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

# CONTROL OF THE MOLECULAR WEIGHT OF LIQUID HYDROCARBONS PRODUCED BY ELECTRICAL DISCHARGE IN ETHANE[1]

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In a recent paper[4] we described the production of a heavy oil obtained, besides various gaseous products, from ethane under the influence of silent electrical discharge in an ozonizer type of discharge tube.

The great viscosity and high average molecular weight (467 by freezing point in benzene) of the oil obtained as a direct product of ethane were notable. According to the original theory[5] for the ionizing effect of $\alpha$-rays on hydrocarbons, there are two ways in which the lower saturated hydrocarbons may be condensed to liquid by ionization: (1) by repeated doubling by means of *successive* ionization until a product is obtained of sufficiently high molecular weight to condense as liquid or (2) by direct condensation of a sufficiently large number of "nascent unsaturates" (those with only one of the double bonds closed) to form liquid directly without repeated ionization.

That the chemical action of $\alpha$-particles on paraffins is not confined to the gaseous members has been shown in several instances. Lind and Bardwell[6] showed that propane yields a liquid under a low intensity of radiation, but that the liquid is transformed to solid upon prolonged radiation. Rutherford and Boltwood[7] found that solid paraffin exposed to $\alpha$-rays had its melting point greatly raised, accompanied by an evolution of much gas. W. T. Richards[8] has recently shown that a gas (principally hydrogen) is evolved under $\alpha$-radiation from both liquid and solid paraffins. Lind[9] has calculated from Richards' results that the quantity of gas per ion-pair is approximately the same as for the gaseous members.

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[4] S. C. Lind and Geo. Glockler, *Tr. Am. Electrochem. Soc.*, Vol. **52**, Preprint No. 6, September, 1927.

[5] S. C. Lind and D. C. Bardwell, THIS JOURNAL, **48**, 2331 (1926).

[6] Ref. 5, p. 2341.

[7] Rutherford and Boltwood, *Science*, **60**, 364 (1924).

[8] W. T. Richards, *Proc. Camb. Phil. Soc.*, **23**, 516–522 (1927).

[9] S. C. Lind, "Chemical Effects of Alpha Particles and Electrons," 2d ed., Chemical Catalog Co., New York, **1928**, p. 150.

Therefore, if the theory proposed for the $\alpha$-ray condensation is valid for electrical discharge, we should expect that the first liquid droplets deposited on the wall of the discharge tube would be subject to much secondary electronic bombardment, since the discharge in an ozonizer enters the gas space entirely through the wall. If then by warming the wall we can prevent liquid from condensing there, and if by putting a low temperature trap in the circuit we stop the earlier condensation products from returning to the region of discharge, we may expect a ma-

TABLE I

PRODUCTION OF CONDENSATES OF LOW MOLECULAR WEIGHT

Variables—Types of discharge, temperature of electrodes and temperature of condensation traps.

| Oil | Type of discharge tube used[a] | Volts | Milli-amps.[b] | Temp. of electrodes,[c] °C. | Temp. of traps,[d] °C. | Mol. wt. of liquid mixture | $n^{20}_{\text{Sun}}$ | Color of liquid | Yield liquid product, cc./hour |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Ozonizer | 11600 | <1 | 25 | 25 | 467 | 1.4900 | Red-brown | 0.028 |
| 2 | Ozonizer | 11600 | <1 | 70 | 25 | 188 | 1.4642 | Slightly yellow | .011 |
| 3 | Ozonizer | 11600 | <1 | 70 | −50 | 184 | 1.4509 | Slightly yellow | .006 |
| 4 | Semi-Pt wire corona | 11600 | <1 | 70 | −50 | 156 | 1.4467 | Slightly yellow | .063 |
| 5–6 | Semi Al rod corona | 11600 | <1 | 18 | −50 | 106[e] | 1.4503 | Slightly yellow | .100 |
| 7 | Semi Al rod corona | 11600 | <1 | 70 | −50 | 105[f] | 1.4294 | Yellow | .100 |
| 8 | Semi Al rod corona | 3000 (Radio) | 135 | 70 | −50 | 95[g] | .... | Red-yellow | .060 |
| 9 | Semi Al rod corona | 10000 (Radio) | 700 | 35 | −50 | 109 | 1.4204 | Light yellow | .100 |
| 10 | Al tube–Pt wire corona | 8000 | <1 | ... | −58 | 81 and 182[h] | .... | Red-yellow | .050 |

[a] For details of construction see below.

