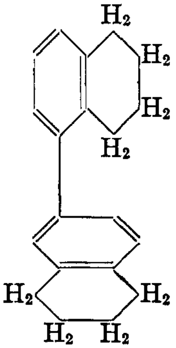
A liquid dimer and a soft brown polymer were obtained by treating menthene in the ozonizer (179).

### *7. Tetralin*

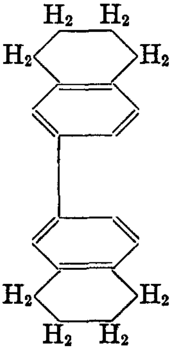
In the presence of air as an auxiliary gas, liquid tetralin gave hydrogen cyanide and probably other nitrogen-containing products when treated in the ozonizer discharge. When hydrogen was used, a part of the tetralin was converted into a thick, almost resinous product. This product was interesting because it possessed air drying properties similar to linseed and tung oils. Owing to the fact that the glass walls of the apparatus became pitted and soon suffered electrical breakdown, the apparatus was changed to the corona type with the inner conductors made of copper. Under these conditions the yield of resinous product was 22.1 g. per kilowatt-hour. Apparatus of this type was also used with tetralin vapor at 5 to 8 mm. pressure. The discharge consumed about 75 watts at 500 cycles. The apparatus was then further changed to the glow type with the electrodes made of copper. With operating conditions of 100 watts, 1 to 2 mm. pressure, 50 cycles, and 2000 volts the resin yield was 75 g. per kilowatt-hour. In a still larger apparatus, using 200 watts at 9550 volts, a small amount of a ditetryl ($C_{20}H_{22}$), m.p. 80–81°C., was isolated (19); just which one of the nine possible ditetryls is not known. If it should be proved to be one of the following compounds:



5,5′-Ditetryl

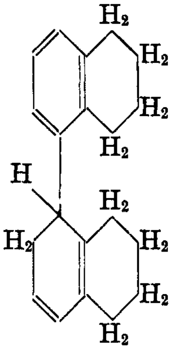


5,6′-Ditetryl



6,6′-Ditetryl

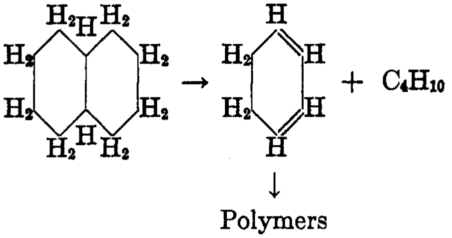
then it is entirely possible that this product is formed in a manner entirely analogous to the formation of diphenyl from benzene in the electric discharge. In this event it seems quite likely that the resinous product having air drying properties would be analogous to the dihydrodiphenyl formed from benzene.



This product would be a dihydroditetryl. Its ability to absorb oxygen from the air and polymerize is entirely consistent with such a structure. Until more work is done on the constitution of these products, these possibilities must remain speculative. Nevertheless, they may be useful in directing the work in trying to identify these products. (2,2′-Ditetryl, m.p. 113°C. (42), and 2,6′-ditetryl, m.p. 53–54°C. (228), are the only ditetryls of known structure.)

### *8. Decalin*

In the ozonizer discharge, decalin gives a gas thought to be butane mixed with hydrogen and unsaturated hydrocarbons. In addition, 25 per cent of material boiling above decalin was formed. A fraction corresponding to 15 per cent of the decalin boiled above 200°C. at less than 1 mm. pressure (19). The reaction was thought to take place according to the scheme:



In another study by a different worker (92) it was found that the primary action of the discharge is the splitting off of hydrogen and the polymerization of the resulting unsaturated compounds. When the reaction is carried out in the presence of oxygen, ozonides are formed; in the presence of nitrogen, nitrogen-containing products are formed.

Several of the cycloparaffins and cycloölefins have been studied in the glow discharge at reduced pressure. The powerful dehydrogenating action of the discharge is indicated by the data summarized in table 9. Cracking reactions also occur, since gaseous olefins, acetylenes, and paraffins are formed. More could be told about the reaction mechanism if the gas analysis were more complete, giving the individual components instead of the hydrocarbon groups (170).

It is well to note the gases produced in the glow discharge with tetralin and decalin (table 9). The gaseous reaction products are not those that would be expected if the reactions in the glow discharge were similar to those in the ozonizer discharge discussed above. Since the analyses are incomplete in both cases, definite conclusions may not be drawn, but it seems that the glow discharge is the more violent in nature, giving more deep-seated changes in the molecule. The present differences serve to emphasize our contention that in any discussion of the electrical reactions it is imperative that the type of discharge used be given as part of the essential data.

There are immense supplies of cycloparaffinic (naphthenic) petroleum oils which might make useful products. The above discussion indicates drying oils for paints as one possibility. Generally speaking, however, the reactions of these hydrocarbons in the electrical discharge need careful study, since the proper data are not available on the reactions of the most common members of this group of hydrocarbons, i.e., the cyclohexane and cyclopentane derivatives. Thus, as far as the chemist is concerned, the field is wide open, from the discovery of the fundamental reactions of these hydrocarbons all the way to the commercial utilization.

### E. PARAFFIN HYDROCARBONS

In many respects the electrical reactions of the paraffin hydrocarbons resemble the corresponding thermal reactions. It will be recalled that, thermally, the paraffins react by dehydrogenation and by cracking and that this primary action is followed by the reactions of the olefins produced by the dehydrogenation or cracking. This same sequence of events seems to take place in the electrical reactions, with this difference: the electrical reactions of the olefins produced in the primary action are different from the thermal reactions. The reactions of the olefins have been purposely discussed before the paraffins in order to give a better understanding of the more complicated overall reactions of the paraffins. In this connection it must be kept in mind that the paraffins are less reactive electrically and therefore require a relatively more intense discharge to make them react at a usable rate. This intense discharge often produces deep-seated changes in the olefins formed in the primary reaction, so that it is difficult to follow the reaction.

In addition to dehydrogenation and cracking, which can be obtained thermally, a type of reaction can occur electrically which does not occur thermally or which is poorly defined. Generally the reaction may be written:

$$2C_nH_{2n+2} \rightarrow C_{n-x}H_{2(n-x)+2} + C_{n+x}H_{2(n+x)+2}$$

So far as the present authors know, no name has been assigned to this reaction. It is a type of disproportionation.

### 1. *Methane*

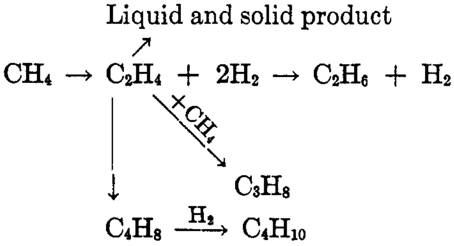
Methane alone can react chemically only by dehydrogenation. In thermal reactions, methane is known to give the reaction

$$2CH_4 \rightarrow C_2H_6 + H_2$$

when caused to react by a heated filament located in a bulb cooled by liquid nitrogen. If the bulb is cooled with liquid oxygen (−183°C.) instead of liquid nitrogen (−195°C.), then acetylene and ethylene form up to 90 per cent of the hydrocarbon reaction product (240). The analogous experiment using the glow discharge with liquid air as the cooling medium indicates that the methane which reacts is quantitatively converted into hydrogen and ethylene (44). In view of the critical effect of the wall temperature in the thermal reaction, it can be argued that ethane and hydrogen might be the initial reaction products in the electrical reactions had the experiment been conducted in liquid nitrogen instead of liquid air. In the absence of data to the contrary, ethylene will be considered the primary reaction product from methane in the electric discharge. On this basis the electrical reaction products of methane would be those of ethylene in the presence of an excess of methane and hydrogen. As near as can be determined from the data available, this is the case. In discussing these data, it must be remembered that methane is one of the very stable hydrocarbons, and any discharge which is powerful enough to change it chemically produces profound changes in the reaction products as soon as these are present in appreciable concentrations.

From a study of methane in the ozonizer discharge at room temperature, the following observations were made (164, 165): (*1*) The volume of gaseous products equals the volume of the original methane. (*2*) An induction period of 20 to 25 min. exists. (*3*) The gaseous product is primarily hydrogen with relatively small amounts of $C_2H_6$, $C_3H_6$, and $C_4H_{10}$. Still smaller amounts of $C_2H_4$ have been found. From 20 to 55 per cent of the reacting methane is converted into the above products; the rest is converted to solid and liquid products. (*4*) A liquid product is formed whose composition agrees closely with $C_nH_{2n}$. The liquid is apparently unsaturated, since it is acted on by light and air. (*5*) The liquid product left in the field of action of the discharge will react with evolution of gas.

The chemistry involved in these processes can be expressed in the following diagram.



In experiments at room temperature (222) in the ozonizer, there may be evidence that ethane is a primary product in the treatment of methane. Certainly ethane is formed in larger amounts than ethylene, although this can be readily explained, since ethylene is known to be much more susceptible to reaction than ethane (166).

Methane also gives liquid and solid products in the semi-corona discharge. Table 10 gives a summary of the conditions used and the results obtained. The apparatus consisted of eleven semi-corona tubes in series for gas flow and in parallel electrically. The central aluminum electrode was $\frac{1}{8}$ in. (0.32 cm.) in diameter and was enclosed in a Pyrex tube 2 cm. in diameter with 1 mm. wall thickness. Traps cooled in ice water were placed between the semi-corona units. The discharge was operated by an 18-kilovolt transformer (161).

Among the earliest products observed from the treatment of methane in the ozonizer discharge were acetylene and hydrogen (27, 25, 30, 222). It seems quite likely that acetylene is a secondary product resulting from the action of the discharge on the ethylene produced from methane.

Owing to the economic importance of acetylene, considerable study has been devoted to the conversion of methane to acetylene. Electrical methods have furnished their share of results in seeking the solution of this problem. The glow discharge has received most attention in this direction. It seems advantageous to heat the discharge tube to about 500°C. The best operating pressure is 40 to 50 mm. and the best electrode distance is 40 to 50 cm.; greater distances cause the formation of higher paraffin hydrocarbons. The voltage does not seem to be critical so long as it is sufficiently high to maintain the discharge. The yields of acetylene are as high as 90 per cent of the methane charged. The energy consumption is 12 to 13 kw.-hr. per cubic meter of acetylene formed (85, 149, 151, 205, 206, 223).

When the above process was altered to produce maximum yields of ethylene instead of acetylene, the energy consumption at the point of maximum yield was 53 kw.-hr. per cubic meter of ethylene (206). The methane was diluted with 0.5 volume of hydrogen. Since the formation of ethylene from methane requires less energy from the thermodynamic point of view than the formation of acetylene, the reason for the larger energy consumption in the case of ethylene formation is not clear. It is possible that a considerable portion of the energy goes to form atomic hydrogen which recombines at the walls of the containing vessel, resulting in a temperature rise of these walls. In this case the energy would be dissipated as heat without doing useful chemical work.

TABLE 10

*Methane in the semi-corona discharge*

| | |
|---|---|
| Flow, liters per hour | 0.57 |
| Time, days | 5.1 |
| Methane used, liters | 64.0 |
| Methane used, grams | 45.7 |
| Liquid yield, grams | 18.25 |
| Molecular weight of liquid | 130–170 |
| Density of liquid | 0.78–0.83 |
| Refractive index of liquid | 1.44–1.46 |
| Solid on glass walls, grams | 4.4 |
| Energy used, kilowatt-hours | 102.7 |
| Carbon on aluminum rods, grams | 0.25 |
| Grams of liquid per kilowatt-hour | 0.178 |
| Grams of liquid and solid per kilowatt-hour | 0.22 |
| Grams of liquid per gram of methane | 0.40 |

The reaction kinetics for methane in the glow discharge have been treated mathematically (262), and the agreement with the published experimental results is said to be good.

