FREE RADICALS IN ELECTRICAL DISCHARGES.

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If any organic gas or vapour is used to carry an electrical discharge, of the type of the electrodeless or the glow discharge, diatomic molecules are formed in which pairs are formed between all of the unlike or like atoms present. These are revealed by the band spectra which they produce. The bands are most prominent in the visible spectrum, but are also numerous in the ultraviolet region. In addition certain atomic and ionic spectra are more or less prominent.

Thus benzene, acetylene, or any other compound of the general formula $(CH)_x$, gives spectra which show that the molecules, presumably most largely by electron impact, are decomposed into neutral hydrogen (H), and carbon (C) atoms, into singly charged carbon ions (C^+), and into molecules of dicarbon (C_2) and monohydrocarbon (CH). These unite with each other very rapidly to form molecules of very high molecular weight of the same general formula $(CH)_x$ in the electrodeless discharge, but with a slight deficiency of hydrogen when produced in the glow discharge (*e.g.* $(C_{1.00}H_{0.89})_n$). As produced by the electrodeless discharge the solid flakes are of a reddish brown colour, while the glow discharge gives solid substances of various colours, such as brown, white and black, together with some liquid material.

In flames produced by the combustion of organic hydrogen compounds in oxygen, molecules of water, of hydroxyl (OH), of dicarbon (C_2), and of carbon monoxide, are present. In electrical discharges through organic compounds which contain oxygen, all of these molecules are formed, together with those formed from benzene, and the spectroscope reveals the presence of the singly charged carbon monoxide ion (CO^+) in the glow discharge.

A spectroscopic study of the decomposition and synthesis of organic compounds in the electrodeless and glow discharges, as carried out by Dr. D. M. Gans,[1] Dr. John M. Jackson,[2] and the writer, gave spectra which revealed the presence in discharges through various organic vapours, of the atoms H, C, and S, of the molecules CO, H_2, S_2, and N_2, of the ions N_2^+, C^+ and CO^+, and of the free radicals, which are also molecules, of hydroxyl (OH), monohydrocarbon (CH), imine (NH), dicarbon (C_2), monocyanogen (CN), and carbon monosulphide (CS). In addition water and ammonia were formed.

By the use of a mass spectrograph Eisenhut and Conrad—Ludwigshafen[3] have found evidence of the presence of the ions C^+, CH^+, CH_2^+, CH_3^+, and CH_4^+, and of similar ions with a larger number of carbon atoms, while Stewart and Olsen[4] found that hydrocarbons with long chains are broken down into those with shorter chains by the impact of the ionising electrons.

[1] William D. Harkins and D. M. Gans, *J. Amer. Chem. Soc.*, **52**, 5165-75, 1930.
[2] William D. Harkins and John M. Jackson, *J. Chem. Physics*, **1**, 37-47, 1933.
[3] H. O. Eisenhut and R. Conrad, *Z. Electrochem.*, **36**, 654, 1930.
[4] H. R. Stewart and A. Olsen, *J. Amer. Chem. Soc.*, **53**, 1236, L 1931.

Apparatus.

(*a*) **Electrodeless Discharge.**—The apparatus used for the decomposition of organic vapours by the electrodeless discharge consisted of a 1 litre quartz or pyrex glass flask (F), (Fig. 1). With a glass flask the

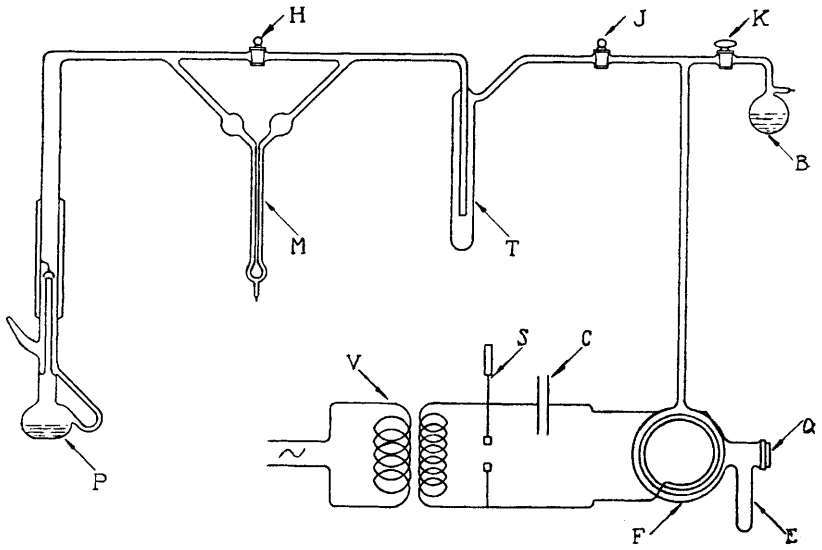

FIG. 1.—Apparatus for electrodeless discharge.

