ferent conditions, and, if possible, to obtain equilibrium values before any definite statement may be made concerning the mechanism of the process.

Other Properties.—Germanic nitride resembles the corresponding compound of silicon in its remarkable stability. It is not affected by air at ordinary temperatures. It is insoluble in water and all the common inorganic solvents. It is not attacked by water at 100°. A boiling solution of sodium hydroxide does not liberate nitrogen as ammonia from the nitride. Strong acids appear to affect it slightly.

Summary

Germanic nitride has been prepared by reacting metallic germanium with ammonia gas at 700°. Germanic oxide may be used in place of germanium in this reaction.

The nitride is readily reduced by hydrogen at 700° to germanium and ammonia. This process serves as a method of analysis for the germanium and nitrogen.

The oxidation of the nitride to germanic oxide by means of oxygen at 850° proceeds rapidly. Chlorine gas reacts with germanic nitride at high temperatures.

The color, dissociation and other properties are discussed.

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A SPECTROSCOPIC STUDY OF THE DECOMPOSITION AND SYNTHESIS OF ORGANIC COMPOUNDS BY ELECTRICAL DISCHARGES. I. THE ELECTRODELESS DISCHARGE

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1. Introduction

While the effects of electrical discharges upon organic gases and vapors have been investigated extensively, little has been known concerning the mechanism of their action. Thus the final condensation products have been studied, but there has been practically no knowledge of the decomposition products formed initially in the discharge.

In certain respects the conditions in low voltage discharges resemble those in flames, although the velocities of the free electrons are commonly greater in the former. In flames produced by the combustion of organic hydrogen compounds in oxygen, molecules of water, of hydroxyl (OH), of carbon (C_2) and of carbon monoxide, are present. These molecules also exist in electrical discharges which pass through organic vapors, provided these contain the elements oxygen and hydrogen as constituents. In flames an excess of oxygen converts the carbon partly into carbon dioxide. In electrical discharges in pure organic vapors such an excess of oxygen is not present, so that practically no carbon dioxide is formed, and oxygen and carbon are combined almost entirely as carbon monoxide. Carbon is present as molecules of C_2, of CH, and as carbon atoms and singly charged positive carbon ions (C^+), while hydrogen is found also as atoms (H).

Such atoms, ions and molecules are obviously extremely active, and unite rapidly to form very complex organic liquids or solids. For example, Lind and Glockler[1] found that silent, semi-corona and corona discharges effect the condensation, with a liberation of hydrogen and some methane, of the lower saturated hydrocarbons and of ethylene. With the ozonizer type of discharge, the products are almost entirely liquid, whereas the corona type of discharge yields as much resinous solid as liquid product. Similarly, Lind and Bardwell[2] found that α-radiation causes the condensation of the lower saturated hydrocarbons with elimination of hydrogen and methane and the formation of higher saturated and unsaturated hydrocarbons, which may be gaseous, liquid or solid. Carbon monoxide gives carbon, carbon dioxide and a solid, presumably a suboxide of carbon. With unsaturated compounds, Lind, Bardwell and Perry[3] obtained solid polymers from acetylene, cyanogen and hydrogen cyanide under the influence of α-particles, and a colorless liquid condensate from ethylene upon elimination of one-sixth of its content of hydrogen.

The effect of canal rays was studied as early as 1906 by Kinoshita,[3a] who worked with several gases, including acetylene, and obtained characteristic line and band spectra. More recently, Kohlschütter and Frumkin[3b] investigated the decomposition of hydrocarbons by canal rays.

The electrodeless discharge, as the writers have reported,[4] is a convenient means of effecting the polymerization or condensation of organic compounds. Thus, when benzene vapor at a pressure of 0.1 mm. (relatively low compared to the pressures used by Lind and his co-workers) is subjected to the electrodeless discharge, a greenish-white, ring-like glow appears, concentric with and adjacent to the coil of wire which supports the discharge. This glow immediately spreads through the entire flask, and is extinguished in a red flash, since the benzene is converted into a solid, so that the pressure falls too low to carry the discharge. If, how-

[1] Lind and Glockler, This Journal, **50,** 1767 (1928); **51,** 2811, 3655 (1929).

