[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

III. THE CHEMICAL EFFECTS OF SEMI-CORONA DISCHARGE IN GASEOUS HYDROCARBONS[1]

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In two previous papers[4] the authors showed that when ethane is subjected to electrical discharge of various types, condensation to liquid by the elimination of hydrogen and methane always takes place. The identity of the gaseous products and of their amounts relative to those found when alpha particles act on hydrocarbons[5] led to the conclusion that the reactions are entirely similar in being due to ionization. Hence the same kind of mechanism is operative in both cases. Especially is that true of the less intense types of discharge such as in the ozonizer or Siemens tube. In corona and semi-corona discharge, while the gaseous and liquid products remain the same, formation of solid on the walls also occurs. In the semi-corona and corona the reaction rate is much more rapid because the energy is more fully expended in ionizing the gases instead of being wasted in getting through the glass wall, as in the Siemen's tube. However, this is not pure gain in the production of liquid because the solid formed in the corona types of discharge is equal in weight to the liquid. The solid hydrocarbons deposit on the glass (or metal) wall in a gummy adherent coating. Their average molecular weights remain unknown as no solvent has been found for them. Free carbon also forms on the metal electrodes in small tree-like deposits. Its amount is, however, relatively small, as will be seen in Table VIII.

In the present work eleven semi-corona tubes of pyrex glass (Fig. 1) were connected in series as to gas flow but in parallel as to electrical flow. The eleven central electrodes of $^1/_8$-inch aluminum rod were connected in parallel to an A. C. source (Thordarson transformer) with 18,000 volts on the secondary. The discharge took place across the annular space of 0.5 inch to the outer glass wall of the tubes, all of which were immersed in an electrolytic solution (sodium carbonate) which was grounded, thus constituting the other electrode. The solution was heated to 70° for the purpose of causing the first liquid droplets formed on the wall to flow off to the trap more readily, thus avoiding production of liquids of high viscosity and molecular weight by continued action of the

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[1] This paper includes part of an investigation of "The Effect of Electrical Discharge upon Gaseous Hydrocarbons," Project No. 8 of American Petroleum Institute Research. Financial assistance has been received from the research fund of the American Petroleum Institute, donated by the Universal Oil Products Company. This fund is administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[4] S. C. Lind and George Glockler, (I) *Trans. Am. Electrochem. Soc.*, **52**, 37–46 (1927); (II) THIS JOURNAL, **50**, 1767–1772 (1928).

[5] S. C. Lind and D. C. Bardwell, *ibid.*, **48**, 2335–2351(1926).

discharge on the liquid already formed (see Paper II). All eleven traps were cooled to a common low temperature suitable to each gas (Table VIII), to cause condensation and to prevent further ionization in successive tubes of heavy gas molecules which would give a still denser liquid. Gas samples were taken from beyond the last discharge tube from time to time. The liquid products were drawn off separately from each tube by cutting its fine glass tip. Solid products were removed (with difficulty) from the wall of each tube after the system had been cut apart.

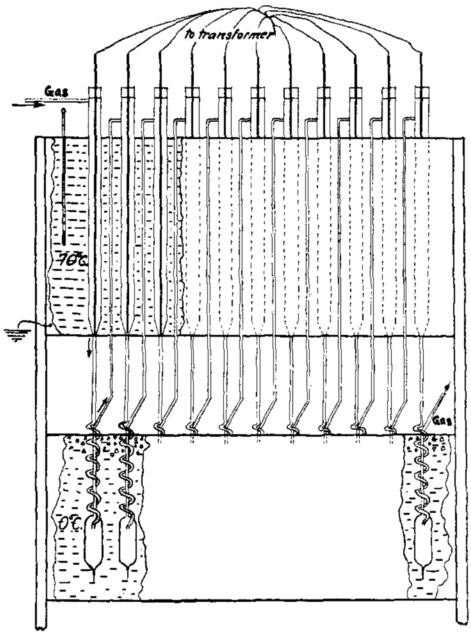

Fig. 1.—Semi-corona apparatus series gas flow.

