REACTIONS IN THE BRUSH DISCHARGE*

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PART I

The Decomposition of Acetone

M. L. Maquenne working with organic vapors in the silent electric discharge found a decided similarity between the products formed by the discharge and the products formed by the pyrolysis of the same compounds. His first work on this subject¹ was with formic acid. He worked with a discharge tube similar to one introduced by Berthelot.² He reduced the pressure in the tube by means of a water pump so that there would be a more uniform discharge. He showed that the volume of hydrogen formed was always very nearly equal to the volume of carbon dioxide formed. This was true also for the gases which Berthelot found were produced by the pyrolysis of formic acid. This, he said, made evident a decided similarity between the two types of decomposition. In both cases the reactions were:

 $HCOOH = CO_2 + H_2$ $HCOOH = CO + H_2O$

In a second paper on silent electric discharges³ he describes work done with the same apparatus. He says that all substances studied *except benzene* (i.e. formic acid, methyl alcohol, ethyl alcohol, acetic acid, acetone, and methyl formate) decomposed rapidly. Quoting from his article: "Tous les corps étudiés, sauf la benzine quí résiste aux tensions électriques employées (15 millimètres d'étincelle avec condensateur), se décomposent rapidement dans un tube à effluves en oxyde de carbone, acid carbonique, hydrogène et carbures: les gaz sont les mêmes qu'on obtient par la chaleur au rouge sombre, et souvent leurs proportions relatives sont extrêmement voisines."

Because of the importance of Maquenne's conclusions it seemed wise to scrutinize carefully his gas analyses. He did not describe them in detail, but he did say that he had to resort to atmolysis in order to separate the hydrogen from the methane and ethane. He analysed for carbon monoxide by absorption in cuprous chloride solution. In some of his analyses he absorbed carbon monoxide and acetylene together in cuprous chloride. The cuprous chloride method for the determination of carbon monoxide is not now considered to be reliable. Concerning his work on ethyl alcohol he says that the gas had the odor of aldehyde and acetylene, and he continues in the same sentence to say that the gas was washed with water before proceeding with the analysis. If

^{*} For an excellent description of electric discharges, see Warner and Kunz, "Corona Discharge," Univ. of Ill. Bull. 114.

¹ Bull, (2) 39, 306 (1883).

² Ann. Chim. Phys., (5) 12, 463 (1877).

³ Maquenne: Bull., (2) 40, 60-65 (1883).

he really wanted to know what was present in the gas it is hard to see what good he expected to accomplish by washing it with water; perhaps he thought it would remove the aldehyde. It is this sort of treatment that causes one to question the value of his analyses.

In summarizing his expectations concerning the behavior of acetone in the discharge he says: "La facilité avec laquelle l'oxyde de carbone se produit dans toutes les décompositions précédentes [decomposition of ethyl alcohol, methyl alcohol, acetic acid, and formic acid] nous a fait penser que l'acétone puorrait se dédoubler, par l'effluve, en oxyde de carbone et éthane; l'expérience a complètement vérifié cette prévision." The gases obtained from acetone in the silent electric discharge were as follows:

discharge tube	low	low	50 mm.	100 mm.
Carbon dioxide	Ι.Ι	o .6	Ι.Ι	0.6
Carbon monoxide	37.5	36.3	40.0	42.1
Ethylene	4 · 3	4 · 4	3 · 5	2.9
Ethane	32.4	33.7	29.7	30.0
Hydrogen	24.7	25.0	25.7	24.4

Acetone decomposed by heat was changed to gas of the following composition:

dull red	above dull red
I,2	o .6
39.5	36.0
7.0	3.3
22.4	21.8
29.9	38.3
	dull red I.2 39.5 7.0 22.4 29.9

These figures are strikingly similar to the ones in the preceding table. From these data Maquenne concluded that the reactions occurring in the silent electric discharge are comparable with those due to high temperature.

Alexander v. Hemptinne¹ working with acetone vapor in an electric discharge decided that acetone was decomposed by it primarily into carbon monoxide and ethane because these were the principal constituents of the gas. This was obviously the main primary reaction but it was probably not the only one. He suggested that methane was probably produced by a secondary reaction. He did not go any deeper into the intricacies of the reactions.

G. Poma and A. Nesti² working with acetone in a discharge tube of the ozonizer type found that it was decomposed by a 42-cycle current into a gas mixture containing

1.6% carbon dioxide

- 5.0 acetylene and ethylene
- 38.1 carbon monoxide
- 55.3 methane and ethane

Prossure in the

¹ Z. physik. Chem., 25, 292 (1898).

² Gazz., 51 II, 87-88 (1921).

The potential difference across the tube was from 5,000 to 10,000 volts. From the gas analysis they concluded that the main reaction was

$$CH_3 - CO - CH_3 = CO + C_2 H_6$$

This was about the only conclusion that could be drawn, because the acetylene and ethylene were not determined separately and the methane and ethane also were grouped together. Their analysis was not complete enough to enable them to draw any further conclusions about the reactions that produced the gas. Their examination of the exposed acetone revealed the presence of a γ -diketone which they said might be acetonyl acetone. The residue that was left after the acetone was evaporated was fractionally distilled. This fractionation demonstrated to them in striking fashion the complexity of the residue. Translating from their article, "a fractional distillation quickly demonstrated the remarkable complexity of the liquid mixture remaining from the proceeding distillation. The thermometer mounted without interruption, showing no tendency to hesitate at any temperature, until the product finished by decomposing and becoming resinous."

Because Maquenne had shown that silent electric discharges and pyrolysis produce similar products, it seemed advisable to look up work done on the pyrolysis of acetone before experimental work was started with the brush discharge.

Barbier and Roux¹ found that gases produced by the pyrolysis of acetone consisted of carbon monoxyde, methane, ethylene, and hydrogen. They were unable to find ethane in the mixture. They explained this by saying that under the conditions under which they were working ethane was known to decompose into ethylene and hydrogen. In the light of later work² it seems probable that ethane was never formed.

Schmidlin and $Bergman^3$ in 1910 reported ketene as a product of the pyrolysis of acetone. Since that time much work has been done on the reaction.