A mixture of methane and an excess of nitrogen was studied with a thyratron circuit capable of giving a glow discharge lasting $10^{-5}$ sec. By varying the constants of the circuit, the number of these pulse discharges could be varied up to 133 per second. Acetylene, hydrogen cyanide, and a solid approximating $(CH)_x$ were formed. The following experimental observations were made under these conditions: (*1*) For the same watt input, the acetylene yield was greater with the pulse discharges than was obtained with A.C. or D.C. (*2*) With a D.C. or A.C. discharge, practically all the carbon of the methane could be converted into hydrogen cyanide. Little or no polymers were formed. (*3*) With a pulse discharge rate of 10 per second an appreciable amount of brown, shellac-like, insoluble polymer was formed. (*4*) As the pulse rate was increased from 10 to 60 per second, the HCN:$C_2H_2$ ratio increased linearly with the pulse rate. (*5*) With pulse rates from 60 to 133 (the limit of the apparatus) per second, the HCN:$C_2H_2$ ratio was constant.

In explaining these observations, it was assumed that CH was the major active particle formed in this discharge. This CH particle may polymerize to $C_2H_2$ or $(CH)_x$, or may react with nitrogen to form hydrogen cyanide by further reaction in the discharge. Since 60 pulses per second were sufficient to utilize all the CH particles, it was suggested that the life period of the particle was of the order of $\frac{1}{60}$ second (270). While this observation on the apparent life of the CH particle is interesting, it is preferred to wait for a more specific description of the experimental details before definite conclusions are drawn. More definite evidence was offered for the methyl radical, for dimethylzinc was formed when the gas was withdrawn through a hollow zinc cathode.

Indirectly, the effect of frequency has been studied in the more conventional glow discharge, using a variable electrical condenser. In the pressure range 1 to 11 mm. of mercury, the amount of methane reacted was a maximum at the maximum condenser capacity, (i.e., at the lowest frequency). At 3.2 mm., 75 per cent of the reacting methane was converted into acetylene, utilizing about 15 per cent of the available electrical energy (192).

Similar experiments at atmospheric pressure using frequencies of 6 and 15 megacycles gave results which indicated that the lower frequency gave a greater per cent conversion, while the higher frequency produced more deep-seated changes in the methane that reacted (204).

Besides the effect of the type of electrical discharge, it has been found that the electrode material may have influence. For example, in the glow discharge under a given set of conditions, it has been found that aluminum, copper, zinc, lead, and iron electrodes gave 1.5 per cent conversion of methane. Mercury electrodes gave 5.2 per cent conversion. Warming the mercury electrodes increased the conversion to 14 per cent. It was concluded that the mercury acted catalytically, probably in the vapor phase (147).

In the spectroscopic investigation of the light produced by the glow discharge in methane, evidence was obtained for H, CH, and $H_2$. In the electrodeless discharge, evidence was obtained for C and $C_2$, as well as H and CH. Brown to black resins were produced on the walls of the discharge vessel in both types of discharge (104, 105, 106, 107).

### 2. *Methane with other hydrocarbons*

*Acetylene.* The silent discharge gave a clear yellow liquid product which could be separated into a viscous liquid soluble in ether and an insoluble solid. The liquid had an average composition corresponding to $C_6H_{10}$, while the solid corresponded to $C_6H_8$ (174). Propene has also been reported (108, 109).

*Ethylene.* Under the same conditions, a 1:1 mixture of methane and ethylene gave a viscous liquid which absorbed oxygen from the air (174).

*Benzene.* A product was obtained which had the average composition $C_{28}H_{36}$ (176).

### 3. *Ethane*

Ethane can undergo both dehydrogenation due to activation of the C—H bond and demethanation due to activation of the C—C bond. The ratio of these two reactions has not been accurately determined. At the beginning of the reaction, in the ozonizer discharge, there is about five times as much dehydrogenation as demethanation, as determined from the gaseous products (222). After the discharge has acted on a given sample of gas for longer times, the amount of methane increases in the gas (159, 222). It seems entirely possible that the primary reaction of ethane would be dehydrogenation if experiments were made under conditions which would minimize secondary reactions. At the present time there is no reported work under such conditions.

In the intense discharge necessary to cause ethane to react at a convenient velocity, the ethylene and acetylene formed are very reactive and polymerize, although they can be readily detected in the gaseous products (25, 30). That they are not always present is indicated by the following gas analysis (159):

| SUBSTANCE | VOLUME PER CENT |
|---|---|
| $H_2$ | 48.4 |
| $CH_4$ | 13.0 |
| $C_2H_6$ | 29.7 |
| $C_3H_8$ | 3.5 |
| $C_4H_{10}$ | 1.9 |
| $C_5H_{12}$ | 3.5 |

More complete (166) analyses giving the major constituents have been converted to moles of product per 100 moles of ethane reacted and are presented in table 11.

The following equations, based on the data in table 11, account for about 85 per cent of the ethane reacted:

| *Reaction* | *Per cent* |
|---|---|
| $C_2H_6 \rightarrow C_2H_4 + H_2$<br>$x(C_2H_4) \rightarrow (C_2H_4)_x$ | 61<br>(50) |
| $C_2H_6 + C_2H_4 \rightarrow C_4H_{10}$ | 5 |
| $2C_2H_6 \rightarrow CH_4 + C_3H_8$ | 15 |
| $C_2H_6 \rightarrow C_2H_2 + 2H_2$ | 3 |

It is to be noted that 50 per cent of the ethane which reacts is converted into liquid products, presumably through the polymerization and condensation of ethylene.

During the study of ethane in an ozonizer discharge, an observation was made which has considerable bearing on the reaction mechanism. The reaction products from the discharge tube were passed into two traps at −50°C. These traps were connected in series, were as close together as possible, and were in the same Dewar vessel. These traps will be designated 1 and 2 in the order of flow. The exit of trap 2 was connected to two similar traps (3 and 4) by a glass tube 15 cm. long. Traps 3 and 4 were also maintained at −50°C. At the end of the run the amount of liquid in the various traps should decrease in the order 1 > 2 > 3 > 4. Instead, the order was 1 > 3 > 2 > 4. Apparently, additional formation of liquid occurs in the relatively long tube connecting traps 2 and 3. This would indicate that some active particle is present which is capable of forming liquid products. At the same time, the particle seems to be fairly stable and has a life of the order of a minute or so, since it has passed through the spirals of both traps 1 and 2 without being deactivated (159).

TABLE 11

*Products from ethane in an ozonizer discharge*

| Time of run, minutes | 20 | 20 | 60 | 60 | 60 |
|---|---|---|---|---|---|
| Products, moles per 100 moles of ethane reacted: | | | | | |
| $H_2$ | 57.4 | 44.4 | 61.1 | 56.8 | 59.6 |
| $CH_4$ | 16.5 | 14.1 | 12.6 | 14.1 | 15.0 |
| $C_2H_2$ | 4.9 | 1.0 | 3.2 | 4.0 | 3.2 |
| $C_2H_4$ | 4.9 | 5.5 | 6.9 | 5.6 | 6.1 |
| $C_3H_8$ | 16.8 | 18.0 | 14.5 | 15.7 | 13.2 |
| $C_4H_{10}$ | 4.7 | 5.1 | 7.0 | 2.2 | 5.2 |
| $C_5^+$ | 1.5 | 3.1 | Trace | 1.0 | 1.4 |
| Expansion | 1.02 | 1.02 | 1.02 | 1.06 | 1.03 |
| Per cent $C_2H_6$ reacted | 15.1 | 18.1 | 36.2 | 46.7 | 43.5 |
| Per cent $C_2H_6$ to liquid | 6.2 | 7.2 | 16.3 | 23.2 | 20.4 |

Since these active particles are intimately connected with the formation of liquid, it seems quite likely that a careful study of their nature and, if possible, their reactions, would be most fruitful in determining the mechanism of the electrical reactions of hydrocarbons. Certainly an understanding of the fundamentals of these particles would help in the development of these electrical reactions (163).

As has been indicated, the ozonizer discharge causes the formation of liquid products from ethane. A yield of 5.12 cc. of liquid has been obtained from 11.66 g. of ethane. In these experiments, 2 kw.-hr. are required for each gram of liquid. The properties of the liquid are as follows (159):

| | |
|---|---|
| Color | Reddish yellow |
| Density | 0.862 |
| $n_{\mathrm{Sun}}^{20^\circ}$ | 1.4900 |
| Molecular weight (cryoscopic in benzene) | 467 |
| Bromine | Unsaturated |
| Per cent C | 85.48 |
| Per cent H | 13.09 |
| Empirical formula | $C_nH_{1.8n}$ |

In attempting to control the molecular weight of the liquid product, it was found that raising the temperature of the ozonizer from 35° to 70°C. lowered the average molecular weight of the liquid from 467 to 105. This was thought to be due to a lowering of the viscosity of the liquid, permitting it to drain from the discharge more rapidly and thus reducing the amount of secondary action of the discharge on the liquid.

Ethane was studied in the ozonizer, in the semi-corona with both low- and high-frequency excitation, and in the corona discharge with the object of determining the effect of the type of discharge and the discharge conditions on the reaction products from ethane (160). The results of this study are summarized in table 12.

From these data it was concluded that the type of discharge had little effect on the properties of the liquid. When a liquid of low molecular weight is desired, the apparatus should be designed so that the liquid originally formed is removed from the discharge as soon after its formation as possible. When a liquid of high molecular weight is desired, the primary liquid should be left in the discharge to undergo secondary reaction.

To obtain sufficient liquid product to examine in more detail, eleven semi-corona tubes were connected in parallel electrically and in series for gas flow. Traps kept at 0°C. were placed at the exit of each semi-corona tube. The properties of these liquids from the traps were as follows: molecular weight, 170 to 210; density, 0.81 to 0.87; $n_{\mathrm{Sun}}^{20^\circ}$, 1.46 to 1.48. Ethane was converted to 48 per cent of liquid and solid. The energy yields were 0.62 g. of liquid or 0.625 g. of liquid plus solid per kilowatt hour (161). (In this experiment, the semi-corona center electrode was an aluminum rod 0.3 cm. in diameter. The voltage was 18,000 volts of 60 cycles.)

When ethane was passed through a glow discharge and the reaction products passed over a silver mirror, the mirror remained unchanged. Hydrogen and a resin were isolated as reaction products (14).