[2] Lind and Bardwell, *ibid.*, **47,** 2675 (1925); **48,** 2335 (1926).

[3] Lind, Bardwell and Perry, *ibid.*, **48,** 1556 (1926).

[3a] Kinoshita, *Physik. Z.*, **8,** 35 (1907).

[3b] Kohlschütter and Frumkin, *Ber.*, **54B,** 587 (1921).

[4] Harkins and Gans, This Journal, **52,** 2578 (1930).

ever, benzene vapor is continuously admitted at the proper pressure, the discharge persists as a brilliant white ball, and a brown solid deposits on the walls of the vessel. The formula of this product is $(CH)_n$. The spectrum from the discharge shows that the benzene is first decomposed into neutral hydrogen (H) and carbon (C) atoms, into singly charged carbon ions (C^+), and into molecules of carbon (C_2) and monohydrocarbon (CH).[5]

Other organic substances form similar compounds and give related spectra. If oxygen is present in the substances, molecules of water, of hydroxyl (OH) and of carbon monoxide are formed as intermediate products, as has already been stated. If nitrogen, but not oxygen, is present, cyanogen (CN), nitrogen (N_2), singly charged N_2^+ ions and imine (NH) molecules are formed.

In general, these atoms, molecules and ions react with each other very rapidly, almost instantaneously, to form products of higher molecular weight. For example, benzene is decomposed and the fragments unite to form a reddish-brown solid almost as rapidly as the benzene vapor can flow into the flask at the proper reduced pressure. One exception is the product water, which is relatively inactive and does not seem to unite to any very great extent with the other materials produced by the decompositions.

2. Apparatus and Procedure

The apparatus used in these experiments is shown in Fig. 1. Here F is a 1-liter pyrex flask which contains the vapor studied. Over the mouth of the flask, a quartz window Q is attached with de Khotinsky cement. The tube E, sealed to the neck of the flask, acts as a trap for any solid product which may be thrown against the window, and, when necessary, as a liquid-air trap. Around the flask, in the plane passing through the

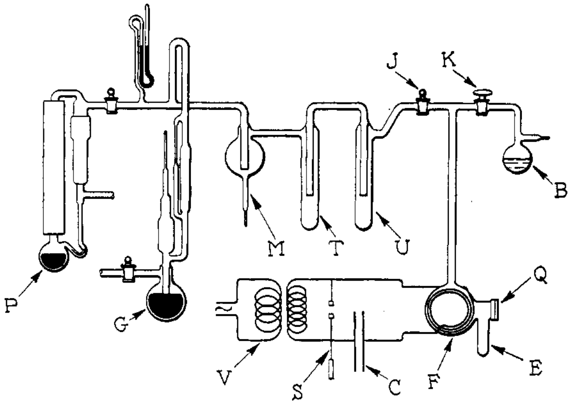

Fig. 1.

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[5] This is confirmed by Austin, This Journal, **52**, 3026 (1930).

window, is tightly wound a vertical coil of six turns of insulated, heavy copper wire. In addition to this coil, the high-frequency circuit consists of a 1 kv. a. Thordarson transformer V which supplies 25,000 volts, a spark gap S capable of adjustment by a screw and made of cylindrical zinc electrodes 1.7 cm. in diameter, and a 0.02 microfarad condenser C of 14 squares of sheet metal immersed in transformer oil between plates of double-strength window glass in a metal container. The frequency of the circuit, as determined with a radio receiver, was about 1100 kilocycles per second.

Vapor is admitted to the flask F from the supply bulb B. Mercury vapor from the diffusion pump P, which is backed up by a Cenco Hyvac pump, is kept from the flask by the liquid-air trap T, while the liquid-air trap U prevents the substance in the bulb from getting into the pumps. The special McLeod gage G is capable of measuring pressures up to several millimeters of mercury.

The compound to be studied, properly purified and dried, is distilled into the bulb B, which is then sealed, except for the outlet through stopcock K. After the air is pumped out of the bulb, stopcock K is closed and the apparatus is completely evacuated. Stopcock J is now closed permanently, the electrodeless discharge is started and vapor is admitted to the flask F through stopcock K. The vapor, as it enters the vessel, is decomposed with emission of light and formation of the products already mentioned.