[b] See paragraph on electrical energy.

[c] In runs 1 to 3 the inner and outer water electrodes were kept at the temperature indicated; in Expts. 4 to 9 the temperature refers to the outer water electrode.

[d] In Expts. 1 to 4 one condensation trap was used. In runs 5 to 8 two traps were used in series. In 9 and 10 four traps were used in series.

[e] Oil No. 5 (mol. wt. 112) was collected in the first trap and oil No. 6 (mol. wt. 100) was collected in the next trap. The molecular weight indicated is the average.

[f] The molecular weight indicated is the average of the liquid collected in the two traps.

[g] The molecular weight indicated is of the lighter fraction obtained from the total mixture by low temperature vacuum distillation into two equal fractions. The heavier fraction was too insoluble in benzene for molecular weight determination.

[h] The total yield of the four traps was separated by vacuum distillation into two nearly equal fractions and their molecular weights are as given.

terial reduction in the degree of condensation or doubling of the liquid product, which will be manifest in a lowering of its molecular weight. The results in Table I demonstrate the truth of these predictions.

**Types of Discharge Vessel Used.**—Four different types of tubes have been used. The ordinary all-glass Siemens ozonizer with inner and outer electrode consisting of water jackets filled with tap water is shown in Fig. 1(I). The inner glass tube has an outer diameter of 2.26 cm. and the glass wall is 0.1 cm. thick. The outer glass tube has an inner diameter of 2.6 cm. and is 0.15 cm. thick. The annular space between the glass walls is 0.17 cm. The semi-wire corona tube shown in Fig. 1(II) has a central platinum wire 0.0324 cm. in diameter fastened in a glass tube of 1.85 cm. inside diameter and of 0.075 cm. wall thickness. Fig. 1(III) shows an aluminum rod semi-corona. The aluminum rod is 0.32 cm. in diameter and is located in the center of a glass tube which is 1.3 cm. in inside diameter and of 0.07 cm. wall thickness. The corona tube shown in Fig. 1(IV) consists of an aluminum tube 2.25 cm. in inside diameter with a platinum wire 0.0324 cm. in diameter fastened centrally.

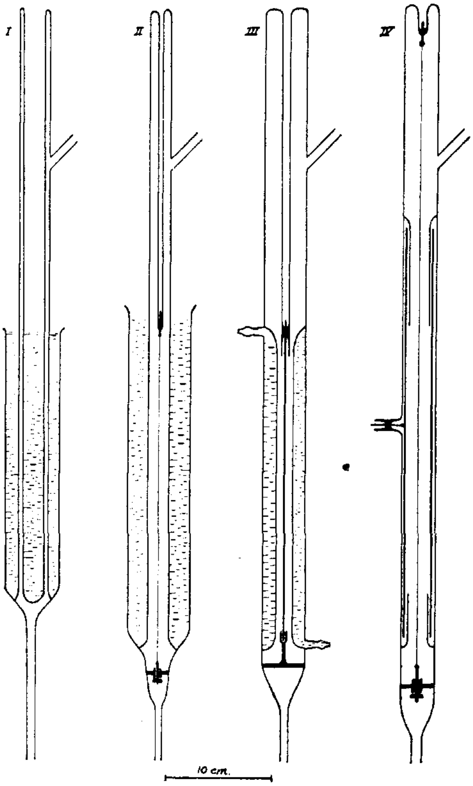

Fig. 1.

**The Reaction Vessel.**—The Circulating System with all glass magnetic pump was the same as described in the previous paper[4] except that the improved horizontal pump[10] utilizing both strokes was employed on account of its higher capacity. The reaction system is shown in Fig. 2. The set of four condensation traps shown there was finally adopted in Expts. 9 and 10 in order to condense all of the reaction products. The traps had spiral inlet tubes which were immersed in a paste of petroleum and aluminum powder contained in solid aluminum blocks which could be kept cool by spraying liquid air into a hole in the block. Pentane thermometers were used to measure the temperature. It was not difficult to maintain −50° within a degree.