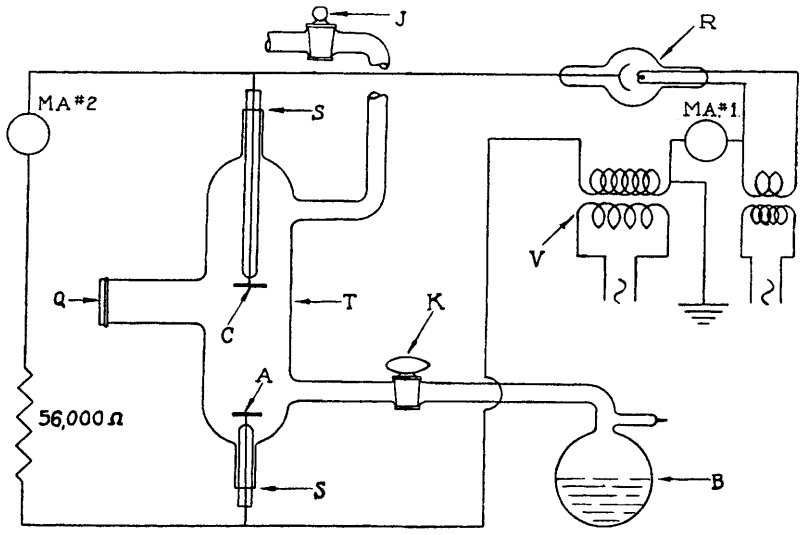

FIG. 2.—Apparatus for glow discharge.

quartz window (Q) was used in front of the slit of the spectroscope. Around the flask in the plane of the window was a coil of six turns of copper wire. The tube (E) served to collect the product formed by the reaction in the flask. In addition to the coil the high frequency circuit consisted

of a 1 k.v.a. Thordarsen transformer (V) which supplies 25,000 volts maximum, a spark gap (S) capable of adjustment by a screw, and made of cylindrical zinc electrodes 1·7 cm. in diameter, and a 0·025 microfarad condenser. The frequency of the circuit as determined by a radio receiver was 800 kilocycles per second.

(*b*) **Glow Discharge.**—The apparatus for the glow discharge was somewhat similar, but a kenetron (R, Fig. 2) was used to rectify the low frequency current from the transformer. The electrodes (C) were aluminium discs 2 cm. in diameter.

Large Hilger quartz, and Steinheil glass spectroscopes were used and the intensity of the radiation emitted was measured by a Kipp thermopile and a Weston galvanometer. The tube (T) was mounted vertically in such a way that the images of the cathode glow, negative dark space, and negative glow, were photographed simultaneously.

Effects of Electrical Discharges.

(*a*) **Electrodeless Discharge.**—Benzene, xylene, mesitylene, and methane, have hydrogen to carbon atomic ratios of 1·00, 1·25, 1·33 and 4, respectively. With benzene vapour at about 0·2 mm. pressure, the discharge used up the gas rapidly, and 5000 litres of vapour could be allowed to pass into the flask and disappear, without changing the characteristics of the discharge. Evidently no gaseous product is formed by the decomposition. If the inflow of the vapour was stopped the discharge was quenched almost immediately. With xylene and mesitylene the discharge would also operate for long periods without the use of a cooling agent on the tube (E, Fig. 1), but stopping the inflow of vapour did not extinguish the discharge. The initial discharge with these substances is a greenish-white ring which changes to a white glow. If the inflow of vapour is stopped the colour becomes a very brilliant red, which shows that the intensity of the α-line of the Balmer series has been greatly enhanced. All of these vapours give a spectrum in the visible region somewhat similar to that of benzene as shown in Fig. 3. The characteristics of the discharges are given in Table I., and Table II. lists the relative intensities of the band and atomic spectra.

As was expected the intensity of the spectra of H and CH relative to C_2 increase as the ratio H/C increase. However no bands corresponding to CH_2 or CH_3 appeared.

TABLE I.