The discharge is very sensitive to pressure changes and operates at low pressures. With a very volatile liquid, the stopcock K must therefore be opened only very slightly, and it is sometimes necessary to surround the bulb B with a properly chosen cooling agent. The vapor pressure of a relatively non-volatile solid or liquid may not be high enough at room temperatures to support the discharge, in which case that part of the apparatus which lies to the right of stopcock J is enclosed in a box which contains an electrical heater capable of maintaining the contents of the box at 60° or more. When the pressure in the flask F is correctly controlled, the decomposition can be continued without interruption for several hours. Should the compound form products whose vapor pressure is too high at ordinary temperatures, the side-arm E is surrounded with liquid air. The discharge causes a considerable evolution of heat, which is dissipated by the use of a fan.

The light which passes out through the window Q is focused on the slit of a spectrograph. In this work a Hilger E1 quartz spectrograph and a Steinheil GH glass spectrograph were used. A small plane silver mirror, placed when desired at an angle of 45° just in front of the quartz window, throws the spectrum of an ion arc on each plate, for comparison. For work in the visible region, panchromatic plates were used. The deposition of a firmly adhering film of product necessitated a change of window after each exposure, which lasted from one-half to two hours.

3. Purification of Compounds

The compounds studied were benzene, acetylene, naphthalene, *n*-heptane, aniline, nitrobenzene, phenol and chlorobenzene. Acetylene was prepared[6] by dropping ethylene dibromide into 30% alcoholic potash at its boiling point. To remove vinyl bromide the gases evolved were passed through a series of two coil condensers, through which ice-water was circulated. The acetylene was collected over water, passed over phosphorus pentoxide and repeatedly through a trap surrounded by carbon dioxide snow to remove water and any remaining vinyl bromide. The acetylene was finally isolated in the bulb B over liquid air. C. P. naphthalene was used. With the other compounds, the middle fractions obtained by distillation of the C. P. reagents were dried over sodium,

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[6] This procedure was suggested to us as the best method for preparing pure acetylene by Prof. M. S. Kharasch.

phosphorus pentoxide, or anhydrous sodium sulfate, and distilled into the bulb B under reduced pressure.

4. Effects of the Electrical Discharge

(a) **Benzene.**—With benzene, no liquid air was required around the side tube E. In half an hour several thousand liters of vapor were admitted continuously to the discharge vessel, and decomposed, yet not enough permanent gas accumulated in the flask to extinguish the discharge, despite its sensitivity to pressure changes. This is evidence that the fragments produced by decomposition reunite completely to form the reddish-brown solid observed. Analysis of the product gave $(C_{1.00}H_{1.00})_n$ as its average composition. It was insoluble in ordinary solvents, although a continuous extraction with xylene in a Soxhlet apparatus for three weeks yielded a brown solution which left a small amount of gummy, viscous liquid on evaporation of most of the solvent. On further heating the product charred before the xylene was completely removed. No fraction could be pumped off from the solid *in vacuo*, although it was heated above 100° and liquid air was used as the condensing medium. A sample of the solid gained 1.0% in weight after being exposed to the atmosphere for twenty days, and 2.5% after sixty-six days, through absorption of oxygen, adsorption of water vapor, or both.

Benzene vapor at a pressure of 0.25 mm. of mercury could be decomposed by the discharge only when the spark gap was increased to 6 mm. At lower pressures, not so long a spark gap was required. Thus, at a pressure of 0.14 mm., a spark gap of 3 mm. sufficed, while at 0.03 mm. pressure, a spark length of 1.5 mm. effected decomposition. At a pressure of about 0.1 mm., approximately 1.2 g. of solid was produced per hour.