TABLE 12

*Condensates of low molecular weight from ethane*

| TYPE OF DISCHARGE | VOLTS | MILLIAMPERES | TEMPERATURE OF ELECTRODES | TEMPERATURE OF TRAPS | MOLECULAR WEIGHT OF LIQUID | $n^{20^\circ}_{\text{Sun}}$ | COLOR | LIQUID |
|---|---|---|---|---|---|---|---|---|
| | | | *°C.* | *°C.* | | | | *cc. per hour* |
| Ozonizer.......... | 11600 | 1 | 25 | 25 | 467 | 1.4900 | Red-brown | 0.028 |
| Ozonizer.......... | 11600 | 1 | 70 | 25 | 188 | 1.4642 | Slightly yellow | 0.011 |
| Ozonizer.......... | 11600 | 1 | 70 | −50 | 184 | 1.4509 | Slightly yellow | 0.006 |
| Semi-corona(a)..... | 11600 | 1 | 70 | −50 | 156 | 1.4467 | Slightly yellow | 0.063 |
| Semi-corona(b)..... | 11600 | 1 | 18 | −50 | 106 | 1.4503 | Slightly yellow | 0.100 |
| Semi-corona(b)..... | 11600 | 1 | 70 | −50 | 105 | 1.4294 | Yellow | 0.100 |
| High-frequency semi-corona(b)... | 3000 | 135 | 70 | −50 | 95(d) | | Red-yellow | 0.060 |
| High-frequency semi-corona(b)... | 10000 | 700 | 35 | −50 | 109 | 1.4204 | Light yellow | 0.100 |
| Corona(c)......... | 8000 | 1 | | −58 | 81 and 182(e) | | Red-yellow | 0.050 |

---

(a) Platinum corona wire.

(b) Aluminum corona rod.

(c) Aluminum tube and platinum wire corona.

(d) The lighter of two fractions; the heavier fraction was too insoluble in benzene.

(e) Two fractions separated by vacuum distillation.

### *4. Propane*

By using the same eleven-tube semi-corona discharge apparatus described above, results were obtained which are summarized in table 13 (161).

In the ozonizer, propane was decomposed to the extent of 93 per cent to give 74 per cent of a liquid product whose average composition agreed with $C_nH_{2n}$ (163). Later this study was extended to include careful analysis of the gaseous reaction products (166). These analyses have been converted to moles of product per 100 moles of propane reacted. The results are given in table 14.

TABLE 13

*Action of the semi-corona discharge on propane*

| | RUN 1 | RUN 2 |
|---|---|---|
| Rate of flow, liters per hour | 1.45 | 0.514 |
| Time, days | 9 | 10 |
| Propane charged, grams | 550 | 218 |
| Composition of gas produced, per cent: | | |
| $H_2 + CH_4$ | 20.06 | 45.00 |
| $C_2H_6$ | 7.05 | 9.78 |
| $C_3H_8$ | 64.50 | 41.60 |
| $C_4H_{10}$ + higher | 2.39 | 4.53 |
| Liquid, grams | 37.09 | 63.42 |
| Molecular weight of liquid | 115–183 | 120–160 |
| Density of liquid | 0.7424–0.8392 | 0.70–0.82 |
| $n_{\text{Sun}}^{20°}$ | 1.4300–1.4673 | 1.4352–1.4563 |
| Solid, grams | | 63.64 |
| Carbon on aluminum rod | | 1.00 |
| (Grams of liquid per gram of gas charged) × 100 | 6.7 | 29.0 |
| (Grams of liquid and solid per gram of gas charged) × 100 | | 58.5 |
| Grams of liquid per kilowatt-hour | 0.455 | 0.480 |
| Grams of liquid and solid per kilowatt-hour | | 0.985 |

TABLE 14

*Products from propane in the ozonizer discharge*

| | | | | |
|---|---|---|---|---|
| Time, minutes | 24.5 | 24.5 | 73.5 | 73.5 |
| Products, moles per 100 moles of propane reacted: | | | | |
| $H_2$ | 48.2 | 44.0 | 53.0 | 55.8 |
| $CH_4$ | 18.4 | 22.3 | 28.6 | 27.7 |
| $C_2H_2$ | | | 5.5 | 4.5 |
| $C_2H_4$ | Trace | | 6.3 | 6.8 |
| $C_2H_6$ | 10.8 | 3.4 | 5.9 | 7.6 |
| $C_3H_6$ | 39.8 | 48.0 | 15.9 | 17.5 |
| $C_4H_{10}$ | 12.3 | 10.0 | 7.0 | 5.7 |
| $C_5H_{12}$ | 4.8 | 3.4 | 0.8 | Trace |
| Expansion | 1.05 | 1.05 | 1.10 | 1.11 |
| Per cent $C_3H_8$ reacted | 12.3 | 13.3 | 36.0 | 40.4 |
| Per cent $C_3H_8$ to liquid | 2.7 | 3.1 | 18.1 | 20.6 |

The following reaction scheme is proposed to account for these products. As proposed, these reactions can account for about 85 per cent of the reacted propane. The reactions which are proposed as the primary reactions are separated from those thought to be secondary reactions. It will be noted that the ratio of the reactions to one another changes as the reaction time is increased from 24.5 min. to 73.5 min.

| REACTIONS | PER CENT OF REACTION IN REACTION TIME OF | |
|---|---|---|
| | 24.5 min. | 73.5 min. |
| Primary reactions: | | |
| $C_3H_8 \rightarrow C_3H_6 + H_2$ | 46 | 49 |
| $C_3H_8 \rightarrow C_2H_4 + CH_4$ | 16 | 27 |
| $2C_3H_8 \rightarrow C_4H_{10} + C_2H_6$ | 11 | 7 |
| $2C_3H_8 \rightarrow C_5H_{12} + CH_4$ | 4 | 1 |
| Secondary reactions: | | |
| $nC_3H_6 \rightarrow (C_3H_6)_n$ | 2 | 32 |
| $mC_2H_4 \rightarrow (C_2H_4)_m$ | 16 | 16 |
| $C_2H_4 \rightarrow C_2H_2 + H_2$ | 0 | 5 |

The most important primary reaction is the dehydrogenation of propane to propene, which may be isolated as such or, if the action of the discharge continues, secondary reactions involving propene occur. These are indicated as polymerization in the table.

The second reaction of importance is the demethanation of propane, forming methane and ethylene, with the ethylene undergoing secondary reactions, indicated as polymerization. It should be noted that this interpretation of these data indicates that ethylene, under these conditions, is more susceptible to reaction than propene.

The above two reactions, dehydrogenation and demethanation, are also the main thermal reactions of propane. The ratio of the two reactions is quite different; in thermal reactions the ratio of dehydrogenation to demethanation is 0.8 (227), while in the ozonizer experiment above it is about 2.

The reactions proposed to account for butane and pentane are of considerable theoretical interest, although they are of minor importance in accounting for the amount of propane reacted. It seems quite possible that activated propane molecules collide and form an association product that is stable for appreciable periods of time, i.e., long enough for a rearrangement of the valence forces within the molecule.

$$C_3H_8 + C_3H_8^* \leftrightarrows [C_6H_{16}]^*$$

It should be noted in passing that increased pressure should favor this type of reaction to the detriment of the dehydrogenation and demethanation.

If the valence forces within this activated complex do not rearrange, it reverts to propane; if they do rearrange, then it breaks down into butane and ethane or pentane plus methane. It is quite possible that the rearrangement of the valence forces could extend so far that appreciable amounts of isobutane and isopentane are formed. Further, it is quite possible that the complex could decompose to give hexanes and hydrogen, although it is not possible to decide from the data available.

This type of reaction has been proposed to account for the reactions of hydrocarbons caused by alpha-particles and has been extended to include the electrical reactions (162, 163). The theory has been called the "ion cluster" theory and in the case of propane would apply as follows:

$$\begin{aligned} C_3H_8 &\rightarrow C_3H_8^+ + e && \text{(ionizing)} \\ C_3H_8^+ + C_3H_8 &\rightarrow [C_3H_8 \cdot C_3H_8]^+ && \text{(clustering)} \\ [C_3H_8 \cdot C_3H_8]^+ + e &\rightarrow C_6H_{14} + H_2 && \text{(de-ionization or neutralization)} \end{aligned}$$

This theory is a very useful one. It seems to the present authors that it is possible of even broader application than to ions. As we have indicated in the discussion above, the clustering or at least association between molecules with either or both activated, is a useful concept. In the ion cluster theory, the charge on the ion gives a physical reason for expecting association, while in the activated molecule no such obvious reason is apparent. We see no immediately apparent reason why two saturated molecules with a certain combined energy of activation should not be able to form an unstable molecule within which valence changes could occur before dissociation without ionization occurring at any time. The dissociation of the rearranged product gives two new paraffin molecules.

### 5. *Butanes*

Using the eleven-tube semi-corona discharge apparatus described, the results summarized in table 15 were obtained (161).

The same butane mixture has also been studied in an ozonizer system consisting of twelve discharge vessels connected in parallel as to gas flow and electrically. The applied voltage was 20,000 volts of 60 cycles. The run lasted 659 hr., during which time 5420 g. of butane was charged and 1041 cc. (833 g.) of liquid was produced. The liquid product boiled from 0°C. at 740 mm. to 230°C. at $10^{-4}$ mm. Careful fractionating of the liquid gave only one fraction (8.0 g.), which had the properties of an octane containing 22 per cent of octene (162). This (833 g.) is the largest amount of liquid so far reported as produced from a hydrocarbon gas by electrical means.

Later (166) the gases formed in the treatment of a mixture containing 75 per cent of *n*-butane and 25 per cent of isobutane in an ozonizer were analyzed. The time of treatment was 24.5 min. We have calculated the analyses to moles of product per 100 moles of butanes reacted (table 16).

TABLE 15

*Semi-corona discharge in butane**

| | |
|---|---|
| Gas flow, liters per hour | 0.60 |
| Time, days | 5.7 |
| Gas used, grams | 192 |
| Volts | 18,000 |
| Liquid yield, grams | 71.1 |
| Molecular weight of liquid | 110–140 |
| Density of liquid | 0.74–0.78 |
| $n^{20°}_{\text{Sun}}$ | 1.43-1.45 |
| Solid on glass wall, grams | 70.0 |
| Carbon, grams | 1.0 |
| Yield, (grams of liquid per gram of gas) × 100 | 37 |
| Yield, (grams of liquid and solid per gram of gas) × 100 | 73.5 |
| Grams of liquid per kilowatt-hour | 1.09 |
| Grams of liquid and solid per kilowatt-hour | 2.23 |

* The butane used in this experiment was 75 per cent *n*-butane and 25 per cent isobutane (private communication).

TABLE 16

*Products from mixed butanes in the ozonizer*

| | |
|---|---|
| Products, moles per 100 moles of butanes reacted: | |
| $H_2$ | 16.6 |
| $CH_4$ | 11.2 |
| $C_2H_4$ | 1.2 |
| $C_2H_6$ | 5.3 |
| $C_3H_6$ | 19.3 |
| $C_3H_8$ | 51.5 |
| $C_4H_8$ | 5.3 |
| $C_5H_{12}$ | 1.5 |
| Expansion | 1.05 |
| Per cent $C_4H_{10}$ reacted | 34.3 |
| Per cent $C_4H_{10}$ to liquid | 11.3 |

We have not been able to set up equations which will explain these results. The original workers prefer to regard the data as preliminary, since they were unable to separate closely the propane and isobutane by their method of fractionation. They do make the interesting observation that isobutane seems to be formed in the reaction.

From a knowledge of the thermal reactions of butane and by analogy with the propane reactions we think that the following equations will express the primary reactions of the butanes. No attempt is made to estimate the relative importance of the various reactions.

$$C_4H_{10} \rightarrow C_4H_8 + H_2$$
$$C_4H_{10} \rightarrow C_3H_6 + CH_4$$
$$C_4H_{10} \rightarrow C_2H_4 + C_2H_6$$

$$2C_4H_{10} \rightarrow C_5H_{12} + C_3H_8$$
$$2C_4H_{10} \rightarrow C_6H_{14} + C_2H_6$$
$$2C_4H_{10} \rightarrow C_7H_{16} + CH_4$$
$$2C_4H_{10} \rightarrow C_8H_{18} + H_2$$

It is quite possible that the isomerization reaction can be explained adequately by the equation:

$$n\text{-}C_4H_{10} + n\text{-}C_4H_{10}^* \rightarrow (C_8H_{20})^* \rightarrow i\text{-}C_4H_{10} + n\text{-}C_4H_{10}$$

using the intermediate activated complex device employed with propane. In the case of propane, the complex could decompose back to propane and not be noticed, but in the case of butane, it is quite possible for a rearrangement to occur and the product decompose into isomerized butane, either or both contributing molecules being isomerized.