**Electrical Energy Used.**—We have not been able to make satisfactory current measurements in the secondary current circuit. As electrical leakage was reduced by improving the discharge tubes, the readings in the hot wire milli-ammeter were di-

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[10] W. S. Funnell and G. I. Hoover, *J. Phys. Chem.*, **31**, 1099 (1927).

minished until it was evident that certainly less than a milli-ampere flowed through the reaction vessel. In Expt. 8 the reaction vessel was placed in the secondary of a Tesla transformer which was fed from an oscillating circuit containing condenser (0.0018 microfarad) and rotating spark gap. In Expt. 9 the reaction vessel was placed in the oscillating circuit itself. It is seen that the currents flowing were then very large but the chemical reaction produced was not augmented thereby. These large currents do not cross the reaction space as conduction currents, they only serve to charge the reaction vessel (as an electrical condenser) and do not contribute to the ionization in the gas space on which the chemical reaction is believed to depend.

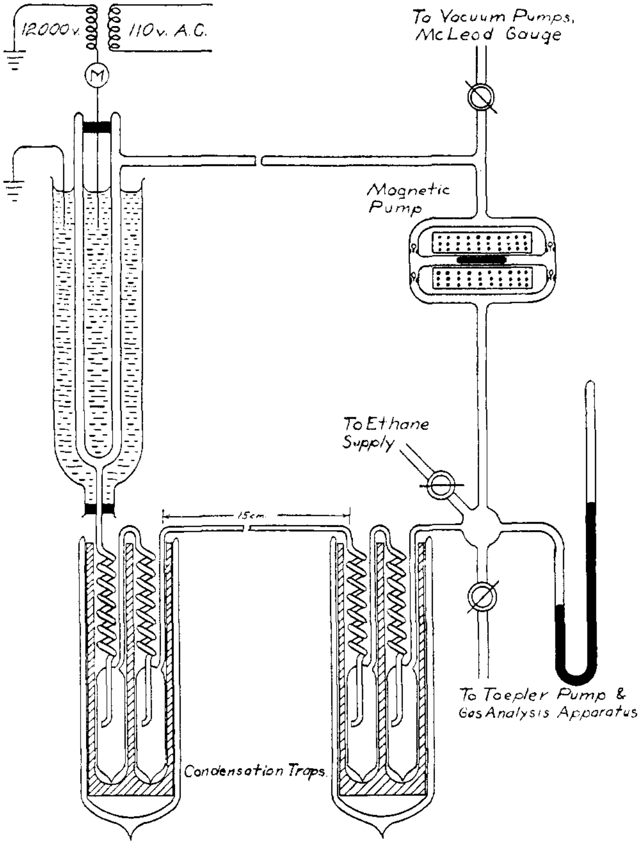

Fig. 2.

## Discussion

The type of discharge employed does not seem to influence the reaction products greatly.[11] This would be expected if ionization is the primary

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[11] If the results with electrodes at 70° and the traps at $-50°$ be considered separately, there do appear to be some consistent differences in average molecular weight for the different types of discharge. It is to be remembered, however, that even at 70° liquid product flows down the walls rather slowly and the slower the less liquid is formed

step. Some secondary differences, however, were found. In the semi-corona and corona discharges (Expts. 4 to 10, Table I) there was some cracking to give free carbon, and always in corona there is formation of a solid film on the wall, which peels off readily in a coherent skin that rolls into small hollow cylinders when removed. This solid burns easily but is inert toward solvents—unlike the liquid products. Its smooth, glistening appearance might suggest its formation by a process of electrical deposition. On the other hand, it should be recalled that a similar solid film (suboxide of carbon) was formed in carbon monoxide[12] under action of $\alpha$-rays where there was no electrical field, so that the action may be merely a surface condensation.