These data are summarized in Table I. The first column gives the color of the initial ring discharge, greenish-white in the case of benzene. In the second column is the color of the brilliant glow within the flask when decomposition is in progress. This glow completely fills the flask at intermediate pressures, but shows a non-luminous core at higher pressures. It was this glow, white for benzene, which was photographed. The next column of Table I gives the color of the product. The solid formed on the walls, and peeled off as a powder, as thin flakes or as thick scales, depending on the substance decomposed. The physical form of the product is listed in the fourth column. That part of the solid which did not peel off clung tenaciously to the glass, but could be cleaned away by filling the flask with water, which seemed to get between the glass and the film with great ease. A fresh, dry flask was used for each substance. In the last column is given the approximate rate of formation of the product in grams per hour at an intermediate pressure. Data for all the substances studied are presented in Table I.

TABLE I

Substance	Color of discharge Ring	Glow	Color of product	Form of product	Rate of formation of product, g. per hour
Benzene	Greenish-white	White	Medium brown	Powder and small scales	1.2
Acetylene	Bluish-white	White	Medium brown	Powder and small scales	1.3
Naphthalene	Violet-white	White	Very dark brown	Thick scales	1.2
n-Heptane	Bluish-white	Reddish-white	Yellow brown	Very thin scales	0.00
Aniline	Violet-white	Bluish-white with red spots	Medium brown	Powder and scales	0.9
Nitrobenzene	Bluish-white	White	Dark brown	Thick scales	0.7
Phenol	Violet-white	White with red spots and greenish-blue center	Medium brown	Powder and scales	0.4
Chlorobenzene	Greenish-white	Greenish-white with red at center	Black	Powder and thick scales	0.4

Photographs of the decomposition spectrum for benzene are shown in Figs. 2 and 3. The fainter portions, easily visible in the original plates, are here indiscernible, because of repeated reproduction. The spectrum taken with the Steinheil instrument, Fig. 2, extends from 6600 to 3800 Å., and that taken with the Hilger spectrograph in the first position, Fig. 3a, from 6600 to 3300 Å. Spectrograms were also secured with the Hilger instrument in the second position, which carried the work down to 2400 Å. in the ultraviolet.

The decomposition spectrum of benzene showed all five groups of Swan bands very prominently. The other C_2 bands, discovered by Deslandres and D'Azambuja[7] and analyzed and discussed by Dieke[8] and by Johnson[9] were also present, though faintly, at λ4102, λ4068, λ4041, λ3852, λ3826, λ3607, λ3593, λ3588, λ3400 and λ3398. The CH bands at λ4300 and λ3900 were both prominent, and the first five lines of the Balmer series of hydrogen, H_α to H_ϵ, were very apparent. The line spectrum of C^+ and the line due to C at λ2478 were also present. The relative intensities are tabulated in Table II, which lists similar data for all of the compounds investigated.

When the decomposition was carried out at the lowest possible pressures, the nature of the spectrum was changed. The glow itself became

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[7] Kayser, "Handbuch der Spektroscopie," Vol. V, 234.

[8] Dieke, *Nature*, **125**, 51 (1930).

[9] Johnson, *ibid.*, **125**, 89 (1930).

TABLE II

RELATIVE INTENSITIES

	Substance							
	Benzene	Acetylene	Naphthalene	*n*-Heptane	Aniline	Nitrobenzene	Phenol	Chlorobenzene
Exposure, hrs....	0.5	0.75	0.5	0.5	1	2	1.5	1
Intermediate decomposition product								
CH	4	3	2	2	3–4	2	3	
Swan C_2	5	4	4		4	3	3	1
C_2[a]	2	2			1	1	2	
C^+ (C)	3	2	2	1	3	3	3–4	1
H	4	4	3	5	3	3	3	3
CN					5	5		
NH					2–3			
N_2					2	2		
N_2^+					2	2		
CO						2	1	
OH						3	3	
Cl								5

[a] C_2 bands other than Swan bands.

1, Very weak; 2, weak; 3, average; 4, intense; 5, very intense.

much redder and weaker and what bands appeared were very feeble in intensity. The Balmer series for hydrogen became relatively more prominent, and, despite the precautions taken to keep mercury vapor out of the discharge vessel, there appeared an intense line spectrum of mercury corresponding to that excited by the spark, rather than the arc.