Normal butane in the glow discharge gives fragments (radicals) that remove lead and antimony mirrors. The reaction products were not identified (213).

### 6. *Isobutane*

It has been stated (166) that isobutane in the ozonizer "did not show appreciable differences compared with its isomer". Presumably this statement applies only to the rate of the reaction, for no analysis of the reaction products is given.

Experience with the thermal reactions of isobutane leads one to expect it to give different ratios of the dehydrogenation and demethanation reactions compared to *n*-butane, even though the overall reaction rates are of the same order of magnitude.

### 7. *n-Pentane*

At "reduced pressure" in an ozonizer, *n*-pentane gives a decane, a decene, and a yellowish brown compound having the empirical formula $C_{46}H_{78}$ (179). An analysis of the gas produced is not available.

In the glow discharge (213) fragments (radicals) are produced that removed lead and antimony mirrors. The other products of the reaction have not been reported. The spectrograms made from the light emitted by the electrodeless discharge in *n*-pentane give lines which are due to to hydrogen atoms and CH radicals (11). A solid brown deposit formed in the discharge tube.

Table 17 gives an analysis of the gas formed from *n*-pentane in the glow discharge.

TABLE 17

*Paraffinic hydrocarbons in the glow discharge*

| HYDROCARBONS | ANALYSIS OF GAS IN VOLUME PER CENT | | | | $dp/dt$ | $W$ |
|---|---|---|---|---|---|---|
| | $H_2$ | Acetylenes | Olefins | Paraffins | | |
| | *per cent* | *per cent* | *per cent* | *per cent* | | |
| *n*-Pentane | 60.2 | 10.0 | 17.7 | 12.1 | 60 | 1.21 |
| *n*-Heptane | 46.0 | 9.7 | 26.9 | 17.5 | 101 | 0.35 |
| *n*-Octane | 48.9 | 13.8 | 16.6 | 20.8 | 105 | |
| 2,2,4-Trimethylpentane | 53.2 | 3.5 | 27.1 | 16.2 | 97 | 1.32 |
| 2,7-Dimethyloctane | 56.6 | 15.1 | 15.5 | 12.9 | 118 | 0.62 |
| *n*-Docosane | 55.7 | 11.2 | 25.7 | 7.4 | 155 | 1.54 |

$dp/dt$ = rate of gas formation, in cubic centimeters per milliampere per second × $10^4$.
$W$ = rate of solid formation, in grams per milliampere per second × $10^6$.

## *8. Isopentane*

In the ozonizer, isopentane gives a gas containing hydrogen and methane along with 5 per cent of unsaturated hydrocarbons. Fractionation of the liquid product gave a liquid boiling at 100–110°C. and having a molecular weight of 118.6. This fraction was thought to contain an octane (177).

Isopentane has also been studied in an ozonizer in the presence of ammonia. The products consisted of olefins and a base thought to be a hexenylamine (178).

## *9. n-Hexane*

Hexane gave a gas containing 40 per cent of hydrogen, 58 per cent of saturated hydrocarbons, and 2 per cent of unsaturated hydrocarbons when treated in an ozonizer. The liquid product formed simultaneously was separated by steam distillation into a colorless, mobile liquid and a yellowish, thick, clear mass. Fractions of the volatile liquid separated by distillation contained from 0.19 to 4.32 per cent of oxygen. One of the fractions had a vapor density corresponding to a heptane (177).

It was observed that hexane was more stable than isopentane under comparable conditions (177).

By conducting similar experiments at reduced pressure, dodecane $(C_6H_{13})_2$, a colorless liquid having the formula $(C_6H_{12})_2$, and a yellowish brown product ($C_{36}H_{64}$) were observed (179).

When a high-frequency discharge was used to excite the ozonizer, hexane at the boiling point gave a gas having the following composition: 43 per cent $H_2$; 12 per cent $CH_4$; 6 per cent $C_2H_6$; 21 per cent $C_2H_4$; 11 per cent $C_3H_6$; 6 per cent $C_3H_8$. In addition to this, a −70°C. trap in the exit line contained liquefied gas which analyzed as 70 per cent $C_3H_6$ and 30 per cent $C_3H_8$. The residual liquid contained 5 per cent of 1-hexene and a liquid boiling at 45–120°C. at 15 mm., besides the unchanged hexane. This higher boiling liquid contained a small amount of olefinic hydrocarbons. The olefinic constituents were saturated by hydrogenation. The fraction boiling above 100°C. at 15 mm. was judged to be cyclic in nature by its hydrogen content. The cyclic compounds were thought to arise from the bivalent radical $—CH_2CH_2CH_2—$ (222).

The differences between the composition of the gases reported to result from the treatment of hexane are worthy of note. These differences emphasize the fact that all the factors in the electrical treatment are probably not known and not readily controlled. While the frequencies of the discharges are different, it seems that this is not the only difference (*cf.* 56).

### *10. n-Heptane*

When nickel electrodes were used in a glow discharge, heptane liberated hydrogen and formed a brownish yellow solid which would slowly absorb oxygen. It was partly soluble in organic solvents and reacted with sulfuric and nitric acids and with bromine (53) (see also table 17).

The spectrum analysis of the glow discharge in heptane indicates the presence of carbon and hydrogen atoms and of CH, $C_2$, and $H_2$ molecules (104, 105, 106).

A spectrometric study of the electrodeless discharge in heptane indicates the presence of $C^+$ ions as well as CH molecules and carbon and hydrogen atoms (104, 107).

Heptane in the glow discharge gave fragments that removed antimony mirrors (213).

### *11. 2,2,4-Trimethylpentane*

A spectrogram of the light emitted by this hydrocarbon in the electrodeless discharge has been made (11), but none of the details have been reported.

Table 17 gives an analysis of the gas produced from 2,2,4-trimethylpentane in the glow discharge.

### 12. *Higher paraffinic hydrocarbons*

A number of the higher hydrocarbons, including some of those already discussed, have been studied in the glow discharge. The studies were made at reduced pressures and the gaseous products analyzed. The results are summarized in table 17. The table clearly indicates (*a*) the powerful dehydrogenating action of this type of discharge and (*b*) the formation of unsaturated gaseous products (168, 170).

A comparison of the data on the two octanes, *n*-octane and 2,2,4-trimethylpentane, indicates that the branched-chain isomer reacts more slowly (lower $dp/dt$) but gives more dehydrogenation and more gaseous olefins, while the straight-chain compound gives more acetylenes and more paraffinic gases (167).

"Liquid paraffins" in the ozonizer lose hydrogen and increase in molecular weight and viscosity (78).

We may now ask what the available data indicate towards the commercial utilization of natural gas and gasoline. First, it must be noted that in cases where the power requirements have been measured they are high compared to the amount of chemical changes produced. With more work, it is certain that the power requirements can be reduced. Before any extensive program is undertaken in this direction, it is advisable that the antiknock quality of some of the products in the gasoline boiling range be determined. This will help to decide a part of the potentialities in this direction.

## F. THEORETICAL DISCUSSION

The theory of the various types of silent discharge has been excellently presented recently (96, 172), so there is no reason to repeat it here. It does seem worth while to review a few of the essentials and this can be done most clearly with the glow discharge. Particular attention will be paid to the source of chemical action.

### *Essentials of the glow discharge*

The glow discharge has been studied in sufficient detail with elemental gases so that it is fairly well understood (43, 44, 224, 253). The discharge takes place at pressures from about 0.01 to 20 mm. of mercury, so that particles in the discharge have a much longer mean free path than at atmospheric pressures. A diagram of this type of discharge is given in figure 2 with the characteristic portions of the discharge labeled.

In the cathode glow there exists a region of high positive-ion density due to the electrostatic attraction of the negative electrode (cathode). The luminosity is probably due to excitation of molecules by positive-ion collision.

The negative glow is usually the region of greatest luminosity. In it the electron, positive ion, and probably the excited molecule densities are highest. It is a region of almost constant potential.

The Crookes dark space accounts for most of the potential drop of the discharge, and this is where a large portion of the energy dissipation occurs (10). It contains electrons moving towards the anode and positive ions moving towards the cathode.

The Faraday dark space resembles the Crookes dark space, but the energy dissipation and potential drop are much less.

The positive column is a region of uniform ion density and energy unless the column is striated, in which case the energy and ion density vary with the striations. In both cases the electron energies are less than those obtained in the Crookes dark space. The positive ion and electron densities are about 1/100th as great as the densities in the negative glow.

In the anode glow the electron energy is a little higher than in the positive column.

The properties of the individual zones of the discharge and the changes occurring will be discussed, starting with an electron close to the cathode. (The source of the electron at this point will be dealt with later.) Owing to the electrostatic repulsion of the cathode, the electron moves into the Crookes dark space, i.e., the region of greatest potential drop. Owing to this potential the electron is accelerated, its final velocity depending on the potential drop and the pressure in the discharge vessel, i.e., the number of molecules in its path. During this acceleration three types of collisions with molecules occur: (*1*) Elastic collisions; no energy lost or gained. (*2*) Ionizing collisions; a positive ion and electron result. (*3*) Activating collisions; the quantum state of a molecule is raised. This energy may in turn be converted into vibrational energy.

Methods for accurately determining the magnitude of each of these processes are not available. It is known that each electron leaving the cathode forms from fifty to one hundred secondary electrons by ionizing collisions (55, 168). The energy required for an ionizing collision is usually greater than that for an activating collision. Therefore each electron leaving the cathode will undergo many activating collisions. Only ionized and activated molecules have the energy necessary for chemical reaction, so the elastic collisions may be neglected.

Following the electron through the discharge, we have just shown that it receives most of its energy in the Crookes dark space. In the negative glow the effects of this energy are made manifest, as these electrons continue the loss of this energy in collisions. In this region the electrons must complete the process of forming enough positive ions to maintain the discharge.

Since we are concerned with the chemical action of the discharge, we can regard the rest of the discharge as a diffusion of electrons towards the anode, where they are neutralized, and a diffusion of positive ions towards the cathode.

Consider now the positive ions, which are formed mainly in the negative glow and the Crookes dark space. These ions will tend to move towards the cathode, owing to electrostatic attraction. Even in the Crookes dark space region where this action is greatest, it is quite improbable that these ions will obtain sufficient kinetic energy to cause the activation of other molecules by collisions unless the pressure is low (0.1 mm. or less). The ions do not obtain this energy, (*1*) because they are heavy when compared to electrons and (*2*) because of their large collision area it is more probable that they will lose what excess energy they gain, by decelerating collisions. In this respect the positive ions are quite different from electrons (*cf.* 198).