The entire reaction takes place in a closed glass system (pyrex) out of access to air, so that products containing only hydrogen and carbon were obtained. The first experiment using the series flow apparatus (Fig. 1) was made with propane. These results will be described in detail, and the same procedure and apparatus were used with the other hydrocarbons, methane, ethane, butane and ethylene, data for which are also given in this paper.

Propane. Experiment No. 1.—In this experiment no heater was used for the discharge tubes, as it was hoped that the electrical energy applied would maintain their temperature at 60–70°. Actually the sodium carbonate electrolyte surrounding these tubes and hence controlling the temperature of their outer walls, in which we were most interested, would heat only to 35°. The accumulation of liquid in the traps being open to observation, the run was ended when any trap first became full of liquid, in this case the last one, No. 11. By collecting a sample of gas of definite volume and then condensing all gases in the sample at liquid-air temperature, only hydrogen and methane are left. Since they are always the principal gaseous products (Paper I), the course of the reaction can be followed by determining their combined partial pressure. The following data show how the reaction gradually became slower in the whole system, due to the

Table I

Decrease in Reaction Rate Due to Deposition of Solid on the Glass Wall Experiment No. 1 with Propane

Time	Pressure, mm.	Remarks
2-14-28	299.3	Partial pressure of reaction products, $H_2 + CH_4$, after condensing C_3H_8 and other gases from one atmosphere of total pressure.
2-15-28	320.0	
2-17-28	270.0	
2-21-28	180.0	

decrease in efficiency of each tube owing to the deposition of the solid hydrocarbons on the wall, which diminishes the current and hence the ionization and chemical action in each tube.

The distribution of liquid products in successive tubes in the series is shown in Table II. The total yield of liquid in this experiment was 37.09 g. from 550 g. of propane, using 81.5 kw. hours.

Properties of Liquid Condensates.—The following properties have been determined for the liquid condensate of each tube: index of refraction for sunlight at 21°, density, average molecular weight and the color (arbitrary scale of the Union oil colorimeter).

TABLE II

LIQUID HYDROCARBON CONDENSED FROM PROPANE IN INDIVIDUAL TRAPS IN ELEVEN SEMI-CORONA SERIES SYSTEM. FIRST EXPERIMENT

Trap no.	Yield of liquid product, g.	Av. mol. wt.	Density	Index of refrac. 21° n_{Sun}	Color (Union Oil Colorimeter)	Glass wall thickness (inches)
1	0.372	183.1	0.8393	1.4673	7.88	0.0359
2	0.739	157.5	.8062	1.4573	4.25	.0329
3	1.276	139.9	.7882	1.4512	2.75	.0334
4	1.500	138.7	.7872	1.4499	3.32	.0360
5	4.030	145.7	.7894	1.4486	4.50	.0306
6	3.349	126.7	.7814	1.4450	3.44	.0346
7	4.780	130.4	.7672	1.4400	3.38	.0365
8	4.056	118.0	.7658	1.4380	3.00	.0312
9	4.548	114.0	.7540	1.4315	1.94	.0301
10	5.056	109.3	.7611	1.4326	1.82	.0315
11	8.997	133.9	.7827	1.4454	4.67	.0380
	36.699					
12[a]	0.391	115.1	.7424	1.4300	.06	...
	37.090					

[a] The twelfth trap was not related to any ozonizer. It was an additional condensation trap, placed at the exit end of the apparatus. Its purpose was to catch any condensable material not caught in the eleventh trap.

The properties given in Table II are shown graphically in Fig. 2. It should be remembered that the liquids are all very complex. No efforts to fractionate them will be reported in the present paper. All data refer to the liquids as obtained.

Correlation of Properties.—Inspection of the curves of Fig. 2 shows at once that index of refraction, density, average molecular weight and color are all correlated properties and hence show similar curves when plotted in the order of the successive traps. All four properties show a marked fall when proceeding in the direction of flow. Irregularities are probably due to accidental variations in individual tubes, either wall thickness or eccentricity of the central electrode.