The spectrum thus indicated the intermediate existence of C^+ ions, C and H atoms and CH and C_2 molecules during the decomposition of the benzene.

(b) **Acetylene.**—The product obtained with acetylene resembled that for benzene. To cool the side tube E was not necessary. The spectrum was the same as for benzene. The details are given in Tables I and II.

(c) **Naphthalene.**—Naphthalene produced a very dark brown product, which flaked off the glass in thick scales. No liquid air was required around tube E. The initial electromagnetic ring discharge did not show as great a tendency as with benzene to spread through the flask to give decomposition. The decomposition spectrum differed from that for benzene in its lower intensity for the same time of exposure.

(d) ***n*-Heptane.**—*n*-Heptane reacts differently from the unsaturated hydrocarbons. Although an amber-colored solid was formed on the walls, the quantity was very slight. When the discharge vessel was filled with *n*-heptane vapor at the proper pressure and stopcock K was closed, the pressure on decomposition seemed to rise slightly, rather than to fall. If fresh vapor was admitted to the flask, the discharge was extinguished because of the increase in pressure. Nor was the passage of the discharge made possible when the side tube E was immersed in liquid air, if vapor was continuously admitted to the flask. No liquid products were visible. The gaseous products could not be condensed with liquid air. The spectrum consisted of the Balmer series, which was very prominent, of the CH bands, which were faint, and of the C line at λ2478. In addition, an intense mercury spectrum was present, as it was for benzene when decomposed at the lowest pressures.

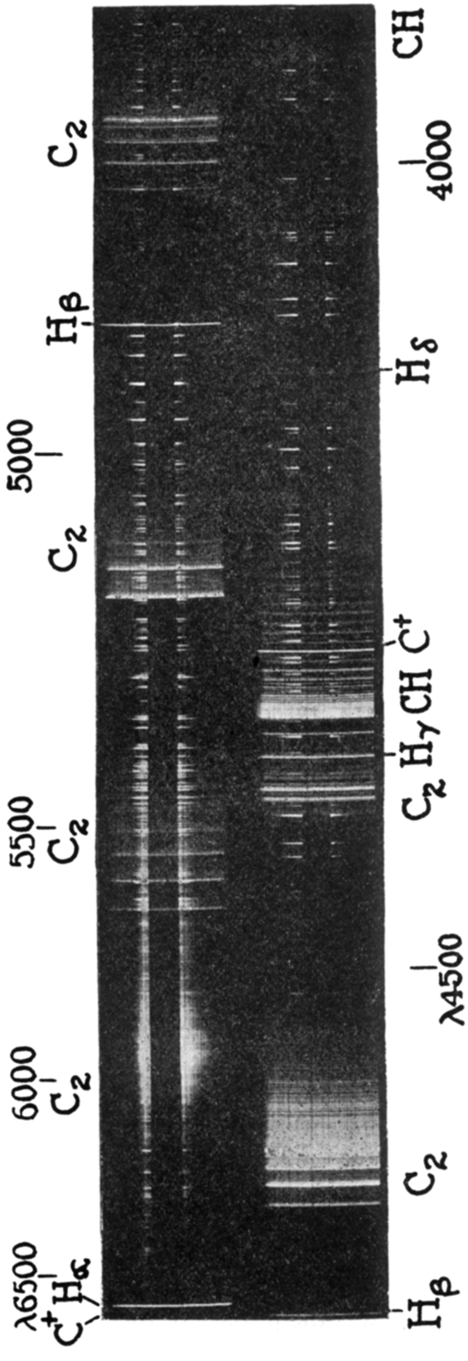

Fig. 2.—Spectrum obtained when benzene is decomposed in the electrodeless discharge. Taken with a Steinheil GH glass spectrograph. The spectrum of the iron arc is also shown.

(e) **Aniline.**—With aniline, it was necessary to immerse the side tube E in liquid air in order to keep the pressure low enough for the discharge to pass. The product had a strong odor of bivalent carbon compounds, which made difficult the detection by smell of ammonia and the lower amines, but neutral litmus paper, when inserted into a freshly opened flask F, rapidly turned blue.