Peytral⁴ passed acetone vapor through a short platinum tube heated to 1150°C. She concluded from her analyses of the gaseous products that the main primary reaction was the formation of ketene, thus:

$$CH_3COCH_3 = CH_4 + CH_2CO$$

She thought that this reaction was followed by a secondary reaction in which some of the ketene was broken up into ethylene and carbon monoxide. The ethylene thus formed was decomposed to some extent into acetylene and hydrogen. She did not list ethane as a product. This is in accordance with the observations of Barbier and Roux,⁵ but not in accordance with the data eited by Maquenne.⁶

¹ Bull., (2) 46, 268 (1886).

² Peytral: Bull., (4) 31, 122 (1922).

³ Ber., 43, 2821 (1910).

⁴ Bull., (4) **31**, 122 (1922).

⁵ Bull., (2) 46, 268 (1886).

⁶ Bull., (2) 40, 60-65 (1883).

The most favorable conditions for the production of ketene by pyrolysis have been worked out by Hurd¹ and his associates. These conditions give consistent yields of ketene that range from thirty-five to forty-five percent based on unrecovered acetone.

Considering the extent to which this reaction takes place under favorable conditions when acetone is pyrolyzed, it seemed worth while to look for ketene in the products formed when acetone is decomposed by a brush discharge. It is not surprising that it was not listed as a product by Poma and Nesti² in their work on electric discharges through acetone vapor. In the apparatus used by them, if ketene had been formed, it would probably have been dissolved by the acetone in their reflux condensers and carried back to the flask of boiling acetone. The ketene would then have boiled rapidly out of the solution and would have been exposed again to the discharge. The process would have repeated until it was decomposed.

Ketene is very soluble in acetone. Schmidlin and Bergman³ report that twenty-three percent of the total yield of ketene was dissolved in the condensed acetone. The apparatus that gives the best yields of undissolved ketene⁴ was designed so that it would separate the ketene from the condensed acetone as quickly as possible. The solubility of ketene in acetone was used to advantage in the present research. The apparatus that was used was designed so that the gas that was being collected would have to pass through the condensed acetone. Thus most of the ketene was retained by it.

It seemed probable that ultra-violet light emitted by the discharge might play an important part in the decomposition of acetone. Berthelot and Gaudechon⁵ have shown that acetone is rapidly decomposed by a 110-volt quartz mercury lamp into a gas containing 40% carbon monoxide, 5%methane and 46% ethane. The predominating reaction in their work was:

$$CH_3COCH_3 = CO + C_2H_6$$

Apparatus

The apparatus used in this work on acetone is shown in Fig. 1. It consists of a flask, A, in which acetone is vaporized; the discharge tube, B; a heater, C, for the discharge tube; a pneumatic trough, H; a water-jacketed tube, FG, for collecting the gas; a leveling bulb, M, which is used to run mercury into FG; and a source of high frequency current.

The discharge tube was simply two concentric glass tubes, R and S, with an aluminum foil electrode, D, around the outside tube and a two millimeter copper wire electrode inside the inside tube. All the important dimensions except the diameter of the small tube are given on the drawing. This small inner tube had an outer diameter of four millimeters and an inside diameter of slightly more than two millimeters.

¹ "Organic Syntheses," 39 (1925).

² Gazz., **51** II, 87-88 (1921).

³ Ber., 43, 2821 (1910).

⁴ Hurd: "Organic Syntheses," 39 (1925).

⁵ Compt. rend., 151, 478-481 (1910).





The High-Frequency Alternating-Current Apparatus

When a charged condenser discharges through a circuit of low resistance the current that flows has a very high frequency. This principle was utilized in the production of the high-frequency current. Three Leyden jars charged by means of a sixty thousand volt transformer were allowed to discharge through a closed circuit of low resistance. The high-frequency current that was thus generated was made available for laboratory use by including the primary of an air-core transformer in the closed circuit. The secondary of the transformer was connected to the discharge tube. The circuit used in this work was very similar to the old-fashioned wireless spark-transmitter hook-up. The main difference was that the wires that ordinarily would lead to an antenna and ground were connected instead to the two electrodes of the

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discharge tube. The circuit is shown in Fig. 2. Morecroft¹ discusses such circuits in a very enlightening way. He says, concerning the function of spark gaps in these circuits: "In order that the condenser may be charged to the high potentials required for large energy storage, and to permit its discharge in a suitable closed circuit of low resistance, that circuit must contain an element whose resistance decreases instantaneously when the condenser discharges and remains at a very low value during the period of discharge. This requirement is fulfilled by the ordinary spark gap, the resistance of the gap being very high before breakdown occurs, but decreasing to a very small value when the gap has broken down under the increasing potential impressed



across its terminals. The spark gap and spark are thus essential to transmitters generating high-frequency oscillations by means of condenser discharges."

The parts of the high-frequency current generator and their functions may be summarized as follows: A is a 3 KVA transformer capable of transforming 110 volts to 60,000 volts. It was used to charge the three Leyden jar condensers, C. The spark gap, B, automatically closed the condenser circuit when a high enough potential had been reached. While sparks were passing across the gap the condensers were discharging and therefore a high-frequency current was passing in the circuit, BCD. The air-core transformer, E, transferred the high-frequency current from the closed circuit to the electrodes of the reaction tube. The primary of the air-core transformer consisted of six turns of heavy copper wire. The secondary was made up of sixty-five turns of annunciator wire. Both the primary and the secondary were supported by a wooden frame. The choke coils, F, were mounted directly on the terminals of the transformer. They were placed in the circuit so that the high frequency current could not pass back into the transformer.

A Description of the Discharge

Warner and $Kunz^2$ say that "electrical discharges in gases at pressures near that of the atmosphere may be divided into five classes. These are:

1. "The dark discharge, where a small current passes through gas without making itself visible.

¹ "Principles of Radio Communication," 330, 357 (1927).

² Univ. Illinois Bull., 16, No. 114 (1919).

2. "The glow discharge, where a larger current passes and the gas in the immediate neighborhood of the electrodes becomes faintly luminous.

3. "The brush discharge, such as that from points where the glow is irregular and extends into the gas some distance from the electrodes.