This fall in average molecular weight, etc., is closely but inversely related to the yield per trap. The greater the yield per tube, the faster the flow of liquid from the walls, hence the shorter the time of exposure to further discharge which has already been shown (Paper II) to be the cause of *high* condensation, average molecular weight, color, density, viscosity, etc.

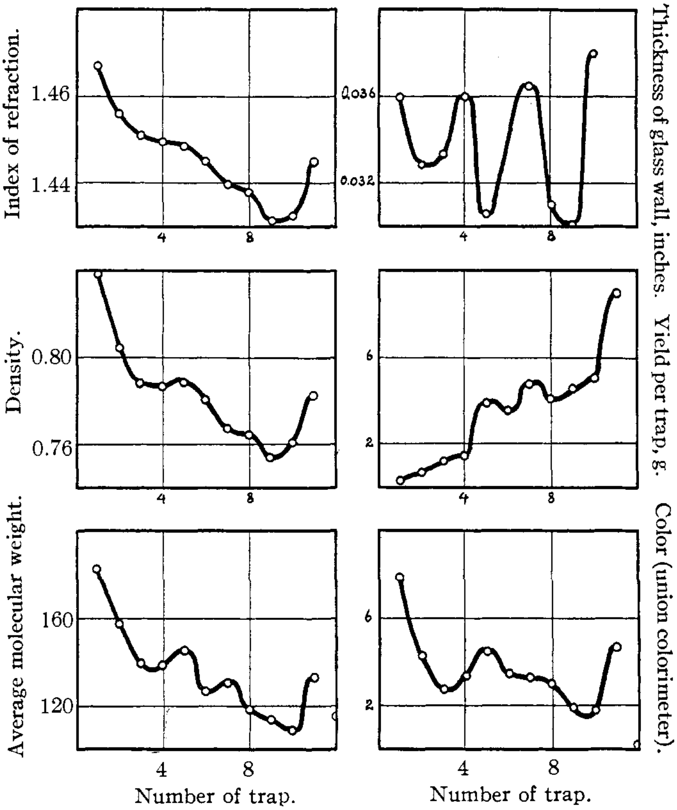

Fig. 2.—First propane run—eleven semi-coronas in series.

In order to demonstrate more clearly the correlation of index of refraction to density and to molecular weight, the data of Run No. 1 with propane have been plotted in two curves (Fig. 3). These curves have been used to obtain the density and molecular weight of the liquid product of other gaseous hydrocarbons from their indices of refraction. The agreement with values found directly by the freezing point lowering in benzene was fairly satisfactory, as is seen in Fig. 5, where the double circles show the actual check determinations in comparison with the predicted curves.

Yield per Tube.—As has just been seen the yield per trap increases on passing to successive tubes in the direction of gas flow. Three causes are to be considered: (1) a purely physical inefficiency or lag in vapor condensation, which would give an increased concentration in later tubes, further augmented by electrical generation of new condensable vapor. This effect might not be expected to increase through many tubes but to reach a steady state; however, it should be remembered that presumably the more of heavy molecules reaching a given tube, the easier it is to produce ionization there and hence more of the condensable product is formed. (2) The carrying over to higher tubes of molecules already condensed (chemically) but not sufficiently so to condense physically to liquid. These heavy readily ionized molecules also supplement the yield. (3) A *delayed chemical* condensation exists, as demonstrated in Paper II, p. 1771. All three of these effects work in the same direction to give more liquid in successive tubes. It is not now possible to evaluate the influences separately. It is evident that there would be a limit to this increase though it is not reached in this case, but is in propane Run 2, where, on account of a slower rate of flow and consequent earlier depletion of reactant gas, a maximum is passed. The conversion of total propane to liquid product is only 6.7% in Run 1 (see Table VII).[6]

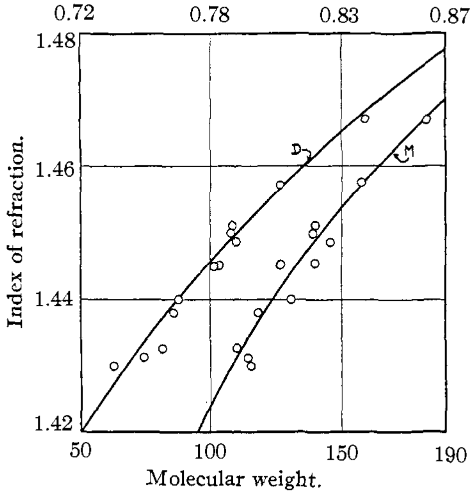

Fig. 3.—Molecular weight and density as functions of index of refraction. First propane run in eleven semi-corona apparatus.