In the spectrum, the violet cyanogen bands were prominent, from Group II at λ4532 to Group V at λ3590. The β-bands of NH, at λ3360 and λ3370, were visible. The second positive group of N_2 appeared at λ3577, λ3371 and λ3159, and the first negative group, due to N_2^+, showed at λ3914. The spectrum characteristic of benzene was also present, although subdued. The spectrogram obtained for aniline with the Hilger spectrograph in its first position is reproduced in Fig. 3b, next to that for benzene.

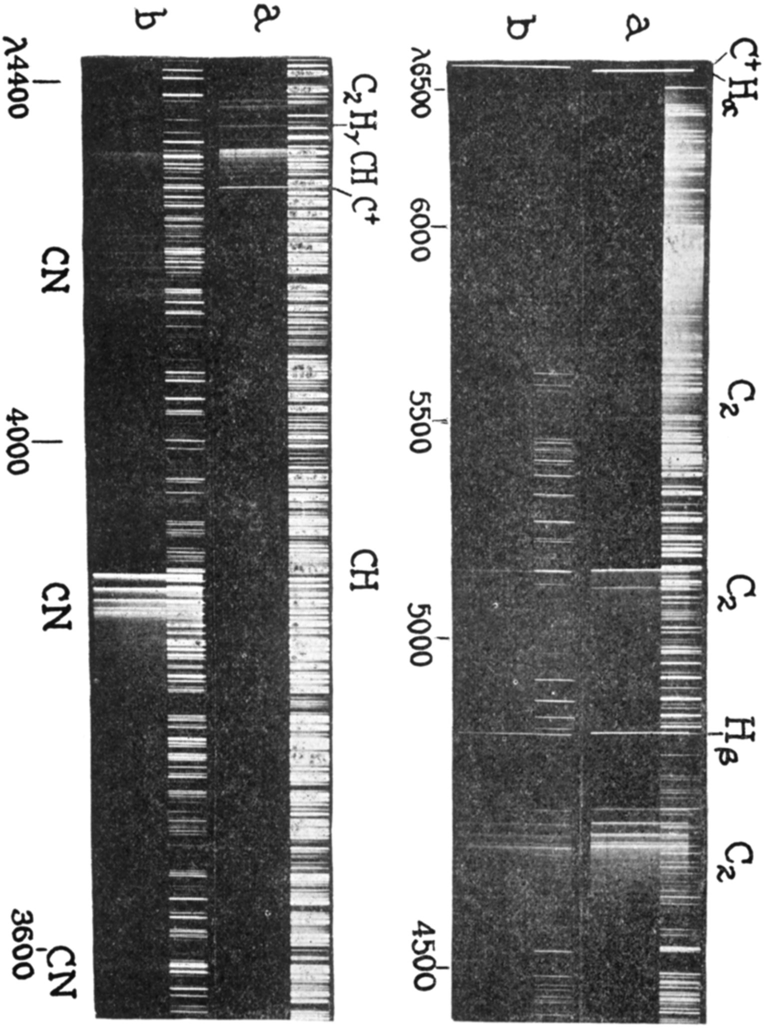

Fig. 3.—(a) Spectrum given by benzene when decomposed in the electrodeless discharge. Taken with a Hilger El quartz spectrograph. The narrow spectrum is that of the iron arc. (b) Spectrum obtained with aniline, showing cyanogen bands not found with benzene.

(f) **Nitrobenzene.**—For continuous decomposition, nitrobenzene required liquid air at E. The product did not have the strong odor of the solid from aniline, and was dark and coarse, although a slight deposit that formed at the neck of the tube E was much lighter in color, a characteristic that was observed also with other compounds. Moist neutral litmus paper was not affected when it was held in a flask F opened just after the end of an exposure. The spectrum was in general like that for aniline, but showed also the OH band at λ3064 and the CO bands at λ2974 and λ2832, as for phenol. A search for NO bands was made down to λ2200, but none was found after a two-hour exposure.

(g) **Phenol.**—To condense the water vapor which phenol forms on decomposition, liquid air was kept around the tube E. In addition to the typical benzene decomposition spectrum, phenol showed the water vapor band, for which the carrier is OH, at λ3064, and, faintly, the third positive group of carbon, due to CO, at λ2974 and λ2832.