Eventually most of the positive ions reach the cathode and are discharged. In this discharging process many of the positive ions cause the liberation of an electron from the cathode surface. This is the source of the electron at this point, referred to earlier in this discussion. *For the discharge to be maintained it is essential that every electron leaving the cathode surface form a positive ion which will reach the cathode and liberate another electron.*

When an alternating current is used instead of a direct current in the glow discharge, each electrode alternately acts as the cathode. When the alternations are of the order of 60 cycles per second, the discharge gives the appearance of having a Crookes dark space near each electrode with the positive column in the center. As the frequency is further increased, the length of the Crookes dark space decreases. This in turn means a greater potential gradient in this region, which in turn produces electrons having greater energies (velocities). Since the length of the Crookes dark space is shortened, the total number of electrons formed and accelerated in this region probably decreases. This readily explains the observation that methane, ethylene, and acetylene undergo more profound changes with frequencies of $15 \times 10^6$ cycles per second (20 meters wave length), while the total amount of reaction is greater at $6 \times 10^6$ cycles per second (48 meters) (65, 204).

Considering the chemical action of the discharge applied to hydrocarbons, we must admit that little is known about the chemical reactions of hydrocarbon ions. We do not know even whether chemical reaction accompanies the neutralization of a hydrocarbon ion at the cathode. A little more is known about the activated molecules from thermal activation in pyrolytic work. There are essential differences between thermal activation and electrical (or to be more exact, electronic) activation. In thermal activation, energy must be put into the entire aggregation of molecules and there is only a certain limited probability that the energy will be concentrated in a given bond and cause chemical reaction. In electronic activation the electron collides with the electron which forms a part of the chemical bond, producing activation directly without adding to the translational or rotational energy of the molecule. From this point of view the electrical method is the more efficient method of activating the molecule to cause chemical reaction.

We can sum up the discussion with the statement that accelerated electrons and ions cause the activation of molecules so that chemical reaction may take place at pressures below about 0.1 mm. Above this pressure the ions activate fewer molecules, so that at atmospheric pressure the electron can be regarded as the primary activating agency.

It will be noted from the above discussion that *it is not necessary for a molecule to become ionized to react chemically in the discharge* (73). If we assume that a hydrocarbon ion can be discharged at the cathode without undergoing chemical reaction, then it would seem that only a very minor portion of the reaction product would be due to ions. (The above assumption can be partly justified by noting that the energy of neutralization at the cathode can be used to liberate an electron from the cathode, a process which is essential to the maintenance of the discharge.)

The fundamentals of the glow discharge may be summarized (43) as follows: (*1*) The major part of the chemical reaction takes place in the negative glow. (*2*) The reaction rate in the negative glow is independent of pressure within the limits 0.2 to 20 mm. (*3*) The rate of reaction is proportional to the current. (*4*) Reactions in the negative glow have a zero or negative temperature coefficient. (*5*) In synthesis (combination of two or more molecules) the rate of reaction is accelerated by the addition of the gas having the higher ionization potential and retarded by the addition of the gas with the lower potential.

In addition to the above theory of the glow discharge, there are several interesting points about the ozonizer discharge which should be noted (*cf.* 148):

1. If the glass acts as an electrode, then we might well expect some change in the glass. This has been noted in several cases. The action is an erosion of the glass until it assumes the appearance of a ground-glass surface. As the eroding action continues, the glass is finally punctured by the electrical potential and becomes useless for further service (78).

2. When the ozonizer apparatus is supplied with a 60-cycle alternating current, it has been found that the electrical condenser (capacity) characteristic comes into resonance with the inductive part of the circuit causing

high-frequency oscillations (144, 65, 99). It is thus not possible to say what part of the chemical action of the discharge is due to the frequency supplied and what part due to the resonance frequency.

3. Chemical action taking place in the ozonizer apparatus *increases* the electrical conductance of that apparatus. For example, an ozonizer causing chemical reaction in a gas conducts more current than the same apparatus with the reaction space filled with mercury (144).

By studying several hydrocarbons under comparable conditions, relative reaction rates are obtained from the per cent of hydrocarbon reacted in a given time (166) (see table 18).

If we knew the number and energy of the electrons causing the reaction, we would be able to calculate the relative reaction rates in more fundamental terms. The technique for such a determination has not been worked out. Nevertheless this has been approximated by Lind and Schultze (166), using similar data obtained with alpha-particles where the energy and number of activating particles are known. This approximation uses the following quantities: $M$ = number of molecules reacting; $N$ = number of ion pairs (alpha-particles); $k$ = total specific ionization of the reacting molecule; and $s$ = ion-stopping power of the reacting molecule. $k$ and $s$ are obtained in terms of Bragg's equations (41).

TABLE 18

*Relative stability of hydrocarbons in the ozonizer discharge*

| HYDROCARBON | PER CENT REACTED |
|---|---|
| $CH_4$ | 7.9 |
| $C_2H_6$ | 17.0 |
| $C_3H_8$ | 12.9 |
| $C_4H_{10}$ (both isomers) | 32.8 |
| $C_2H_4$ | 39.6 |
| $C_3H_6$ | 65.0 |
| $C_2H_2$ | 75.5 |

It is then assumed that the quantity

$$\frac{M}{N} ks$$

governs the electrical reactions of hydrocarbons.

In the alpha-ray work, $M/N$ and $ks$ are known for several hydrocarbons. For example, $M/N$ for methane is 2 and $ks = 1$, so that

$$\frac{M}{N} ks = 2$$

Now if this quantity $\frac{M}{N} ks$ governs the rate of reactions in the electrical discharge, then the per cent conversion should be proportioned to $\frac{M}{N} ks$ under comparable conditions, i.e.,

$$\text{per cent conversion} = C \frac{M}{N} ks$$

where $C$ is a function of the apparatus, the conditions of the experiment, etc. As these were fixed, $C$ is a constant and should be applicable to all hydrocarbons studied under those fixed conditions. In the case of methane the per cent conversion is 7.9 per cent under these conditions. Using the above values of $M/N$ and $ks$ for methane we get

$$7.9 = 2C$$

$$C = 3.95$$

We can now use $C$ to calculate $\frac{M}{N} ks$ for the electrical reactions and compare them with the experimentally determined alpha-ray studies. The values are summarized in table 19. With the exception of propane and acetylene the agreement is good. The reaction of acetylene is known to involve some inhibiting factor whose nature is unknown. No explanation can be given for the result with propane.

This work of Lind and Schultze indicates that the fundamentals of the electrical reactions are beginning to be understood. At first sight, it would seem that, by using the total specific ionization, $k$, every molecule

TABLE 19

*Relative stability of hydrocarbons to the ozonizer discharge compared with the stability to alpha-particles*

| | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $C_4H_{10}$ | $C_2H_4$ | $C_3H_6$ | $C_2H_2$ |
|---|---|---|---|---|---|---|---|
| $\frac{M}{N}$ from alpha-ray work | 2 | 2 | 2 | 2 | 5.5 | 4.9 | 19.2 |
| $ks$ | 1.0 | 2.0 | 3.0 | 4.0 | 1.7 | 2.58 | 1.4 |
| Per cent conversion (table 18) | 7.9 | 17.0 | 12.9 | 32.8 | 39.6 | 48.0 | 75.5 |
| Calculated $\frac{M}{N} ks$ (electrical) | 2* | 4.5 | 3.3 | 8.3 | 9.9 | 12.2 | 19.1 |
| $\frac{M}{N} ks$ (alpha-ray) | 2 | 4 | 6 | 8 | 9.4 | 12.6 | 27.7 |

* This value was used in evaluating $C$.

must become ionized to react. An analogous factor, "the total specific activation", can be introduced and, if the total specific activation is proportional to the total specific ionization, the same relationships still hold. Our contention that ionization is essential to maintain the discharge but is not essential for reaction is unchanged.

## IV. Reactions in Arc and Spark (Disruptive) Discharges

"The arc discharge is characterized and distinguished from other types of discharge by its exceptionally low cathode fall of potential and its high current densities" (that is, amperes to thousands of amperes per square centimeter; 172, page 605). The spark is "an unstable and discontinuous occurrence marking the transition from one more or less stable condition of current between electrodes in a gas, to another one" (172, page 408). Thus, in many cases the spark is a precursor of the arc. (For an excellent bibliography and theory of the spark see reference 184.)

The arc and spark are also closely related in the types of reactions that they cause when the discharge takes place in hydrocarbons. In both cases the reactions are those that would be expected if the hydrocarbons were exposed to high temperatures, i.e., 1500°C. and perhaps higher. In dealing with such high temperatures it must be remembered that the reaction zone is restricted and consequently the contact time can be made very short so that the reaction is controlled. While there may be electrical effects on the hydrocarbon in the spark discharge, there is reasonable doubt that there is any such effect in the arc (81).

While the thermal effect is probably the outstanding effect in these discharges, it is noticeable that the electrode material in many cases plays an important rôle in the reaction. This may be due to a catalytic effect, as in the case of iron or nickel, or it may be a definite chemical reaction where the electrodes actually take part in the reaction, as has been noticed in some cases with carbon electrodes. Undoubtedly there are also electrons and ions in these discharges. Just how much they influence the final reaction products cannot be told at this time.

With these effects in mind it is not possible as yet to present any satisfactory mechanism for the reactions taking place.

### A. REACTIONS OF HYDROCARBONS IN THE SPARK DISCHARGE

#### *1. Methane*

It was realized quite early (1798) that electric sparks caused reactions in hydrocarbon gases (115) with the formation of higher boiling products. It was also soon found that the spark also decomposed the hydrocarbons into carbon and hydrogen (60, 115, 209). It is quite possible that acetylene was also present but remained undetected in the large volume of hydrogen. It remained for Berthelot (23), in his comprehensive studies on acetylene, to show its presence. Table 20 gives a summary of the work that has been done.

TABLE 20

*Gaseous paraffins in the spark discharge*

| HYDROCARBON | REACTION PRODUCTS | REFERENCE |
|---|---|---|
| Hydrocarbon gas.. | $H_2$, C, liquids | (115) |
| Hydrocarbon gas.. | $H_2$, C | (35, 47, 60, 89, 156, 209, 250) |
| $CH_4$ | $H_2$, $C_2H_2$, C; 80% increase in volume | (23) |
| $CH_4$ | 12.5% $C_2H_2$ (50% yield on methane reacted) | (21, 24) |
| $CH_4$ | Up to 14% $C_2H_2$, 65% $H_2$. Carbon, and liquid and solid hydrocarbons | (236) |
| $CH_4$ | 5 volumes $H_2$ and 1 volume $C_2H_2$ | (93) |
| $CH_4$ | $H_2$, $C_2H_2$ | (58) |
| $CH_4$ | One or both electrodes metal: $H_2$ and C<br>Both electrodes carbon: $H_2$ and $C_2H_2$ | (182) |
| $CH_4$ | 7 volumes $H_2$ and 1 volume $C_2H_2$ | (30) |
| $CH_4$ | Olefins and acetylenes | (132) |
| $CH_4$ | $H_2$, $C_2H_2$ | (3) |
| $C_2H_6$ | $H_2$, $CH_4$, $C_2H_2$, and $C_2H_4$ | (93) |
| $C_2H_6$ | $H_2$, $C_2H_2$ | (3) |
| $C_3H_8$ | $H_2$, $C_2H_2$ | (3) |
| $n$-$C_4H_{10}$ | $H_2$, $C_2H_2$ | (3) |
| $i$-$C_4H_{10}$ | $H_2$, $C_2H_2$ | (3) |

TABLE 21

*Products formed by treating methane with electric sparks*

Volume per cent of products in final gas at pressures indicates

| TIME OF SPARKING | OLEFINS | | | ACETYLENES | | |
|---|---|---|---|---|---|---|
| | 40 cm. | 60 cm. | 70 cm. | 40 cm. | 60 cm. | 70 cm. |
| *minutes* | | | | | | |
| 1 | 1.10 | 2.05 | 3.90 | 7.50 | 4.85 | 5.20 |
| 2 | 1.55 | 3.15 | 5.35 | 8.45 | 7.40 | 7.75 |
| 3 | 1.90 | 3.70 | 5.90 | 8.90 | 7.55 | 7.80 |
| 4 | 2.20 | 4.05 | 6.00 | 9.00 | 7.00 | 7.85 |

By controlling the pressure and the time of sparking (platinum electrodes), the reaction products can be controlled to some extent. This is indicated in table 21.