Table III

Experiment No. 1 on Propane. Analysis of Initial and Effluent Gases

Initial gas		Effluent gas	
Permanent gases	0.12%	$H_2 + CH_4$	26.06%
C_2H_6	0.51	C_2H_6	7.05
C_3H_8	99.12	C_3H_8	64.50
C_4H_{10} (and higher)	0.42	C_4H_{10} (and higher) by difference	2.39
Total	100.17	Total	100.00

Solid Deposits.—The glass walls were covered with a resinous inert solid deposit of the character already described, the amount of which was

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[6] The efficiencies given always refer to the amount of initial gas sent through the apparatus. The efficiency of the ozonizers decreased during the experiments (see Tables I and IV) and it was not possible to calculate the actual amount of initial gas used from the gas analysis.

not determined in this run. The aluminum rod electrodes had a deposit of carbon in tree-like formation, the amount of which was relatively small but undetermined (compare Table VIII).

Propane. Experiment 2.—The same sample of gas was used as in Experiment 1, and the same apparatus (Fig. 1), the chief difference being that the rate of flow was reduced from 1.45 in Run 1 to 0.54 liters per hour in Run 2. Due to this slower rate of flow, a number of differences are observed owing to the more rapid depletion of propane, as may be seen by comparing the following with corresponding data for Run 1.

TABLE IV

DECREASE IN REACTION RATE DUE TO DEPOSITION OF SOLID ON THE GLASS WALL

EXPERIMENT 2

Time	Pressure, mm.	Remarks·
3-2-28	396.0	Partial pressure of reaction products, H_2 + CH_4, after condensing C_3H_8 and other gases from one atmosphere pressure.
3-5-28	320.0	
3-10-28	220.0	

Owing to the higher utilization of propane (60% to solid and liquid against 6.7% to liquid or 13% estimated for liquid and solid in Run 1) the yield per trap passes a maximum at the eighth tube and then falls off in the ninth, tenth and eleventh (Fig. 4 and Table V). The data are given in Table V and plotted in Fig. 5. Inspection of the latter shows the same kind of correlation between index of refraction and color as in Run 1, and in addition a close correlation, almost equality, between the

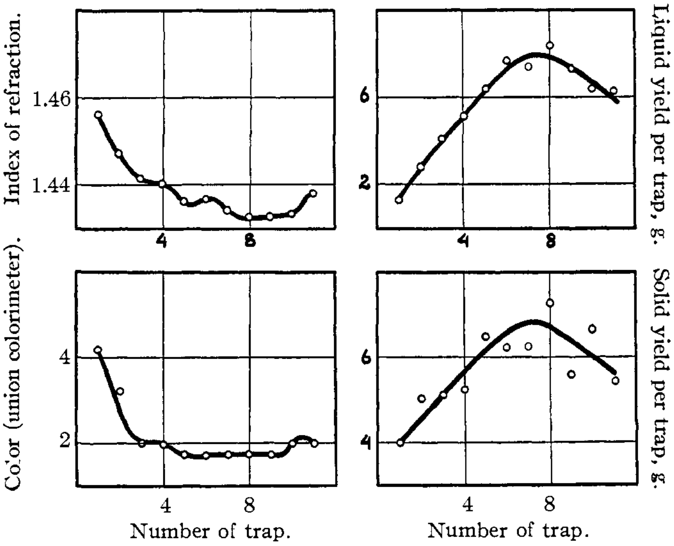

Fig. 4.—Second propane run—eleven semi-coronas in series.

amount of solid and liquid product, though the distribution per tube is somewhat different.