(h) **Chlorobenzene.**—With chlorobenzene, also, the tube E was cooled with liquid air. The product was black, and neutral litmus thrust into a freshly opened flask quickly turned red, indicating the presence of hydrogen chloride. The spectrum consisted almost entirely of the line spectrum of chlorine, as excited by the spark, but the first three lines of the Balmer series for hydrogen were present. Also, some of the lines due to C^+ and C and part of the Swan bands were very faintly visible.

4. Discussion

The electronic energy utilized in breaking up the molecules is in part given off as radiation, and the energy of this radiation gives some idea of the range of the electronic energy and velocity involved. This range is from 1.8 to 5 volts, which corresponds to velocities from 8×10^7 to 1.3×10^8 cm. per sec. and to energies from 41 to 115 kg. cal. per mole. Undoubtedly electron velocities below this are effective in breaking up the organic molecules, but such velocities correspond to the infra red spectrum, which has not been investigated. According to Hittorf[10] and J. J. Thomson[11] the electrodeless discharge is due to electromagnetic induction, but Townsend and Donaldson[12] consider it to be caused by the electrostatic potential. MacKinnon[13] has shown that Thomson's work has been confined to the ring discharge, which is electromagnetic in origin, while the relatively weaker glow discharge investigated by Townsend and Donaldson is electrostatic. In the present work both types of discharge existed, but the decomposition always started as a ring discharge.

It may be assumed that the decomposition of the organic vapors into simpler molecules, atoms and ions is due to free electrons. These gain velocity, due to the field, between impacts. The higher the pressure of the gas, the smaller the mean free path of these electrons, and the more rapidly must the electrons gain velocity in order to attain any definite final velocity at the time of impact with a molecule. For this reason

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[10] Hittorf, *Wied. Ann.*, **52**, 473 (1884).

[11] J. J. Thomson, *Phil. Mag.*, [7] **4**, 1128 (1927); [5] **32**, 321, 445 (1891).

[12] Townsend and Donaldson, *ibid.*, [7] **5**, 178 (1928).

[13] MacKinnon, *ibid.*, [7] **8**, 605 (1929).

it is necessary to increase the voltage on the coil as the pressure of the gas increases, if the discharge is to continue to pass. Since there are great differences in the individual electron mean free paths as well as differences between the electrostatic and the electromagnetic fields, the individual electrons attain very different velocities before impact. If the velocities are in general too small, the discharge will not pass through the gas, since not enough ions and free electrons are produced.

It is not the intention of the preceding paragraph to indicate that the effects of ions, produced by electron bombardment, in causing ionization and dissociation by collisions of the second kind are negligible. There may be, in addition, some dissociations produced by collisions of the first kind, other than those due to electrons.

The writers wish to thank the National Research Council for a grant which has enabled them to secure a Steinheil GH glass spectrograph for use in this and other spectroscopic work.

5. Summary

1. In the electrodeless discharge organic vapors are commonly decomposed into simpler molecules, atoms, ions and electrons. For example, benzene is rapidly decomposed into molecules of monohydrocarbon (CH) and of carbon (C_2), into atoms of carbon (C) and of hydrogen (H), and into singly charged positive ions of carbon (C^+). Phenol gives all of these products and molecules of hydroxyl (OH), of water (H_2O) and of carbon monoxide (CO) in addition. Aniline gives the same decomposition products as benzene, and also single molecules of cyanogen (CN), of imine (NH), of nitrogen (N_2) and singly charged molecular nitrogen ions (N_2^+). Acetylene and naphthalene give the same products as benzene.

2. The intermediate decomposition products listed in (1) are extremely active and unite very rapidly to form brown or black solids which are insoluble in water and organic liquids, and which doubtless have high molecular weights.

3. *n*-Heptane, unlike the unsaturated hydrocarbons, gives very little solid in the type of apparatus here employed. During the decomposition of this saturated compound there exists much atomic hydrogen (H), relatively few molecules of monohydrocarbon (CH) and some neutral atoms of carbon (C).

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