It will be noted that the higher pressure favors the olefin yield, but is slightly unfavorable to the acetylene yield. For the maximum yield of useful products the higher pressure is definitely indicated (132).

Methane has also been studied using a wide sheet of spark produced between two flat strips of copper. The methane was passed perpendicular to the spark sheet. The gaseous product contained 14 per cent of acetylene, "large quantities of hydrogen," 2 per cent of ethylene, traces of hydrogen cyanide, and higher hydrocarbons (236).

The liquid product was thought to be mainly dipropargyl ($CH\equiv CCH_2CH_2C\equiv CH$) along with small amounts of benzene. The yield of this liquid varied from 0.007 to 0.026 g. per liter of methane.

The tar produced contained naphthalene and acenaphthene along with other substances not identified. The yield of tar varied from 0.01 to 0.051 g. per liter of methane.

In other experiments electrodes of copper, gold, aluminum, or platinum did not seem to alter the course of the reaction, while iron electrodes seemed to favor carbon formation (236).

The use of metal electrodes or one metal electrode and one carbon electrode is said to favor carbon formation, while acetylene formation is favored if both electrodes are carbon (182) when treating methane by sparks.

Methane was treated with sparks of about 50 kilovolts at 100 kilocycles. The yield of acetylene increased with increasing rate of flow and decreased with the reaction time and the rate of decomposition of the methane. The methane reacted varied from 73.7 to 100 per cent and the acetylene yields from 38.4 to 47.3 per cent of the methane reacted. Dilution of the methane with an equal volume of hydrogen or carbon monoxide increased the acetylene yield. Nitrogen changed the yield slightly and carbon dioxide, oxygen, or water vapor decreased the acetylene yield greatly (3).

The physical changes taking place in a spark between nickel or copper electrodes in methane have been observed through a low-powered microscope. The electrical source was a high tension D.C. magneto. When there is no added resistance in the circuit, small incandescent particles pass to the anode, then fly suddenly to the center of the gap and deposit on the cathode. With 5,000 to 100,000 ohms resistance in the circuit, a carbonaceous thread-like deposit builds up on the cathode. This deposit is conducting, so that the discharge takes place from the anode to the end of the deposit. Reversing the polarity of the discharge gradually removes a preformed deposit (128).

### 2. *Ethane*

Ethane when passed through 8- to 47-kilovolt sparks between spherical electrodes gave hydrogen, acetylene, methane, and ethylene (93). Ethane when treated with 50-kilovolt 100-kilocycle sparks gave hydrogen and acetylene, along with minor amounts of ethylene and other saturated and unsaturated hydrocarbons. Dilution with hydrogen increased the acetylene yield (3).

### *3. Propane, n-butane, and isobutane*

These gases, when treated with 50-kilovolt sparks at 100 kilocycles gave hydrogen and acetylene as the major products in yields of 61.1 to 87.3 per cent of theory. Small amounts of ethylene and other olefins and paraffins were simultaneously formed (3).

### *4. n-Pentane*

Sparks passed between platinum electrodes immersed in boiling *n*-pentane gave a gas containing hydrogen, methane, and probably ethane, ethylene, and acetylene. No carbon was deposited (254).

### *5. Ethylene*

Hydrocarbons from ethyl alcohol and from ethyl ether, presumably containing ethylene, gave oily droplets on sparking (87).

The uncontrolled action of sparks on ethylene is to form carbon and hydrogen. This has been observed with platinum (60) and copper electrodes (182, 209). The carbon-forming action of aluminum electrodes is intense compared with gold electrodes (189).

TABLE 22

*Products from ethylene upon passage through a 33,000-volt spark*

| ETHYLENE | ETHYLENE REACTED | VOLUME PER CENT COMPOSITION OF GASEOUS PRODUCTS | | |
|---|---|---|---|---|
| | | $C_2H_2$ | $H_2$ | $CH_4$ |
| *cc. per hour* | *per cent* | *per cent* | *per cent* | *per cent* |
| 754 | 85.2 | 28.8 | 67.8 | 3.4 |
| 3115 | 58.0 | 33.4 | 64.8 | 1.8 |

If the action of the sparks is controlled, the gas produced contains 14 per cent of acetylene and 86 per cent of hydrogen (22). It has also been noticed that under comparable conditions ethylene reacts more slowly than acetylene. The ethylene forms a small amount of a liquid product that has the odor of turpentine or petroleum (269).

A mixture of equal volumes of ethylene and argon gave hydrogen and a small quantity of methane as the gaseous reaction products (34). The effect of the argon is not clear.

A more quantitative study (93), using 33,000 volts across the spark gap, indicates that the extent of decomposition was proportional to the time of contact and that some of the acetylene formed originally was decomposed into carbon and hydrogen. Table 22 indicates the type of results obtained (93).

It is claimed (121) that a spark discharge passed between copper electrodes 8 cm. apart with the current adjusted so that the discharge consumed 60 watts will give products containing 9.1 per cent of propene, 1.4 per cent of butene, and 7.7 per cent of butadiene when ethylene is passed through the discharge at 20 liters per hour.

Ethylene treated with 50-kilovolt 100-kilocycle sparks gave mainly acetylene and hydrogen (3).

### *6. Propene, 1-butene, and 2-methylpropene*

When treated in 50-kilovolt 100-kilocycle sparks these hydrocarbons gave acetylene and hydrogen as the main products, with small amounts of ethylene and other olefin and paraffin hydrocarbons. When the reacting gases were diluted with hydrogen, the amount of ethylene was increased (3).

### *7. Pentenes*

Sparks passed between platinum electrodes dipping in boiling "amylene" caused the separation of small amounts of carbon and the evolution of a gas containing hydrogen, methane, acetylene, ethylene, and probably ethane (254).

### *8. Acetylene*

Acetylene gives primarily the elements in the spark discharge (20, 26, 33, 88, 194, 268), although small amounts of liquid and polyacetylenes have been detected (28). The tendency for acetylene to revert to carbon and hydrogen can be vividly illustrated by the observation that an electric spark in acetylene at 3 atmospheres pressure caused a violent explosion (48).

### *9. Butadiyne*

When a spark was passed through gaseous butadiyne, decomposition occurred with production of a dazzling white light. The main decomposition was to carbon and hydrogen, although there was a 4.5 per cent contraction in volume, indicating that some hydrocarbon, presumably methane, had been formed (243).

### *10. Benzene*

A spark between platinum wires dipped in benzene gave carbon and a gas containing 42 to 43 per cent of acetylene and 57 to 58 per cent of hydrogen (64, 80). Carbon electrodes under somewhat similar conditions gave a gas containing 44 per cent of hydrogen, 53 per cent of methane, and 3 per cent of acetylene and other unsaturated hydrocarbons. A liquid residue was formed which boiled above 250°C. and had an average molecular weight of 300 (88). Whether the difference in the electrodes is the sole cause of the observed differences in gas composition in the two experiments is not known.

### *11. Toluene*

With platinum electrodes a spark discharge in toluene gave carbon and a gas containing 76 to 77 per cent of hydrogen (64).

## B. ARC DISCHARGE

### *1. Methane*

A carbon arc in a closed vessel filled with methane gave, after 1 hr. of arcing, 9 per cent of acetylene, 2 per cent of methane, and 89 per cent of hydrogen. A gas of the same final composition was obtained when the original gas was hydrogen, clearly indicating that the carbon of the electrodes is actually part of the reaction system (37, 38).

When methane is passed through the arc, acetylene forms in yields of 6 to 12 per cent of the methane passed or 26 to 32 per cent of the methane reacted. The rest of the methane is converted into a fine soot-like carbon and hydrogen. Dilution of the methane with hydrogen tends to reduce the formation of carbon. With a mixture of 1 volume of methane and 2 volumes of hydrogen, the arc treatment gave acetylene equivalent to 51 per cent of the methane charged or 68 per cent of the methane reacted, in a single pass (91, 153).

Instead of diluting the reacting gas with hydrogen, a similar effect can be obtained with a high-tension arc at reduced pressures (39, 40). At pressures of 100 to 200 mm. of mercury the exit gas contained 12 to 14 per cent of acetylene with an energy consumption of 12 kw.-hr. per cubic meter of acetylene produced. The effect of either hydrogen or reduced pressure is to decrease the amount of carbon formed, so that the reaction is more selective.

A study of arcs with different intensities (energy consumption) indicated that an arc consuming up to 150 watts promotes cracking to acetylene, while arcs of higher energy promote the formation of carbon and hydrogen (39, 193). It seems likely that factors other than energy consumption, e.g., electrode material, size, cooling, etc., are also pertinent.

Butadiyne has been isolated from the gases produced by the arc in methane. There is also some evidence that allene, methylacetylene, and butadiene are formed (248).

It is to be noted that heating the chamber enclosing the arc promotes the formation of more carbon and hydrogen, probably owing to the secondary reaction of acetylene. For this reason it is desirable to cool the arc vessel when acetylene is the product sought (217).

Electrodes of iron and nickel have also been used in the study of methane in the arc discharge. At 110 volts and 4 to 5 amperes D.C. the rate of decomposition of the methane and the concentration of acetylene in the gas produced were higher with carbon electrodes than with iron or nickel electrodes, but the yield of acetylene on the basis of the methane reacted was the same in all cases. At a contact time of 0.002 sec. in the carbon arc, 18 per cent of the methane reacted. The acetylene yield was 9 per cent of the original methane or 50 per cent of the methane reacted. A mixture of methane and hydrogen increased the acetylene yield (146).

### *2. Ethane*

Ethane gave ethylene and acetylene in nearly equal amounts when treated in the electric arc (126). Low gas velocities through the arc caused the formation of carbon and hydrogen.

### *3. Ethylene*

Passing an arc between platinum electrodes in ethylene until the maximum expansion occurred (about 10 min.), produced hydrogen as the only gaseous product. Presumably the other product was carbon (47).

### *4. Acetylene*

Using carbon electrodes, an arc in acetylene gave predominantly carbon and hydrogen, along with a small amount of methane and enough naphthalene so that it could be recognized by its odor (37, 38).

### *5. Pinene*

Pinene gave ethylene, acetylene, and isoprene, in addition to unidentified substances (260).

### *6. Liquid paraffin hydrocarbons*

When hexane vapor was studied with a 3- to 4.5-ampere, 60- to 80-volt arc between copper or iron electrodes a gas was produced which analyzed as follows: paraffins, 4 per cent; olefins, 0.5 per cent; acetylene, 1 per cent; hydrogen, 94.5 per cent (116).

When the conditions were altered so that the electrodes were still in the vapor space but were kept wet by the refluxing hydrocarbon, the gas contained 10 to 16 per cent of olefins and 4.8 to 5.6 per cent of acetylene. The olefins were not identified, except that the presence of butadiene was proved by isolating the solid tetrabromide. In addition to hexane, the hydrocarbons heptane, octane, nonane, and decane were studied with both iron and copper electrodes. The higher boiling hydrocarbons seemed to favor slightly higher yields of olefins, although the trend is slight. The iron electrodes gave more carbon deposits than the copper electrodes, but no significant effect was noted on the olefin or acetylene concentration in the gas. The carbonaceous deposit formed in the presence of iron contained 20.1 per cent of iron; the analogous deposit with copper electrodes contained 0.59 per cent of copper. The deposit on the iron electrode was bright and lustrous, while the copper electrode deposit was dull (116).