TABLE V

SECOND EXPERIMENT ON PROPANE CONDENSATION IN ELEVEN SEMI-CORONA APPARATUS

Trap	Yield of liquid, g.	Index of refraction, 21° n_{Sun}	Color of liquid (Union oil colorimeter)	Yield of solid on glass wall, g.
1	1.315	1.4563	4.25	4.03
2	2.896	1.4472	3.25	5.09
3	4.118	1.4415	2.00	5.15
4	5.150	1.4403	2.00	5.29
5	6.432	1.4362	1.75	6.50
6	7.648	1.4370	1.75	6.26
7	7.431	1.4342	1.75	6.26
8	8.355	1.4327	1.75	7.28
9	7.158	1.4328	1.75	5.62
10	6.390	1.4334	2.00	6.69
11	6.328	1.4380	2.00	5.47
12[6]	0.200	1.4352	0.00	
	63.42			63.64

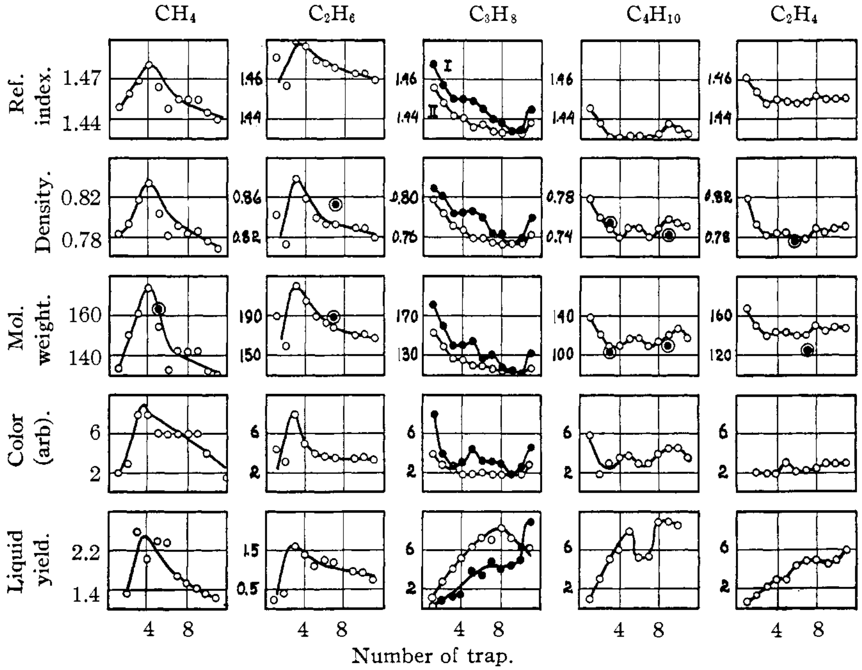

Fig. 5.—Properties of liquid condensates obtained from gaseous hydrocarbons in semi-corona discharage.

TABLE VI

EXPERIMENT NO. 2 ON PROPANE. ANALYSIS OF INITIAL AND FINAL GASES

Initial gas, %		Effluent gas, %	
Permanent gases	0.12	$H_2 + CH_4$	45.00
C_2H_6	0.51	C_2H_6	9.78
C_3H_8	99.12	C_3H_8	41.60
C_4H_{10} (and Higher)	0.42	C_4H_{10}	2.90
		C_5H_{12}	1.63
Total	100.17	Total	100.91

Table VII contains a summary and comparison of the principal results for Propane in Runs 1 and 2.