4. "The spark discharge, which is a transient phenomenon bridging the whole distance between the electrodes, accompanied by a bright light and a comparatively large current.

5. "The arc, in which a large current passes between the electrodes in the gas and the ionized vapors of the electrodes producing a continuous light.

"Any one of the first forms of discharge may be converted into one of the latter forms by an increase in the potential between the electrodes, depending upon the nature and pressure of the gas and the spacing, size, capacity, and shape of the electrodes."

This classification is obviously an arbitrary one. The discharge used in the work on acetone was, according to this classification, more a brush discharge than anything else. The discharge was made up largely of streamers. A large number of fine sparks also were passing. When the potential was raised gradually it was difficult to tell just when the sparks started to pass. At high potentials the tube seemed to bristle with these very fine hair-like sparks. Whether or not the sparks were passing, the predominating discharge seemed to be due to streamers.

Experimental Part

Acetone was placed in the flask, A. The temperature of the water bath around A could be kept uniform at any desired temperature. Thus with a uniform application of heat the acetone vapor would pass through the discharge tube at a more uniform rate. When the work was started it was not known whether or not the rate of flow of vapor through the tube would affect the results. Therefore the water bath was used as an aid in obtaining reproducible conditions and also to prevent superheating. Later it was found that this precaution was unnecessary.

The acetone vapor passed up through the heated discharge tube and was expelled under mercury at I. After all air had been swept out of the tube the mouth of the mercury filled bulb, FG, was placed over I. The high-frequency current was then turned on and a stop-watch was started. As the acetone vapor and gas passed up through the water-jacketed tube, G, the acetone was condensed and the gas collected over the liquid acetone. When F was filled with liquid acetone and gas, the discharge was turned off and the time read on the stop-watch.

It was necessary to correct the results of the gas analyses for gases dissolved in the condensed acetone and also to remove the acetone vapor from the gas sample before the analysis was started. Solubilities of the gases in acetone were found in Seidell: "Solubilities of Organic and Inorganic Substances." Due to the fact that acetylene is extremely soluble in acetone it was not considered necessary to analyse for it in the gas. At 25° C and one atmosphere, one liter of acetone dissolves 15.231 grams of acetylene. Analysis of the condensed acetone showed that there was only a small amount of acetylene present. This justified leaving it out of the gas analysis. The acetone vapor was removed from the gas samples by passing it through a coil of glass tubing immersed in a bath made from solid carbon dioxide and ether. Since the temperature of this bath was never below -78° , none of the constituents of the gas except the acetone were condensed. All other constituents except ketene boiled at temperatures below -78° C. The percentage of ketene was so low in the samples that its very low partial pressure would prevent it from condensing at -78° C.

The condensed acetone had to be analyzed for two constituents, acetylene and ketene. The total volume of the acetone condensed was measured. A known portion of this was used for each.

The analysis for acetylene was made as follows: About a half gram of copper sulphate was dissolved in 25 cc of hot water. Ammonium hydroxide was added until the solution was dark blue. Hydrazine sulphate was then added to the warm copper solution until it became pale blue. The acetone that was to be analyzed for acetylene was added. Cuprous acetylide was precipitated as a red powder. This was filtered off by suction and washed with dilute ammonia and finally with water. The precipitate was dissolved on the paper with hot 6 N hydrochloric acid. The paper was washed with dilute ammonia. About 2 cc of nitric acid and 5 cc of concentrated sulphuric acid were added. The solution was then evaporated until sulphur trioxide fumes were given off. This treatment converted all cupous ions to cupric. The copper was then titrated with thiocyanate using a method described in Scott's "Standard Methods of Chemical Analysis," third edition. The thiocyanate solution was standarized in cc's of acetylene under standard conditions.

Ketene was determined by a method similar to one used by Schmidlin and Bergman.¹ Water was added to the portion of the acetone that was to be analysed for ketene. The solution was then heated to boiling and the acetic acid was titrated with standard sodium hydroxide using phenolphthalein as indicator. The alkali was standardized in cubic centimeters of ketene at standard conditions.

The gas was analysed in a Hempel apparatus using the following methods of determination:

Gas	Method of determination
Ketene	Absorption in potassium hydroxide
Ethylene	Absorption in fuming sulphuric acid
Oxygen	Absorption in alkaline pyrogallol
Hydrogen	Combustion with copper oxide at 270°C
Carbon monoxide	Combustion with copper oxide at 270°C
	followed by absorption of carbon
	dioxide in potassium hydroxide.
Paraffins	Combustion with oxygen in a Dennis
	combustion pipette.

¹ Ber., 43, 2823 (1910).

			TA	BLE I					
	-	ы	3	4	5	9	7	×	6
Time of run (min and sec)	6^{-28}	001	004	12-46	14-26	11-36	11-00	8-00	001
Temp. discharge tube $\pm 5^{\circ}$	285.	285.	285.	285.	285.	285.	285.	285.	285.
cc of gas formed	221.8	206.0	202.0	170.0	192.0	196.6	189.8	209.5	169.4
ce of acetone condensed	18.9	31.6	21.5	65.o	43.4	30.3	50.2	48.8	76.8
Summary of gas analyses	Air-free	e.—Correct	ted for Dis	solved Ga	ses.				
Ketene	ri.8	6.9	4.7	6.2	6.7	4.9	5.2	5.8	6.3
Ethylene	7.5	9.1	8.2	8.5	9.3	5.3	7.0	9.9	8.9
Acetylene	trace	trace	trace	trace	trace	trace	0.8	0.0	Ι.Ι
Hydrogen	13.9	14.6	14.I	11.4	12.6	12.I	14.0	15.5	16.6
Carbon monoxide	34.2	34.9	38.4	37.8	36.3	35.8	38.6	35-3	35.5
Ethane	20.1	23.0	21.6	23.7	23.4	25.5	26.0	25.6	1.91
Methane	12.4	11.4	13.2	12.5	11.6	16.4	8.6	6.9	12.5
	10	11	12	13	14	15			
Time of run (min and sec)	3.18	2^{-43}	2-55	2-52	26	2-57			
Temp. discharge tube $\pm 5^{\circ}$	110.	110.	110.	110.	285.	285.			
ec of gas formed	153.0	129.0	189.0	187.6	129.4	178.1			
cc of acetone condensed	122.0	80.2	17.5	16.3	70.8	87.0			
Summary of gas analyses	-Air-free	e.—Correct	ted for Dis	ssolved Ga	scs.				
Ketene	5.7	4.5	3 . 1	0.4	4 · 5	3.8			
Ethylene	14.0	10.9	11.0	11.2	13.8	9.1			
Acetylene	0.0	1.6	0.7	0.7	1.5	2.2			
Hydrogen	18.0	19.2	19.4	19.6	21.0	23.0			
Carbon monoxide	34.7	33 - 5	37.8	38.0	32.9	36.4			
Ethane	0.0	11.7	18.7	15.2	11.4	IO.0			
Methane	17.8	18. 5	0.5	15.0	14.0	15.4			