When the experimental conditions were further altered so that the arc was immersed in the liquid, it was found that hexane, heptane, and decane gave a gas that contained 5 to 16 per cent of olefins and 13 to 15 per cent of acetylene. It is thus apparent that the method of conducting the arcing of the hydrocarbon greatly affects the composition of the gas produced (116).

### *7. Benzene*

Benzene has a distinct tendency to form carbon and hydrogen in the arc; at the same time there are usually formed liquid products boiling above benzene. The gas formed is 80 to 90 per cent hydrogen (202).

To study the reaction more carefully, 17 liters of benzene were treated in the carbon arc and the products passed through traps at room temperature and at −36°C. Under these conditions there were 8 liters of product in the arc vessel, 540 cc. in the trap at room temperature, and 320 cc. in the trap at −36°C. The residue in the arc vessel was 95 per cent benzene and 5 per cent higher boiling material. From the higher boiling material phenylacetylene, diphenyl, and anthracene were isolated. Butadiyne was recovered from the −36°C. trap. In a separate experiment 194 g. of carbon was obtained during the treatment of 780 g. of benzene (195).

When the arc is immersed in liquid benzene under some conditions, the carbon formed builds a bridge across the arc and shortcircuits it. Metal electrodes were found to prevent this, because the carbon was kept in suspension. With metal electrodes, acetylene and ethylene were formed as well as hydrogen (261).

An arc between iron or copper electrodes that were in the vapor but were kept wet by refluxing benzene gave a gas that contained 0.2 to 0.3 per cent of olefins (116). No other analyses are given.

### *8. Toluene*

Toluene gave a gas containing 2 to 2.5 per cent of olefins when subjected to an arc between iron or copper electrodes that were in the vapor but were kept wet by refluxing toluene (116).

### *9. Naphthalene*

Only carbon and hydrogen have been reported as products from naphthalene in the arc (171).

## V. Commercial Processes

From the literature available it is not possible to give complete details on the commercial processes for the electrical treatment of hydrocarbons. Neither is it possible to say just which of the proposed processes have actually been commercialized. Nevertheless it is instructive to review briefly the processes which have been proposed, along with such pertinent characteristics as may be obtained from the issued patents. We fully realize that the information obtained from patents may not always be reliable.

### A. ACETYLENE PRODUCTION

The current method of producing acetylene is from calcium carbide. The main reaction in preparing the carbide is

$$CaO + 3C \rightarrow CaC_2 + CO; \quad \Delta H_{298} = 108{,}000 \text{ cal.}; \Delta F^0_{298} = 88{,}400$$

It is also possible to prepare acetylene from methane (or natural gas) by the reaction

$$2CH_4 \rightarrow C_2H_2 + 3H_2; \quad \Delta H_{298} = 91{,}000 \text{ cal.}; \Delta F^0_{298} = 75{,}400$$

Thus the theoretical energy requirement for the carbide reaction is more than 15 per cent greater than that of the methane reaction. Converting the $\Delta H$ requirement into electrical units, the carbide reaction requires 5.6 kw.-hr. per cubic meter of acetylene, while the methane reaction requires 4.7 kw.-hr. per cubic meter.

In actual practice the energy requirements are greater. It has been stated that 8.5 kg. of 310 liters per kilogram carbide can be produced per kilowatt day (259). This indicates a practical energy requirement of 9.1 kw.-hr. per cubic meter. Further, to get the power requirement this low, very large furnaces (15,000 to 25,000 kilowatts) must be used. On smaller furnaces the energy requirements may be as high as 15 to 18 kw.-hr. per cubic meter of acetylene.

The corresponding practical energy requirements for acetylene from methane are not known. From the information available, however, it seems that the following factors would tend to favor the production of acetylene from methane: (*1*) The theoretical or limiting energy requirement for the methane reaction is lower. (*2*) The raw material, methane, is cheaper in many localities than lime and coke. (*3*) Gaseous methane is readily transported in pipe lines to the centers of "cheap" electrical power.

The factor favoring the carbide process is that the acetylene produced is comparatively pure, while that from methane is mixed with hydrogen and unconverted methane.

Not only has methane been used as a source of acetylene in the arc, but also various hydrocarbon mixtures from both petroleum and coal. In all cases carbon, as a more or less light soot, is formed as a by-product. Much of the study has been in the direction of minimizing this carbon formation and devising mechanical schemes for operating the process without the soot plugging the necessary pipes and valves.

In the case of petroleum products, graphite electrodes are much better than copper or iron for making high yields of acetylene and reducing the soot formation (83).

In the Claude process (173) the liquid hydrocarbon is atomized into the arc through one of the electrodes. The soot is removed by an oil scrubber and the acetylene separated from the hydrogen and other gases by compressing to 10 atmospheres and extracting with water in which the acetylene is considerably more soluble than the other constituents.

It is stated that 1 cubic meter of acetylene requires 2.2 kg. of raw oil, 14 kw.-hr. for the furnace, 1.5 kw.-hr. of pumping energy, and 3.4 g. of electrodes. At the same time about 1.4 cubic meters of hydrogen is produced (173; also 77, 82, 99, 171, 193, 216).

In the case of a petroleum fraction boiling in the hexane range it was found that at the beginning of the arc treatment the gas contained 18 per cent of acetylene. After a short time of operation the hexane became heavily laden with soot and the acetylene in the gas increased to 33 to 34 per cent. Removal of the soot by filtration and again treating the hexane in the arc gave 18 per cent of acetylene. Thus the soot seems to be intimately related to the acetylene-forming process. Lamp black or coal dust added to the hexane produced no effect, but soot produced in one run could be added to fresh hexane and the 33 to 34 per cent of acetylene realized immediately (58).

In view of the high hydrogen yields in the arc cracking of methane or natural gas, this method has been proposed as a method of making hydrogen. Using an arc of 400 to 500 volts and 7 to 12 amperes, the hydrogen yield was 88 per cent of the theoretical in one pass through the arc (67, 124, 267).

The patents pertinent to making acetylene from hydrocarbon materials by treatment in the electric arc deal mostly with types of apparatus and operative details (16, 17, 70, 71, 98, 100, 103, 119, 123, 131, 150, 186, 200, 218, 232, 233). The main generalization is that it is desirable to dilute the reacting gas or vapor. Hydrogen is the diluent most frequently mentioned (41, 46, 72, 123, 142, 155, 170, 232), although carbon monoxide, carbon dioxide, and steam have been claimed.

It has been proposed that acetylene be made from hydrogen plus carbon monoxide or carbon dioxide in the arc (15, 57).

The carbon that is regarded as a nuisance in the preparation of acetylene is, in many cases, so light, fluffy, and black that it has value as a black pigment and as the carbon black component of rubber articles. Special techniques have been designed for its manufacture from hydrocarbons in the arc (103, 130).

When anthracene oil was subjected to impulse discharges (the spark discharge from an electrical condenser) a gas containing 22 to 30 per cent of acetylene was obtained. The energy requirement was 11 to 12 kw.-hr. per cubic meter and was independent of condenser capacity in the range 5 micromicrofarads to 0.25 microfarad (154, 216).

It is claimed (125) that hydrogen can be activated in the arc and that when the activated hydrogen is brought in contact with hydrocarbons, olefins and acetylene are formed. Or, if the hydrocarbon is ethylbenzene, phenylacetylene is formed (120).

The electric spark has also been proposed as a means of converting coal gas into acetylene on a commercial scale (100).

### B. LUBRICATING OILS

The polymerizing and dehydrogenating action of the silent discharge have been used advantageously to produce and improve lubricating oils (5, 6, 7, 9, 18, 36, 45, 49, 68, 79, 90, 94, 101, 102, 112, 118, 122, 126, 136, 139, 145, 196, 197, 201, 203, 207a, 210, 212, 215, 230, 235, 237, 258, 264, 265, 271, 272, 273). A commercial process is known as "Elektrionization" or "Voltölization".

The apparatus used for this treatment consists of a series of aluminum electrodes in the form of flat plates about 80 cm. square and 1 mm. thick. The electrodes are built up as a bank of plates of alternating polarity until a total area of about 190 square meters is obtained; each plate or electrode is separated and insulated from its adjacent plate by glazed pasteboard 2 mm. thick. The pasteboard extends beyond the edges of the plate electrodes to prevent sparking from plate to plate.

The reaction vessel consists of a horizontal cylinder which contains four of the electrode banks described above, to give a total plate area of 750 square meters (8050 sq. ft.). The electrodes are mounted so they can be rotated about a central shaft at 1 R.P.M. During this rotation the electrodes dip into the oil contained in the cylinder (one-quarter full of oil). At the same time appropriately placed buckets dip into the oil and gradually pour the oil over the electrodes. In this way the oil on the electrodes is continually replaced so that overexposure to the discharge does not occur.

The reaction vessel is equipped with a few coils of pipe which are used at the start to heat the charge up to 80°C. and during operation are used as cooling pipes to keep the temperature down to 80°C. Also attached to the reaction vessel is a small suction pump which maintains the pressure in the vessel at about 60 mm. of mercury (Absolute).

The electrical energy is supplied by a special alternator producing 500-cycle current. This is stepped up by transformers to give the desired voltage. Most of the published work indicates that this voltage is 4300 to 4600 (126, 203), although a photograph of part of the equipment in one of the plants shows a vessel labelled 50,000 volts (49). For the type of equipment described above, the 50,000 volts would be much too high.

In use the apparatus is filled one-quarter full of the oil to be treated (about 2000 gallons) and the air in the vessel is replaced by hydrogen at 60 to 65 mm. of mercury pressure (Absolute). When the current is turned on, the vessel is filled with light from the discharge. The action of the discharge causes dehydrogenation of the oil and the hydrogen must be pumped off. The dehydrogenated oil polymerizes to form larger molecules. This dehydrogenation and polymerization action of the discharge is analogous to the reactions which have already been discussed in connection with the pure hydrocarbons. The net result of the action of the discharge is to increase the viscosity of the oil. It is possible to continue the action of the discharge until the oil coagulates and forms a gel.

When a pure mineral oil is treated in the discharge, the rate of reaction is usually too slow to be economical (203). On the other hand, the fatty oils (fish, animal, and vegetable) polymerize much faster. As a result, it is customary to start with a fatty oil or a fatty oil–mineral oil blend and treat this. The treated product is diluted with mineral oil and re-treated until the final product contains about 15 per cent of the fatty oil. The properties of the oil so produced are as follows (8):

| | |
|---|---|
| Specific gravity at 15°C. | 0.925 |
| Viscosity at 100°C. | 2000 centipoises |
| Flash point (open cup) | 225°C. |
| Conradson carbon | 0.4 per cent |
| Pour point | −5°C. |
| Acid number | 1 |
| Saponification number | 90 |
| Ash | 0 |

It is indicated that this oil is to be blended with mineral oils up to 15 per cent. The following changes take place when this is done: (*1*) the viscosity increases; (*2*) the viscosity–temperature coefficient is decreased; (*3*) the pour point is lowered; (*4*) the sludge-forming tendency of the oil is decreased; and (*5*) the tendency to form emulsions with water is increased.