Substance.	Colour of Discharge.		Maximum Pressure, 1·5 cm. Gap.	Colour of Product.	Form of Product.	Rate of Formation of Product, gm. per hour.
	Ring.	Glow.				
Xylene .	Greenish-white	White to red	0·26 mm.	Light brown	Powder and scales	1·0
Mesitylene .	Greenish-white	White to red	0·30 ,,	Light brown	Powder and scales	0·8
Methane .	Greenish-white	White to red	1·01 ,,	Light brown	Scales	0·0
Pyridine .	Greenish-blue	Bluish-white to brown	0·28 ,,	Dark brown	Powder and scales	1·8
Benzaldehyde	Greenish-blue	Blue and red to red	0·37 ,,	Dark brown	Powder and scales	1·2
Thiophene .	Intense green	Purple to red	0·19 ,,	Dark brown to black	Some powder and heavy scales	0·7

(*b*) **Glow Discharge.**—In contrast with the effect of the electrodeless discharge in benzene vapour, the glow discharge, after being well started, will operate continuously without the admission of fresh vapour, which seems to indicate that not all of the hydrogen is chemically combined. The spectrum is shown in Fig. 4, while Fig. 5 exhibits the corresponding spectrum of methane.

With continuous admission of benzene vapour it was found in one experiment that about 10 moles of benzene were decomposed per equivalent of current passed. The average wave-length of the radiation was estimated to be about 4200 Å, and about 100 molecules of benzene were decomposed per quantum of radiation which escaped through the quartz of the discharge tube used for this experiment. Probably a considerable amount of radiation is absorbed inside the vapour.

The characteristics of the effects in the glow discharge are exhibited by Tables III., IV. and V.

TABLE II.—Relative Intensities.

	Substance.					
Exposure, hours.	Xylene. 0·5.	Mesitylene. 5·5.	Methane. 3.	Pyridine. 1.	Benzaldehyde. 1.	Thiophene. 1.
Intermediate Decomposition Product.						
CH	4	4-5	3-4	3	3	3
Swan C_2	4	4-5	2	3	3	3
All other C_2	2	3	1	1	0-1	0-1
C+(C)	3	2-3	4	3	4	3-4
H	4-5	4-5	5	4	4	4
CN				5		
NH				3		
N_2				2		
N_2^+				2		
CO					1	
OH					2	
S						4
S_2						3
CS						5

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

TABLE III.

Substance.	Colour of Discharge.	Colour of Product.	Form of Product.	P.D. in Volts.	Rate of Formation of Product, gm. per hour.	Moles per Equivalent of Current.	Molecule per Quantum of Radiation.
Benzene	Blue-green to white	Black to yellow	Powder and gum	800	0·5	9·87	102
n-heptane	Blue-green to pink	Black to brown	Powder	800	0·15	2·47	25·5*
Methane	Blue-green to pink	Black to brown	Powder	450 to 650	0·03	3·28	38·2*
Pyridine	Blue to violet	Black to brown	Powder and scales	800	0·14	2·75	
Phenol	Blue-green	Black to brown	Powder and scales	650	0·16	2·40	

* Estimated assuming radiation equal to that from benzene decomposition.

TABLE IV.—Relative Intensities for Glow and Electrodeless Discharges.

	Substance.									
	Benzene.		*n*-heptane.		Methane.		Pyridine.		Phenol.	
Exposure, hours .	*G.* 4.	*E.** 0·5.	*G.* 5.	*E.** 0·5.	*G.* 3·5.†	*E.* 3.	*G.* 4.	*E.* 1.	*G.* 2.†	*E.* 1·5.
Intermediate Decomposition Product.										
CH . .	4	4	4	2	4	3	3	3	2	3
Swan C_2 . .	3	5	3	0	0	2	1	3	2	3
All other C_2 .	2	2	2	0	0	1	0	1	0	2
C . .	1	3	1	1	?	3	3	3	4	3-4
C^+ . .	0	3	0	1	0	0	0	3	4	3-4
H . .	5	4	5	5	5	5	4	4	4	3
H_2 . .	3	0	4	0	4-5	0	1	0	1	0
CO . .									4-5	1
CO^+ . .									4-5	0
OH . .									3	3
CN . .							5	5		
N_2^+ . .							4	2		
N_2 . .							0	2		
NH . .							3	3		

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

* Data taken from previous paper (reference 11). Heptane is not a fair comparison because there was no pumping out in the electrodeless experiment.

† Time is for Steinheil instrument, others are for Hilger.

TABLE V.—Relative Intensities in Different Parts of the Discharge.