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The data obtained from fifteen runs are given in Table I. The information obtainable from analytical data concerning the happenings in a discharge tube is fragmentary. It must be pieced together in order to give it meaning. After it all has been fitted into its proper place, a story more or less complete, should result. The completeness of the data determines the completeness of the reconstructed story. If every carbon, hydrogen, and oxygen atom originally present in the decomposed acetone vapor is accounted for by the analysis the whole story can probably be reconstructed.

The limitations of the data obtained in this work may be seen from the percents of carbon, hydrogen, and oxygen in the gas. These values, which are tabulated below, were calculated from the gas analyses. The percentage composition of acetone is given for reference.

	Carbon	Hydrogen	Oxygen
Acetone	62.02%	10.42%	27.56%
Analysis No. 1	60.3	10.2	29.5
2	61.5	II.O	27.5
3	60.6	10.6	28.8
4	61.2	10.5	28.3
5	61.4	10.7	27.9
6	60.3	10.8	28.9
7	61.3	10.7	28.0
8	62.2	10.9	26.9
9	60.7	10.7	28.6
10	60.4	10.5	29.I
II	60.5	II.2	28.3
I 2	60.4	10.7	28.9
13	60.3	II.I	28.6
14	61.3	11.1	27.6
15	58.8	10.4	30.8

It is evident that the composition of the gas is very nearly the same as the composition of the acetone. Therefore when a molecule of acetone is broken up into gaseous products it is changed completely to gas. Condensations with elimination of a gas do not occur to any great extent.

With these facts in mind one can proceed with confidence to the actual solution of the problem.

In the light of previous work on the decomposition of acetone by electric discharges, and the work on decomposition by pyrolysis it seems probable that some of the following reactions would be the ones that take place:

I.
$$CH_3COCH_3 = I CO + I C_2H_6$$

2.
$$CH_3COCH_3 = I CH_2:C:O + I CH_4$$

3. $CH_3COCH_3 = I CH_2:C:O + \frac{1}{2}C_2H_6 + \frac{1}{2}H_2$

There may be other reactions in which acetone is changed entirely to liquid or solid products. Such reactions were not looked for or investigated in any way. The only observation related to that subject made during this research was that a small amount of a brown solid material (a few milligrams) collected on the electrodes during a long series of runs.

In all of the reactions listed above, one volume of acetone vapor decomposes to give two volumes of gas. The volume of acetone vapor decomposed to form the sample of gas is equal to the volume of CO plus the volume of ketene since these constituents contain all the = CO groups originally present in the acetone. The sums of these volumes are tabulated below:

Analysis Number	Volume of CO plus ketene	Analysis Number	Volume of CO plus ketene
I	46.0 cc	9	41.8cc
2	41.8	10 •	40.4
3	43.I	II	38.0
4	44.0	I 2	40.9
5	43.0	13	38.4
6	40.7	14	37.4
7	43.8	15	40.2
8	41.1		

If the reactions listed above were the only ones taking place, the sum of the volumes of carbon monoxide and ketene should be fifty in each analysis because the analyses are calculated for a 100 cc air-free sample. The volumes range from $_{38}$ to $_{46}$. Since these values are equal to the volume of acetone decomposed, the corresponding volume of gas formed according to the above reactions would range from 76 to 92. In each case it should be 100.

The first secondary reaction that suggests itself is the decomposition of ketene. Under ordinary conditions ketene is very reactive.

4. $_2CH_2CO = CH_2 + CO$

This reaction may be written without the intermediate formation of ketene.

5. $2 \text{ CH}_3\text{COCH}_3 = \text{CH}_2\text{CH}_2 + 2\text{CO} + 2 \text{ CH}_4$ 1 volume $2\frac{1}{2} \text{ volumes}$

The volume of acetone decomposing according to this last equation is equal to two times the volume of the ethylene. If the formation of ethylene and carbon monoxide from ketene is the only secondary reaction the following relation should be true:

 $2\frac{1}{2}(2 \times \text{vol. CH}_2\text{CH}_2) + 2$ (acetone decomposed $-2 \times \text{vol. of ethylene}) = 100$ The calculated values are tabulated below:

Analysis No.	Calculated value	Analysis No.	Calculated value
I	99.5	9	92.5
2	92.7	10	94.8
3	94 - 4	II	88.7
4	96.5	I 2	92.8
5	95.3	13	88.0
6	86.7	14	88.6
7	94.5	15	89.5
8	92.I		

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These values range from 86.7 to 99.5. This brings out in striking fashion the fact that all of the reactions have not been accounted for.

If the predicted reactions were correct the sum, volume of ketene $+ 2 \times$ the volume of ethylene, should equal the amount of ketene originally formed, because when two ketenes decompose one ethylene is formed. The amount of ketene formed should also be equal to the sum of the volume of methane and twice the volume of hydrogen, because according to the predictions methane and hydrogen are formed only during the formation of ketene. These two sets of values are tabulated below for comparison:

Analysis No.	Ketene + $2(C_2H_4)$	$\mathrm{CH}_4+2\mathrm{H}_2$
I	26.8	40.2
2	25.I	40.6
3	21.1	4I.I
4	23.2	35.3
5	25.3	36.8
6	I5.5	40.6
7	19.2	36.6
8	25.6	37.8
9	24.I	45.7
10	33 · 7	53.8
II	26.3	56.9
I 2	25.1	48.3
13	23.2	54.2
I.4	32.1	56.9
15	22.0	61.0

The entire lack of similarity between these columns of figures makes it evident that the assumed secondary reaction is not adequate to explain the gas analysis data. It indicates where the trouble lies. Methane and hydrogen are too high.