The variation in the average molecular weight of the liquid product appears to depend (Table I) on the length of time the earlier products remain in the discharge chamber subject to further ionization either in the gaseous or liquid state. Regulation of this factor by the two means already discussed appears to afford satisfactory control of the degree of condensation.

Some evidence of delayed condensation even in the gas phase has been discovered. The efficiency of condensation in long spiral traps at $-50$ to $-58°$ has been surprisingly low. To prove that it was really a chemical condensation taking place in the gas phase and not merely slow physical condensation in the trap or slow solution of low hydrocarbons in liquids already condensed, the following experiment was made. Four traps were placed in series at the same low temperature ($-50°$) with connecting tubes at ordinary temperature, spaced as shown below and in Fig. 2. The order of liquid volumes condensed was $(1) > (3) >> (2) > (4)$, showing that the longer

$$(1) \xrightarrow{\text{short}} (2) \xrightarrow{\qquad\text{long}\qquad} (3) \xrightarrow{\text{short}} (4)$$

time elapsing in passage of gas from 2 to 3 allowed further polymerization at ordinary temperature. This slow polymerization may be attributed to the "open bonds" already referred to, which may, of course, play a role also in delayed polymerization in liquid or solids, the slower there on account of the slower diffusion.

We are indebted to Mr. John L. Wilson, who worked with us as Research Assistant of the American Petroleum Institute.

## Summary

Silent, corona and high frequency discharges all cause the condensation of ethane to liquid with the liberation of permanent gases. The average molecular weight of the liquid products has been regulated between 467

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on account of little head. Since the ozonizer represents the slowest rate of formation, the liquid was there subjected to a greater amount of secondary action than in the other types of discharge and hence higher molecular weights prevail.

[12] Lind and Bardwell, THIS JOURNAL, **47**, 2683 (1925).

and 105 by controlling the time that the first products, either gaseous or liquid, are allowed to stay in the discharge tube—the more secondary action the higher the molecular weight owing to further condensation.

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# THE ABSORPTION SPECTRA OF HYDROQUINOLPHTHALEIN AND HYDROQUINOLSULFONEPHTHALEIN

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The present investigation on the absorption spectra of hydroquinolphthalein and hydroquinolsulfonephthalein was undertaken not only to obtain possible corroborative evidence as to the existence of the meta-quinoid structure in these compounds and their salts, but also to contribute to our knowledge of the effect of hydroxyl substitution in the phthalein and triphenylmethane series generally.[2]

The preparation of hydroquinolsulfonephthalein has been described in a previous paper[3] and from its chemical behavior evidence has been advanced in favor of its possessing the meta-quinoid structure. A study of its absorption spectra, particularly in neutral and acid solution, reveals certain striking characteristics which differentiate it sharply from other sulfonephthaleins now being investigated in this Laboratory. Hence it may be provisionally assumed that to this extent the data support the view that the meta-quinoid configuration has a possible existence in the case of these hydroquinol derivatives. It is felt, however, that primary consideration must be given to the chemical evidence in settling this question, until more extensive data are available concerning the effect of hydroxyl substitution in the phthaleins and until more is known of the intrinsic nature of the several quinoid structures, ortho, meta and para. A comparison of the absorption spectra of hydroquinolphthalein and hydroquinolsulfonephthalein with those of their isomers, fluorescein[4a] and sulfonefluorescein,[4b] brings out a marked distinction. To what extent this difference is to be attributed to the different positions of the hydroxyl groups, or to the existence of different quinoid configurations, is still an unsettled question.

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[1] This article is based on a portion of a thesis presented to the Faculty of the Graduate School of Cornell University by the author, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Orndorff, Gibbs and co-workers, THIS JOURNAL, **47**, 2767 (1925); **48**, 1327, 1994 (1926); **49**, 1541, 1545, 1588 (1927).

[3] Orndorff and Shapiro, THIS JOURNAL, **50**, 1730 (1928).

[4] (a) Orndorff, Gibbs and Shapiro, (a) THIS JOURNAL, **50**, 819 (1928); (b) Gibbs and Shapiro, *ibid.*, **50**, 1755 (1928).