TABLE VII

COMPARISON OF EXPERIMENTS 1 AND 2 ON PROPANE

	Run 1	Run 2
Rate of flow in liters per hour	1.45	0.514
Time of experiment, days	9	10
Amount of propane used, liters (N.T.P.)	280	111
Amount of propane used, g.	550	218
Kw. hours used	81.5	63.42
Secondary volts	18,000	18,000
Molecular weight of liquid product range	183–115	160–120
Yield of liquid product, g.	37.09	63.42
Density of liquid oil	0.8392–0.7424	0.82–0.75
n^{21}_{Sun}	1.4673–1.4300	1.4563–1.4352
Solid deposit on glass wall, g.	[a]	63.64
Efficiency of conversion to liquid, %	6.7	29.0
Efficiency of conversion to liquid and solid, %	[a]	58.5
Liquid per kw. hour, g.	0.455	0.480
Liquid and solid per kw. hour, g.	[a]	0.985

[a] The solid deposit was not determined in Propane Run 1, because it was first discovered there while attempting to clean the apparatus. In cleaning the apparatus with hot chromic acid copious evolution of carbon dioxide from the wet oxidation of the solid on the wall was noticed.

Results for Other Hydrocarbons—Methane, Ethane, Propane, Butane and Ethylene.—Having in the foregoing part of this paper given and explained in considerable detail the results obtained using propane as initial gas, the results for the four other hydrocarbon gases studied can be rather briefly summarized, as they are quite similar in most respects to those obtained for propane.

The eleven tube semi-corona apparatus was again used. All of the hydrocarbons examined give liquid condensates of the same general character. The relation between index of refraction, molecular weight and density is the same for the different liquid condensates, which is interpreted to mean that these liquids are all of the same type. This is supported by our ability to deduce their densities and molecular weights from their indices of refraction by using the corresponding curves from propane. Moreover, all of the condensates have a similar terpene-like odor. The results for all five gases are summarized in Table VIII.

TABLE VIII

COMPARISON OF EXPERIMENTS WITH FIVE GASEOUS HYDROCARBONS IN THE ELEVEN SEMI-CORONA APPARATUS. CENTRAL ALUMINUM ELECTRODE ($^1/_8$" DIAM.) IN PYREX TUBES (2.0 CM. DIAM. AND 1 MM. WALL THICKNESS)

	Methane	Ethane	Propane, Run 2	Butane	Ethylene
Flow, l./hr.	0.57	0.45	0.514	0.60	0.58
Temp. of trap, °C.	0	0	0	10	0
Time, days	5.1	1.5	10	5.7	12.4
Gas used (N.T.P.), l.	64.0	14.9	111	74.1	155
Gas used, g.	45.7	19.9	218	192	193
Volts (secondary)	18,000	18,000	18,000	18,000	18,000
Primary kw. hrs.	102.7	15.7	132.0	63.4	196.3
Yield of liquid, g.	18.25	9.74	63.42	71.10	40.10
Mol. wt. of liq. prod.	130–170	170–210	120–160	110–140	130–160
Density of liq. prod.	0.78–0.83	0.81–0.87	0.75–0.82	0.74–0.78	0.78–0.82
n^{20}_{Sun}	1.44–1.46	1.46–1.48	1.42–1.47	1.43–1.45	1.45–1.46
Solid on glass wall, g.	4.4	0.1	63.64	(70.0)	78.6
Carbon on Al rod, g.	0.25	0.1	1.00	1.00	0.75
Eff. of conv. (g. liquid)/(g. gas used), %	40	48	29	37	21
G. (liq. + solid)/(g. gas used), %	50	48	58.5	73.5	61.4
G. liquid/kw. hour	0.178	0.62	0.48	1.09	0.204
G. (liquid + solid) per kw. hour	0.22	0.625	0.985	2.23	0.605

Discussion of Results

The results for propane, butane and ethylene were obtained under quite comparable conditions. This is not equally true of the experiments with methane and ethane, for which the runs were of much shorter duration due to premature failure of the glass under discharge with the result that formation of solid on the walls had only begun; consequently the clean tubes appear unduly efficient with respect to yield of liquid per unit weight of methane or ethane used or per unit of electrical energy applied to them, in comparison with results for the other gases.

Of course, the most satisfactory basis of comparison of the reaction yields for the different hydrocarbons would be in terms of yield per ion-pair; but since the ionization can neither be measured nor calculated,[7] we must be content with relative rather than absolute comparisons. It has been shown that the reactions have the same general character as those produced in the same gases by alpha radiation, and are presumably due to ionization. In the case of ozone formation by high-speed cathode rays,

[7] Lind, *Trans. Am. Electrochem. Soc.*, **53**, 26 (1928).