The obvious source of the excess hydrogen is from the ethane. The reactions that might occur to produce it are:

- 6. $CH_3CH_3 = CH : CH + 2 H_2$
- 7. $CH_3CH_3 = CH_2:CH_2 + H_2$
- 8. $CH_3CH_3 = CH_4 + C + H_2$

The method of interpretation up to this point has been to assume that the speculative reactions are correct and then test them out with the data. Continuing in this way we see that since acetylene is produced only in reaction number six, it may be considered as a measure of that reaction. The ethane originally formed in reaction one can be calculated by adding the ethane decomposed in reactions six, seven, and eight to the undecomposed ethane. The volume of ethane thus calculated should of course be equal to the volume of carbon monoxide. The ethane decomposed is equal to the volume of hydrogen minus that of the acetylene.

Analysis No.	Ethane undecom.	Ethane decom.	Total	Carbon monoxide
I	20.I	13.9	34.0	34.2
2	23.0	14.6	37.6	34.9
3	21.6	14.1	35.7	38.4
4	23.7	II.4	35 I	37.8
5	23.4	12.6	36.0	36.3
6	25.5	12.1	37.6	35.8
7	26.0	13.2	39.2	38.6
8	25.6	14.6	40.2	35.3
9	I9.I	15.5	34.6	35.5
10	9.0	17.1	26. I	34.7
II	ïI.7	r7.6	29.3	33.5
12	18.7	18.7	37-4	37.8
13	15.2	18.9	34.I	38.0
14	1I.4	19.5	30.9	32.9
15	10.0	20.9	30.9	36.4

In most of the analyses the total ethane agrees with the carbon monoxide as well as could be expected. In numbers x, 5, 7, and 12 the agreement is remarkably good. In S, 10, and 15 the difference is rather large. When the carbon monoxide is larger, it could be explained by saying that some ketene decomposes to produce it. In this case we would expect the ethylene to be somewhat higher than the average. This is, in general, true. The change in ethylene content, however, would not be so marked because one volume of ethylene is formed for each two volumes of carbon monoxide. When the ethane is larger than the carbon monoxide, it could be explained by saying that some ethane has decomposed into carbon and hydrogen. This would cause the ethane to appear larger because the volume of ethane decomposed is calculated from the hydrogen present. It is hardly worth while to push such speculation any farther because of the limitations already pointed out on page 3339.

Conclusions

1. As a general rule, when gaseous products are formed from an acetone molecule, the *whole molecule* is changed to gaseous products. Condensation with liberation of gases does not occur to any great extent.

2. The principal reaction occurring to produce gas is:

$$CH_3COCH_3 = CH_3CH_3 + CO$$

Ethane is produced only in this reaction. A review of the literature has shown that this reaction does not occur during the pyrolysis of acetone. It can not, therefore, be attributed to heat effects in the region of localized discharges. Berthelot and Gaudechon have shown that acetone is rapidly decomposed according to the above equation by ultra-violet light. In our work some or all of the decomposition into carbon monoxide and ethane must have been caused by the light emitted by the discharge. 3. Ketene is produced, just as in the pyrolysis of acetone, by the following reaction:

$$CH_3COCH_3 = CH_2C:O + CH_4$$

Most of the ketene formed remains undecomposed. The percentage of it, however, is small. In most of the runs it was about five percent of the gas formed. Conditions are important in the production of ketene by pyrolysis. It is not surprising, therefore, that the yield of ketene was small in this work for no attempt was made to obtain optimum conditions.

4. The hydrogen, ethylene, and acetylene present in the gas come largely from the decomposition of ethane:

$$CH_3CH_3 = CH : CH + _2H_2$$

$$CH_3CH_3 = CH_2:CH_2 + H_2$$

$$CH_3CH_3 = CH_4 + C + H_2$$

PART II

The Decomposition of Benzene

Mignonac and Saint-Aunay¹ working with benzene in the silent electric discharge found that it was changed into gas and condensation products The composition of the gas was found to be:

Hydrogen	52.0%	Ethylene	7.2%
Acetylene	32.8	Ethane	7.2

They concluded that the discharge caused the following changes:

- 1. Depolymerization of benzene into acetylene.
- 2. Formation of condensation products with the elimination of hydrogen.

A large part of the condensation product was found to be diphenyl. They also isolated a hydrocarbon that had a composition corresponding to dihydrodiphenyl. They explain the formation of these two compounds thus: In the formation of diphenyl an activated molecule and an unactivated one come together and hydrogen is eliminated. Dihydrodiphenyl is formed in the same way but without the elimination of hydrogen. Dihydrodiphenyl is thought to be an intermediate in the formation of the diphenyl.

Studies of the pyrolysis of benzene have shown that diphenyl and hydrogen are the principal products.² Considerable amounts of meta and para diphenyl benzenes also have been isolated but no ortho could be detected.

Bates and Taylor³ working with photosensitization have shown that benzene is decomposed by mercury atoms excited by ultra-violet light. The gaseous products were passed through a trap surrounded by liquid air. The gas that came through was analyzed and found to contain 40% hydrocarbons and 60% hydrogen. A "heavy tarry" deposit formed on the walls of the reaction tube. A strong odor of diphenyl was present.

¹ Bull., (4) 47, 523 (1930).

² Hurd. "The Pyrolysis of Carbon Compounds," 93-5.

³ J. Am. Chem. Soc., 49, 2438 (1927).



When work was started on benzene it was found that, just as Maquenne¹ had pointed out in 1883, benzene gave off gaseous products more slowly than acetone. At first the same apparatus was used and a much higher potential was applied between the electrodes of the discharge tube. It was found that the discharge was much more localized under the high potential. The tubes punctured quickly.