Intermediate Decomposition Product.	Substance.														
	Benzene.			*n*-heptane.			Methane.			Pyridine.			Phenol.		
	a.	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*
CH . .	4	3-4	3	4	3-4	3	4-5	4	4	3	2	1	2	1	0-1
Swan C_2 .	3	3	2	3	3	2	0	0	0	1	1	0-1	2	1	0
All other C_2 .	1	2	1	2	2	1	0	0	0	0	0	0	0	0	0
C . .	1	1	0	1	1	0	?	?	?	3	3	2	5	4	3
C^+ . .	0	0	0	0	0	0	0	0	0	0	0	0	4	4	4
H . .	5	5	5	5	4	4	5	4-5	4-5	4	4	3	4-5	4	4
H_2 . .	0-1	3	3	1	4	4	4-5	4-5	4-5	0-1	1	1	1	1	1
CO . .													5	4	3
CO^+ . .													4	4	4
OH . .													3	2	1
CN . .										5	5	5			
N_2^+ . .										3	3	4			
NH . .										3	3	3			

Key: *a*, cathode glow; *b*, edge of negative glow; *c*, negative glow about 5 mm. from edge. 1, very weak; 2, weak; 3, average; 4, intense; 5, very intense.

Discussion.

A free radical is a molecule in such a peculiar high energy state, with reference to its union with a like or unlike radical, as to be difficult to isolate under ordinary conditions. Free radicals are extremely reactive toward each other and also other compounds.

The principal radicals found in electrical discharges through organic vapours are CH, OH, C_2, NH and CN. These are without exception diatomic. No bands were found which could correspond with the presence of other radicals, such as CH_2, CH_3 or NH_2. From the evidence of positive rays it is known that the positive ions which would be formed by the loss of an electron by each of these radicals, exist under somewhat similar conditions. However positive ray analysis is extremely sensitive to the presence of small amounts of ions. A special search for NH_2 bands in these discharges has been begun.

The absence of the bands of triatomic and higher molecules may be due to either of the following conditions :—

1. The number of such radicals present is small, and since the number of lines produced would be much greater than with diatomic molecules, the energy is distributed over so many lines that they are too indistinct to be apparent.

2. Positive ions of the type of CH_2, etc., which consist of three or more atoms, may dissociate upon taking up an electron, or such radicals may exhibit the phenomenon of predissociation.

The Baldet-Johnson bands of CO^+, which require electrons of the order of one hundred volts of energy for their formation are found in the glow discharge, but not in the electrodeless discharge. This may be due to the higher pressure in the former, but the principal factor is a higher electron energy.

It is probable that the energy of electron impact is the most important factor in the smashing of the molecule into the free radicals, ions, and smaller molecules which are formed in the discharge. There must be many positive ion impacts, but evidence points to the fact that they are ineffective until they acquire velocities comparable to the electron velocities required to produce dissociation or ionisation.[5]

Collisions of the second kind also play an important part in the reaction. The fact that in the glow discharge the rate of reaction is the most rapid, and that one of the most intense portions of the spectrum is located at the edge of the negative glow, where the density of high velocity electrons is the greatest, confirms the importance of electron impacts in the reaction. Inner absorption of the radiation is also a factor, but of unknown importance.

One of the most interesting features of the experiments was the rapidity with which the free radicals (CH and C_2), the atoms (H and C), and the ions (C^+) unite with each other to form a substance of very high molecular weight of exactly the same composition as benzene. This exhibits the very great reactivity of such free radicals. These free radicals are formed by discharges in the insulating sheath which covers the cables which conduct high tension electricity underground. Such cables often cost many thousand pounds per mile, and they are ruined by the union of the free radicals with other products to form substances of high molecular weight.

[5] K. Compton and I. Langmuir, *Rev. Mod. Physics*, **2**, 123, 1930.

In the reactivity and general effects in such reactions as have been discussed in this paper, a free radical is not essentially different from a free atom such as H or C, so free atoms and free radicals may in this sense be considered as constituting a single class.

In the earlier studies of the chemistry of electrical discharges through organic vapours it has been tacitly assumed that the principal reactions are those of large ions, such as $(CH)_6^+$, or $(CH)_6^-$, and that these form ion clusters in such a way as to give the resultant products of high molecular weight. The effects of free radicals and atoms was entirely neglected. The present work indicates that the effects of free atoms and radicals, together with those of ions, which are probably mostly small, are sufficient to explain what occurs. However this does not prove that these particles do not enter into reaction with a part of the molecules initially present.