Busse and Daniels[8] have recently made a satisfactory estimate of the ratio (yield/ion pair) by assuming the total energy reaching their reaction vessel to be wholly expended in producing oxygen ions. Since such a large proportion of energy in the semi-corona discharge is lost to the wall, we cannot make their assumption. It appears more plausible to assume that so much of our energy is lost to the wall that the condition is more like that of alpha particles in vessels so small that all alpha particles cross the entire gas space, and that at the same pressure the amount of reaction in different gases is proportional to the product of the specific ionization yield per ion pair (M/N)—a comparison similar to the one made[9] for the results of Hutchinson and Hinshelwood[10] for the decomposition of NH_3 and N_2O in different tubes under conditions of equal current flow. It is not implied that any single electron traverses the entire gas space, but that under conditions of equal electron flow the total ionization and chemical action in the different gases will be relatively in the proportion given by the product:[11] $ks \times M/N$ where ks is Bragg's specific (molecular) ionization and M/N is the yield of molecules M reacting per N ion pairs.

Two assumptions are involved: (1) that the relative specific molecular ionization by electrons is the same as by alpha particles, which seems by far more plausible than to assume, as has been sometimes done by others, that the probability of ionization by electrons is proportional to the number of molecules present, regardless of their size or nature; and (2) that the yield (M/N) is the same, or, more generally, that the chemical behavior of ions is the same, whether produced by bombardment by electrons or by alpha particles. If the ions produced are identical, this postulate must be true, other conditions being alike. Therefore, we should expect the relative yields to be roughly proportional to those shown for $ks \times M/N$.

TABLE IX

THEORETICAL RELATIVE YIELDS OF LIQUID FROM DIFFERENT GASEOUS HYDROCARBONS UNDER ELECTRICAL DISCHARGE

Hydrocarbon	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4
ks[12]	1.01	1.97	3.05	4.02	1.65
M/N[12]	2.0	2.0	2.0	2.0	5.0
$ks \times M/N$	1.0	1.95	3.02	3.99	4.08
Corrected	0.25	0.98	3.02	3.99	4.08

If by yield we mean *liquid* (and solid) formed, then the relative values for methane and ethane must be yet further reduced because in a reaction

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[8] F. W. Busse and F. Daniels, THIS JOURNAL, **50**, 3271–3286 (1928).

[9] S. C. Lind, *Trans. Am. Electrochem. Soc.*, **53**, 31–32(1928); *Science*, **67**, 567–568 (1928).

[10] W. K. Hutchinson and C. N. Hinshelwood, *Proc. Roy. Soc. London*, **117A**, 131–136 (1928).

[11] S. C. Lind, "Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Company, Inc., New York, **1928**, 2d ed., pp. 36 and 102.

of simple doubling such as $2CH_4 = C_2H_6 + H_2$ and $2C_2H_6 = C_4H_{10} + H_2$, neither of the gases can reach a condensable stage in a single step but must be acted on again (C_4H_{10} once and C_2H_6 twice), so that perhaps the actual relative values would be improved by dividing that for C_2H_6 by *two* and that for CH_4 by *four.* The higher numbers from propane up can all reach the liquid stage by a single doubling.

Some general resemblance, at least to the order given above, can be seen by inspecting the yields per kw. hr. or also per gram of gas used (Table VIII), but the picture is a very distorted one on account of the differences in the amount of solid on the different tubes, which as already mentioned was practically absent for CH_4 and C_2H_6 on account of the short time for accumulation. Hence, the relative yields from ethane and methane appear higher than they should; on the other hand, that of ethylene is depressed on account of the abnormal amount of solid formed.