An apparatus that was satisfactory was finally designed. Instead of running it at a potential that would eventually puncture the glass it was designed to run at a lower potential for a longer period. It is shown in Fig. 3. The benzene was boiled in the flask, A. The vapor passed up through the heated discharge tube, B, and displaced the air. It was condensed in the watercooled condenser, C, and was returned to the flask by means of the small

¹ Bull., (2) 40, 60-65 (1883).

tube, D. All air except a small amount in the condenser was easily and quickly displaced by the benzene vapor. After the air had been displaced, the leveling bulb, E, was placed so that the pressure in the apparatus was about half an atmosphere with the bulb, F, filled with mercury. This slightly reduced pressure seemed to make it easier for the discharge to pass. It also kept the ground joint, I, pressed tightly down on the apparatus. Suction was then applied to H which was closed when the bulb, F, was filled with mercury. The bore of the stopcock, H, was then mercury-sealed by pouring a little mercury into the tube. The current from a Tesla coil was then turned on.

The discharge used in this work on benzene was similar to the discharge used with acetone. The main difference was that there were not so many of the fine sparks.

The gas that was formed was kept from passing back into the discharge tube by benzene vapor which was continually rising up through the tube from the boiling benzene. Polymerized products condensed with the benzene, and were washed down into the flask. The tendency for them to pass again through the discharge chamber was small because their vapor pressures were low at the boiling point of benzene.

The apparatus gave satisfactory results with the benzene because: (1) the products were swept out of the tube rapidly; (2) the products were not reexposed to the discharge, thus minimizing the tendency for secondary reactions to take place; (3) the apparatus could be kept in use for several hours: (4) it was easy to manipulate.

When a sample of benzene was exposed to the discharge a deposit collected on the walls of the discharge chamber. This deposit was heaviest on the inside electrode where the current density was greatest. The color varied from yellow to almost black. At low potential, the deposit was brownish yellow. This material which formed only in small amounts, was dry and brittle. Some of it would peel off the electrodes and some of it could be removed only by scraping. Solvents were ineffective in cleaning the electrodes.

The gas which formed during the exposure of a sample was collected in the bulb, F. It had an odor very similar to that of acetylene generated from calcium carbide.

The benzene in the flask, A, gradually turned brownish red during the exposure. When this benzene solution was evaporated a brown viscous residue remained. It had an odor which was not at all similar to the odor of the gas.

This is a superficial description of the phenomena.

Reconstructing the Story from Analytical Data

The reconstruction of the story of the "adventures of benzene molecules in a brush discharge" from analytical data depended of course on the accuracy and completeness of the data. The gas analyses presented no unsurmountable difficulties. The technique and patience required for good gas analyses are very well discussed by Martin Shepherd.¹ The gas analyses were carried

¹ Bur. Standards J. Research, 6, 121 (1931.)

out in a modified Orsat apparatus. Analysis for acetylene was made on a separate sample of gas. Copper acetylide was precipitated and the acetylene was found by titration of the copper in the same way that it was done in the work on acetone.

Analysis of the solid products was a puzzling problem. The benzene was evaporated from the solid products that had accumulated in it. An attempt was then made to break up the chocolate-brown residue into fractions. Solvents were first tried. The following solvents were used: benzene, ether, carbon tetrachloride, chloroform, petroleum ether, glacial acetic acid, 85% formic acid, acetone, carbon disulphide, ethyl alcohol, methyl alcohol, and ethyl acetate. The residue would dissolve to some extent in all of these, but chloroform was very much the best solvent. It was surprising to find that it was a much better solvent than carbon tetrachloride. This fact was shown by evaporating a chloroform solution of the residue until it was thick and syrupy and then adding a drop of carbon tetrachloride. A light brown precipitate was formed. This precipitate was filtered off and dissolved in chloroform. When the chloroform was evaporated a *dark brown* residue was left. This residue had the same appearance as the original. Repeated attempts to make a separation by extraction with solvents failed. No crystals could be obtained from solutions containing large amounts of the brown material. The first conclusion that was drawn from this was that probably no crystalline products were present.

Fractional distillation up to 180° C at 20 mm., however, yielded a crystalline distillate that was white with a very slight yellowish tinge. Above 180° C the distillate was decidedly yellow. Distillation was not carried on above 250° C because cracking was obviously taking place. The distillate darkened after standing for a week or two. Diphenyl was isolated from the lower fractions by recrystalization from ether. A small amount of a product which melted at 205° C was also isolated. This was assumed to be p-diphenyl benzene. There was not enough of it to identify it by other means. A short time after this, similar work on benzene was published by Austin and Black.¹ They found p-diphenyl benzene in the products formed from benzene vapor which was exposed to the Tesla discharge.

Almost at the same time that diphenyl was isolated from the residue by distillation and crystalization, crystals were discovered in a test tube that contained some of this resinous product. The test tube had lain on its side undisturbed for about three months. The resin had run along the bottom side of the test tube and the crystals had formed along the top side. The crystals were plates so thin that they could hardly be seen edgewise. A sample of these crystals large enough for a melting point was obtained with some difficulty. It melted at $67^{\circ}-69^{\circ}C$, the melting point of diphenyl.

This suggested that perhaps a quantitative estimation of diphenyl in a sample of resin could be made by subliming out the diphenyl. Two methods of sublimation were tried. The resin was placed in a bulb connected to a wide water cooled condenser. The bulb was heated over an electric light

¹ J. Am. Chem. Soc., 52, 4552 (1930).

bulb for several days but no sublimate formed in the condenser. Thinking that the temperature was not high enough, I tried heating the resin in a bulb connected to a long air-cooled condenser. The heat was applied by means of an electric hot plate. The material simply refluxed and no sublimate formed. After these experiments it was evident that even though crystals had been discovered in the test tube, the time required to produce them would make the method of purification by sublimation useless at this time.

The method that eventually succeeded was steam distillation. The resin was steam-distilled as long as any material would distill. The non-volatile residue was collected. The light yellow distillate was redistilled by steam. This time the distillate was perfectly white but melted twelve degrees below the melting point of diphenyl. A reddish brown residue remained from this distillation. It appeared just like the first to which it was added.