The history of this process has been a romantic and turbulent one. It began in 1904, when de Hemptinne (112) found that hydrogen could be activated in the silent electric discharges so that it would hydrogenate oleic acid, converting it into stearic acid. With both hydrogen and oleic acid in the discharge it was found that the oleic acid polymerized, giving viscous oils, instead of hydrogenating to stearic acid. Later it was found that the unsaturated glycerides could be polymerized, giving viscous oils suitable for lubricants. The use of the process for commercial purposes was begun in 1907 (139), when the Société Anonyme Elektrion was formed in Ghent, Belgium. This plant was in operation in 1914 and was commandeered by the Germans when they occupied Belgium. Apparently the Germans operated the Ghent plant throughout the war and also started a plant in Germany with the formation of the Deutsche Elektrion-Oel Gesellschaft. At the end of the war the Germans obtained the right to manufacture these products in Germany but were forced to abandon the name "Elektrion", which was the property of the Belgian company. The Germans coined the name "Voltöl", renaming their company the Deutsche Voltöl Gesellschaft.

Just what mineral oils are most desirable for electrical treatment is not disclosed. It has been found (225) that the oil produced by the alkylation of naphthalene and tetralin by ethylene in the presence of aluminum chloride can be electrically treated. The viscosity is increased, but from the data given it would seem that the viscosity–temperature coefficient has not been decreased.

Other work (207) indicates that the type of original hydrocarbon has a profound influence on the final viscosity characteristics. Several pure compounds have been studied in an ozonizer for 6 hr., using 7500 volts, 1000 cycles, and 10 to 20 milliamperes. The results are given in table 23.

These data indicate that the straight-chain olefins give better products and higher yields than the cyclic and aromatic hydrocarbons. This may not be the whole story, for it has been claimed that non-paraffinic extracts produced by solvent extraction of petroleum oils give suitable "Voltöls" (234). This may arise from the fact that broadening the boiling range of a lubricating oil is known to increase its viscosity index. Where the "Voltöl" is used as a blending oil (as it usually is), it is entirely possible that the viscosity index of an oil could be apparently increased by a "Voltöl" with a very low viscosity index and the entire effect may be due to a broadening of the boiling range. Too little is known about the theory of lubricating oils and viscosity index to offer this as anything more than a possibility.

The optimum conditions for the "Voltölization" process have been studied and the results on a laboratory scale published (249). A cracked kerosene having a kinematic viscosity of 2.88 at 20°C., and 1.68 at 50°C. was used. The experiments were made in an ozonizer that could be oper-

TABLE 23

*Viscosity characteristics of "Voltölized" pure hydrocarbons*

| HYDROCARBON | KINEMATIC VISCOSITY | | | VISCOSITY INDEX* | YIELD | BOILING POINT ABOVE |
|---|---|---|---|---|---|---|
| | At 20°C. | At 50°C. | At 100°C. | | | |
| | | | | | *per cent* | *°C.* |
| Caprylene | 17.2 | 6.3 | 2.0 | | 50 | 200 |
| Cetene | 142.0 | 34.4 | 8.4 | 123 | 60 | Original |
| *n*-Dodecane | 11.43 | 5.00 | 2.02 | | 23 | Original |
| 1,2,4-Trimethylcyclohexane | 1928 | 128 | 12.7 | −56 | 28 | 200 |
| Decalin | 13071 | 399 | 20.7 | −220 | 26 | 200 |
| Cumene | | 1143 | 29.0 | −470 | 17 | 200 |
| Methylnaphthalene | | 5000 | 55.3 | | 15 | 200 |

* We have used a plot of the viscosity–temperature curve to estimate the viscosity index.

TABLE 24

*Effect of conditions of "Voltölization" on the viscosity of a cracked kerosene*

| TIME | CONDITIONS | | | KINEMATIC VISCOSITY | |
|---|---|---|---|---|---|
| | Frequency | Voltage | Current | At 20°C. | At 50°C. |
| *hours* | | *kilovolts* | *milliamperes* | | |
| 2 | 350 | 12.2 | 10 | 6.36 | 3.03 |
| 4 | 350 | 12.2 | 10 | 14.0 | 5.30 |
| 6 | 350 | 12.2 | 10 | 64.4 | 17.2 |
| 2 | 500 | 7.25 | 5.5 | 4.02 | 2.08 |
| 4 | 500 | 7.25 | 5.5 | 5.68 | 2.80 |
| 2 | 500 | 11.4 | 10 | 7.24 | 3.88 |
| 4 | 500 | 11.4 | 10 | 20.2 | 7.2 |
| 6 | 500 | 11.4 | 10 | 66.0 | 18.0 |
| 10 | 500 | 11.4 | 10 | 178.7 | 22.0 |
| 2 | 750 | 9.0 | 10 | 5.64 | 2.82 |
| 4 | 750 | 9.0 | 10 | 10.12 | 4.13 |
| 6 | 750 | 9.0 | 10 | 20.12 | 7.04 |
| 2 | 750 | 7.0 | 6 | 4.38 | 2.26 |
| 2 | 1000 | 5.0 | 7 | 3.82 | 2.09 |
| 4 | 1000 | 5.0 | 7 | 4.60 | 2.44 |
| 2 | 1000 | 7.0 | 10 | 4.60 | 2.46 |
| 4 | 1000 | 7.0 | 10 | 6.88 | 3.20 |
| 6 | 1000 | 7.0 | 10 | 10.64 | 4.26 |
| 8.5 | 1000 | 7.0 | 10 | 35.60 | 10.74 |
| 2 | 1000 | 7.4 | 15 | 5.60 | 2.60 |
| 4 | 1000 | 7.4 | 15 | 9.10 | 4.02 |
| 6 | 1000 | 7.4 | 15 | 17.85 | 6.32 |
| 2 | 2000 | 5.0 | 10 | 4.12 | 2.18 |
| 4 | 2000 | 5.0 | 10 | 5.70 | 2.80 |
| 6 | 2000 | 5.0 | 10 | 9.81 | 4.00 |

ated at reduced pressure (40 to 43 mm.). A slow stream of hydrogen was passed through the oil, causing the oil to froth and be well mixed during the discharge. Table 24 gives conditions studied and the viscosity of the products formed (249).

From the data the following conclusions were drawn: (*1*) With constant electrical conditions, the viscosity increases with time, at first slowly and later more rapidly, especially after 6 hr. (*2*) When the frequency and time are constant, the viscosity increases with the power in the discharge. (*3*) The optimum frequency is 500 cycles per second. This may be limited by the apparatus and kerosene used in the study. (*4*) To produce a given change in the properties of the oil under treatment, a *much* larger change must be made in the electrical conditions.

In conclusion it may be said that, so far as the writers know, these electrically treated oils are not being produced commercially in the United States. They are being produced in Belgium and Germany.

### C. PRODUCTION OF MOTOR FUELS

Electrical methods of producing acetylene and lubricating oils depend upon the application of rather specific conditions to produce the desired results. By the application of still other conditions it is possible to take advantage of the electrical discharge to produce hydrocarbons boiling in the gasoline range and suitable for motor fuels.

The simplest process of this type consists in vaporizing or atomizing the oil to be cracked into a zone where a discharge is occurring and removing the reaction products after a given length of time (52, 66, 86, 95, 113, 129, 214, 226, 231, 255).

There are several variations on this general theme. The one most widely mentioned is the mixing of hydrogen, a hydrogen-containing gas, methane, coal gas, the gas produced in the process, or even water vapor with the hydrocarbons undergoing treatment. It is indicated that in this way the hydrogen can be transferred to quite heavy oils and tars with the production of gasoline (51, 95, 199, 220, 239, 256, 257). Catalysts may or may not be present.

The Cherry process utilizing this principle has been the subject of rather intensive development in the past but has not survived in competition with the thermal-pressure process of cracking oil. It is indicated that the methane or hydrocarbon gas acts as a carrier for the hydrocarbon vapors and furnishes hydrogen so that carbon formation is prevented in the reaction zone. The process resembles the "vapor-phase" process for cracking petroleum, using substantially atmospheric pressure. The hot oil vapors are passed through corona discharge chambers made of metal and arranged so that the inner electrode is insulated from the outer vessel. A fusedquartz insulated lead-in wire connects with the inner electrode. The normal conversion to gasoline is 16 to 25 per cent upon passage through the process. If the process is run without energizing the corona tubes, it is found that the conversion to gasoline drops and the antiknock quality of the gasoline is lower.

The gasoline produced is highly olefinic and resembles "vapor-phase" gasoline in many of its characteristics, especially since it requires special methods of treating to make a marketable product. The gasoline is said to be high in antiknock quality. The reported range was 54 to 77 "benzol equivalent". From this we estimate 68 to 80 A.S.T.M. motor method (50, 219).

The next variation in the electrical process of making gasoline is to combine the use of thermal energy, catalysts, and electrical energy. The catalysts which have been proposed include carbon, uranium, radium, thorium, nickel, silver, cobalt, iron, magnesium, copper, molybdenum, lead, tantalum, and tungsten. The process may be varied so that the catalyst and the electrical energy act on the oil at different stages or they may be combined. One of the methods proposed for effecting this combination has been to maintain a high-frequency field in the catalyst bed (2, 76, 152, 238).

The high-frequency field has also been proposed without the use of any intentional catalyst (114).

It is indicated that natural gas, methane, or other hydrocarbon gases can be converted into gasoline by the simultaneous action of a high-frequency current and a catalyst consisting of coke impregnated with cuprous chloride (190).

Petroleum cracking is also accomplished by passing hydrocarbon gases through an arc, so that highly active particles are formed and pass directly from the arc into oil vapors preheated to 425°C. (244).

### D. MISCELLANEOUS PROCESSES

It has been proposed to crack petroleum gases or coal gas in high-tension silent discharges to lower the molecular weight, decrease the condensing point, and increase the volume (61). Conversely, it has also been proposed that motor fuels and lubricants be made from methane in the silent discharges (74, 75, 211).

Silent discharges in hydrocarbon gases in the presence of metallic lead have been used to produce lead compounds for raising the antiknock quality of gasoline (246).. The same use has been made of arc discharges (245).

It has also been conceived that a petroleum reaction chamber might be made like a giant radio tube having a heated filament to supply electrons by thermionic emission and a charged plate to accelerate the electrons across the reaction zone. The accelerated electrons would cause chemical reaction (183).

The glow discharge in benzene is a potential method for making diphenyl (143).

The manufacture of "higher" olefins and acetylenes by treating ethylene in the arc (84), butadiene from fuel oil in the arc (59), and olefins and diolefins by passing hydrocarbon gases through granular materials heated by an arc (125) has been patented.

## VI. General Discussion

It is readily apparent from the preceding pages that electricity is a powerful tool for causing hydrocarbons to react. So powerful is this tool that the full technique for controlling it completely to cause only desired reactions is not yet known. Yet enough is known to show that many useful reactions can be effected in this manner and, as this control technique is learned, more of these reactions will be used on a commercial scale.

As the main reactions of the discharges are *(1)* dehydrogenation–hydrogenation and *(2)* polymerization (condensation)–depolymerization, probably the earliest advances in controlling the reaction will be to separate these reactions so that any one can be used to the exclusion of the other. As this is done the reactions may be used to make rubber, synthetic resins and plastics, drying oils, antiknock motor fuel, and tough lubricants. Most of the principles are known and most of the reactions are known; the optimum conditions remain to be found. There is every reason to believe that in most cases the power consumption will be within economic reason when these optimum conditions are found.

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