It may appear strange that all of the hydrocarbons in spite of the great differences in their densities, molecular weights, etc., give liquids of about the same properties with respect to density, average molecular weight, etc. Striking as this may appear on first thought, it is a simple consequence of multiple doubling and of the experimental arrangement so as to arrest further doubling by condensing the product in low temperature traps outside of the zone of reaction. By changing the temperature of the discharge region and of the traps, the properties of the liquids could be varied at will, and all of the liquids brought to equal molecular weights of some other value in an arbitrary manner.

The authors wish to thank Mr. J. L. Wilson, who has assisted in this work as American Petroleum Institute Research Assistant.

Summary

1. Like ethane, the other lower hydrocarbons, methane, propane, butane and ethylene condense to liquid and solid hydrocarbons in semi-corona discharge (central aluminum rod in a (pyrex) glass cylinder).
2. The condensation of saturates is brought about by the elimination of hydrogen and some methane as under alpha radiation.
3. In series gas flow through a number of discharge tubes, the amount of liquid condensate increases in successive tubes. If the rate of flow be so slow that depletion of reactant becomes considerable, then a maximum of liquid yield is attained in an intermediate tube.
4. The liquid products obtained from different hydrocarbons or in different tubes from the same hydrocarbon are similar in physical properties, when obtained at the same trap temperature.
5. The liquid products are very complex. Fractionation was not attempted in the present work.
6. Solid hydrocarbons are obtained in slight amount in the Siemens

tube, in larger quantity equal to that of liquid in the corona tubes. The solid is gummy or resinous, inert toward solvents and chemical reagents except strong oxidizing reagents.

7. In corona discharge a small amount of free carbon is deposited on the metal electrode in tree-like formation.

8. A close correlation of index of refraction, molecular weight, density, color and viscosity characterizes all the liquid products. Increase in all these properties is inversely proportional to the *yield*, for which a simple explanation is given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIDDLEBURY COLLEGE]

OXIDATION OF BENZOINS TO DIKETONES WITH IODINE

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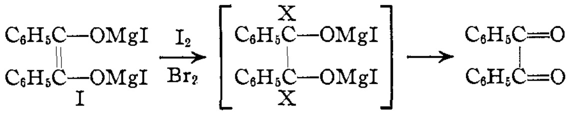
Benzoin, anisoin, piperoin, furoin, etc., are easily oxidized to the corresponding diketones by various methods. On the other hand, the conversion of aliphatic analogs of benzoin such as butyroin, $C_3H_7CHOHCOC_3H_7$, into diketones is not so convenient. We have studied the oxidizing effect of iodine, thinking that the reaction might be applicable to aliphatic acyloins. Solid aromatic acyloins were used in the investigation since they are easier to manipulate than the liquid aliphatic analogs. Although the reaction seems of no value in the preparation of aliphatic diketones, some of the results which came to light are of general interest.

The reaction is based on a recent observation of Gomberg and Bachmann[1] that benzil results from the action of iodine or bromine on stilbenediolate (I).



$$\begin{array}{c} C_6H_5C{-}OMgI \\ \| \\ C_6H_5C{-}OMgI \\ \text{I} \end{array} \xrightarrow[Br_2]{I_2} \left[\begin{array}{c} X \\ C_6H_5\overset{|}{C}{-}OMgI \\ | \\ C_6H_5\underset{|}{C}{-}OMgI \\ X \end{array}\right] \longrightarrow \begin{array}{c} C_6H_5C{=}O \\ | \\ C_6H_5C{=}O \end{array}$$

We have obtained 90–95% yields of benzil by the addition of iodine to alkaline solutions of benzoin. Benzoin was dissolved in methyl alcohol and sodium methylate was added, followed by iodine. Due to the extreme sensitiveness to oxidation of an alkaline solution of benzoin, the reaction mixture must be protected from air. This was accomplished either by working in an atmosphere of dry nitrogen or by keeping the alcohol solution boiling throughout the duration of the reaction. Similar yields of diketone (80 to 90% of the theoretical amount) were obtained from anisoin, piperoin and furoin.

It seems quite likely that the mechanism of this reaction is that described by Gomberg, namely, the removal of sodium from the dienolic

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[1] Gomberg and Bachmann, THIS JOURNAL, **49**, 2584 (1927).