The perfectly white distillate was re-steam-distilled and again a considerable amount of a brown residue remained and a white distillate formed. It was decided to continue the distillations until a white distillate and no residue resulted. Melting points of some of the distillates were taken. Each time the melting point came up nearer that of diphenyl. Finally after twenty-six steam distillations, a pure white distillate resulted and no residue remained. The melting point was the melting point of diphenyl. The distillate was identified as diphenyl by a mixed melting point. These results were disappointing from one point of view. It was desirable not only to get out pure diphenyl but also to get it out easily and completely enough that it could be weighed and called a quantitative estimation. Procedure requiring twentysix steam distillations certainly could not be called quantitative. The most extreme care could not prevent loss of material during such a long process.

Ether was used to dissolve the diphenyl out of the condenser, etc. All beakers used in the work were kept meticulously clean. Whenever a sample of distillate was transferred from a beaker, the beaker was washed inside and out with ether. This was absolutely necessary because of the tendency for diphenyl to "crawl" over the edge of the beaker from the ether solution.

The analysis of the first sample exposed to the discharge showed the following results:

Benzene vapor	13.7%
Acetylene	28.8
Ethylene	9.65
Oxygen	0.3
Nitrogen	2.15
Hydrogen	41.5
Paraffins	3.9
	100.0
Total gas	164. cc.
Room temperature	26.5
Barometer	741. mm.
Time of run	5. hours
Diphenyl isolated	0.5873 gm.

The diphenyl was dried in a desiccator over calcium chloride before it was weighed. Its melting-point was $66^{\circ}-68^{\circ}$. Pure diphenyl melted at $67^{\circ}-68^{\circ}$ C. The mixed melting point was $67^{\circ}-69^{\circ}$ C. The above weight of diphenyl corresponds to 96.3 cc. of hydrogen at 741 mm. and 26.5°C, since diphenyl must have been formed according to the following equation:

$$_{2} C_{6}H_{6} = C_{6}H_{6}.C_{6}H_{6} + H_{2}$$

The hydrogen actually in the sample, $6_{7.2}$ cc, was less than the hydrogen that should have been there due to the formation of diphenyl. A secondary reaction using up some of the hydrogen must have taken place. In the original benzene molecule there was one hydrogen atom for each carbon atom. Hydrogen must have been used up to form the 9.65% ethylene and the 3.9% paraffins. Supposing that the paraffin gas was all ethane we see that 27.6 cc of hydrogen was used to produce these compounds in which the ratio of carbon to hydrogen is 1:2 and 1:3 instead of 1:1 as in the original benzene molecule. The calculated volume of hydrogen added to the volume found in the gas gives 94.8 cc.

This volume was so near the volume calculated from the diphenyl (96.3) that it seemed too good to be true. If these values could be checked in other runs it would mean that all hydrogen, paraffins, ethylenes, and diphenyl had been accounted for. Acetylene would of course be formed by the depolymerization of benzene. The brown resinous product could be accounted for by the polymerization of acetylene. This could then be checked by combustion analysis. This beautiful air castle did not survive the next two analyses; but the data obtained from them were more interesting than those from the first.

When all the information that had been collected concerning the resinous product was rescrutinized for the purpose of speeding up the quantitative estimation of diphenyl it was found that in several instances light colored products changed to darker ones after standing for some time. Thus, the perfectly white distillate from the vacuum distillation turned brown after standing for several weeks. Even before a systematic examination of the resinous product was started, it was noticed that if benzene was left in the discharge apparatus for several days after a run it would change from an amber to a darker brown. There was one other bit of information concerning this color change. A brown residue was formed from a perfectly white material during a steam distillation. With this evidence the following conclusions were drawn: (1) Some material in the diphenyl was slowly changing to a colored form that would not steam distill. The form that would steam distill was colorless. (2) Heat (as in a steam distillation) accelerated this change from colorless to dark brown.

The following procedure was adopted for the purification of diphenyl: Steam distill once and collect the crystalline distillate, remove the water from it, and let it reflux on a hot plate all night. Repeat this process till there is no color change during the refluxing. It was gratifying to find that a perfectly white distillate would turn dark brown after a few minutes refluxing on a hot plate. After six alternate distillations and refluxings and a final distillation pure diphenyl was obtained. During the last period of refluxing there was no color change and *crystals of diphenyl formed inside the neck of the flask*. It should be pointed out that the apparatus used to carry out these refluxings was the same as was used in the first attempts to obtain pure diphenyl by sublimation from the resin. Thus we see that crystals of diphenyl did form in this apparatus but it was after the diphenyl had been purified.

The results from the analysis of the second sample are as follows:

Benzene vapor	12.8%
Acetylene	24.4
Ethylene	10.3
Oxygen	0.6
Nitrogen	2.4
Hydrogen	44.2
Paraffins	5.3
	100.0
Total gas	174.1 CC.
Room temperature	24.5°C
Barometer	740. mm.
Time of run	4. hours
Diphenyl isolated	0.8421 gm.
H ₂ corresponding to diphenyl	127.5 CC.
Volume of H_2 in sample	76.8 cc.

Thus we see that the volume of hydrogen actually in the sample was less than the volume that should have been there. This result is similar to that from the first sample. If corrections are made for hydrogen used to produce ethylene and ethane, the calculated volume of hydrogen is 113.1 cc. This brought to light a very remarkable fact. The hydrogen that should have been present calculated from the weight of pure diphenyl actually isolated was 14.4 cc more than could be accounted for in the gas. This was such an unexpected result that it seemed advisable to check it by another complete run.

The third run was made at a much lower potential. It was supposed that lower potential would decrease the yield of diphenyl. It should, it seemed, decrease the tendency for the localization of the discharge. This in turn would decrease the tendency for localized energy dissipation and localized high temperatures. Since diphenyl is formed by the pyrolysis of benzene, a rise in temperature above the ordinary temperature of the discharge tube should favor the formation of diphenyl. Therefore it seemed that low potential should produce less diphenyl than high. In the first run 33 cc of gas were produced per hour; in the second 43.5 cc; and in the third 6.7 cc. Measurements of voltage were not made, but it is evident from the rates of gas formation that the voltage in the third run was much lower than in the previous runs. The results for the third run were as follows:

Benzene vapor	12.2%
Acetylene	38.4
Ethylene	14.7
Oxygen	0,2
Nitrogen	0.7
Hydrogen	28.1
Paraffins	5 · 7
	100.0
Total gas	128.9 cc.
Room temperature	23.0°C
Barometer	746.0 mm.
Time of run	19.0 hrs.
Diphenyl	1.2865 gm
H_2 corresponding to diphenyl	206. cc.
H ₂ in the sample	36.3 cc.

These data show in a very striking way that hydrogen produced during the formation of diphenyl had been used up in a secondary reaction. The volume of hydrogen used to produce ethane and ethylene from acetylene brings the volume of hydrogen that can be accounted for up to 69.9. There are 136.1 ce that can not be accounted for in the gas.

The material that was left after the steam distillations in these runs was all put together, because quantitative work on it was not planned at that time. The resin from the steam distillation of the third sample, however, was weighed before it was added to the other. There was 2.744 grams. Before making this weighing the last traces of solvents were removed by placing it while hot into a vacuum desiccator.

A combustion analysis was made on the combined resin from the three samples. Careful practice runs were made on commercial sucrose, before analysis of the resin was attempted. The results were as follows:

	Sucrose		Resin	
	I	2	I	2
Carbon	41.1%	41.2%	88.54%	90.55%
Hydrogen	6.3	6.0	5.03	5.07
Oxygen	52.6	52.8		

Some difficulty was experienced in getting the samples of resin to burn slowly and evenly. This fact shows up more plainly in the percentages, of course, than it does in the calculated C to H ratios. This ratio was 6:41 for the first sample of resin and 6:40 for the second.

It will be noticed from the combustion analyses that the hydrogen and carbon do not add up to 100% of the sample. Austin and Black¹ working

¹ J. Am. Chem. Soc., 52, 4554 (1930).

with a similar product from benzene found 73.38% carbon and 4.77% hydrogen. Quoting from their article, "It will be seen that there remains to be accounted for from 15 to 20% of these compounds. Qualitative tests for nitrogen made with a method, which under ordinary conditions detects nitrogen in a sample containing 0.1% NH₄Cl, gave completely negative results; hence it has been assumed that the remaining portion is oxygen which is the only other element likely to be present under the circumstances.

"The difference between our powders and those of Harkins and Gans¹ is, however, easily accounted for, since they took great precautions to dry their vapors and in our work at least a trace of water vapor was undoubtedly present. Indeed on making a careful study of our plates we find a faint band at about λ_{3064} which is the position of the so called water vapor bands."

The work of Harkins and Gans was done on benzene vapor at 0.1 mm pressure using an electrodeless discharge. The walls of their tube became coated with a reddish brown deposit which on analysis proved to be $(CH)_n$.

The presence of a high percentage of oxygen in the reddish brown deposit obtained by Austin and $Black^2$ can not be satisfactorily explained by the presence of a *trace* of water vapor. It seems more probable that such a large percentage of oxygen would come from a source that could supply a large amount of oxygen. Handling the material in air would open up the possibility of absorption of oxygen from the air.

It seems that the presence of oxygen in the polymerized product indicates unsaturation; unsatisfied valences in the hydrocarbon take up oxygen from the air. In the very stable benzene molecule there is one hydrogen for every carbon. Any rearrangement of its structure would doubtless bring out the "latent unsaturation" of the molecule. Perhaps this "latent unsaturation" could be satisfied by oxygen from the air. The work of Harkins and Gans³ is not published in sufficient detail to enable one to judge whether or not it is in agreement with these ideas.

The combustion analyses of the resin formed in our tube did not tell what became of the hydrogen that was used up by secondary reactions. Furthermore they showed that the resin itself was deficient in hydrogen. When benzene changed into the resin, $(C_6H_4)_n$, 8_{31} cc of hydrogen must have been eliminated. The total amount of hydrogen that can not now be accounted for is 967 cc.

The hydrogen could have been used to produce liquid products. Cyclohexane very probably was one of the principal products. Although benzene is usually written with double bonds it does not react as members of the ethylene series do. For example it does not react readily with bromine. We say that it is *not* actively unsaturated. Cyclohexadiene which may be formed from benzene by saturating one double bond is actively unsaturated. It is probable that it would be more difficult for the first hydrogen to react with the benzene

¹ J. Am. Chem. Soc., 52, 2578 (1930).

² J. Am. Chem. Soc., 52, 4554 (1930).

³ J. Am. Chem. Soc., 52, 2578 (1930).

than it would be for others to react with the partly saturated ring. Therefore it seems probable that if the reaction once got started it would not stop until cyclohexane was formed.

The fact that so much gas could disappear in an electric discharge is not surprising when one considers the work of Harkins and Gans.¹ They say that "the spectrum indicates that benzene molecules rapidly decompose into molecules of C_2 and CH, and atoms of C^+ and H. The C_2 , CH, C^+ , and H seem to combine completely to form the reddish brown hydrocarbon, as evidenced by the fact that several thousand liters of benzene vapor decompose without giving enough gaseous residue to raise the pressure sufficiently to extinguish the discharge."

Conclusions.

r. The main reaction taking place is the formation of a resinous product which contains hydrogen and carbon atoms in the ratio of 6 to 4. The best solvent for the resin is chloroform.

2. The reaction next in importance is the formation of diphenyl. A small amount of p-diphenyl benzene also was isolated. These products are known to be formed also by the pyrolysis of benzene. Bates and Taylor have shown that diphenyl may be formed by a process sensitized by ultra-violet light. Conditions in the last run were made so as to minimize the tendency for localized discharges and the consequent localized heat effects, yet the largest yield of diphenyl was in this run. It seems probable, therefore, that some of the reaction forming diphenyl and hydrogen may have been brought about by the ultra-violet light.

3. Hydrogen, that should have been produced at the time of the formation of diphenyl and the resin, did not appear in the gas. It must have been used up in some secondary reactions.

4. The electric discharge caused gas to form much more rapidly from acetone than from benzene.

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¹ J. Am. Chem. Soc., 52, 2578 (1930).