

This reaction was also carried out in the cold, using a vacuum to concentrate the solution.

Other semicarbazones are indicated in Table I. All were prepared by J. G. Park except No. 4, which was prepared by W. N. Pritchard, Jr. In all cases the reacting compounds were dissolved in alcohol and the products were recrystallized from alcohol.

Summary

The preparation of *p*-bromophenylurea by three methods is described and procedure is given for its conversion into *p*-bromophenyl-4-semicarbazide. The usefulness of the semicarbazide as a ketone reagent has been tested by the preparation of several semicarbazones.

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

IV. THE CHEMICAL EFFECTS OF ELECTRICAL DISCHARGE IN BUTANE. FRACTIONATION OF THE LIQUID PRODUCT¹

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RECEIVED AUGUST 5, 1929

PUBLISHED DECEMBER 11, 1929

Introduction

In a former paper⁴ it was shown that butane, as well as other hydrocarbons, yields liquid condensates when subjected to the semi-corona electrical discharge. At the same time, however, it was found that solid condensation products are also formed on the inner walls of the discharge tubes. From previous experience it was known that this solid formation does not occur in an all-glass ozonizer, or at least that such action is very slow.

Since the *object of the present work was the production of a fairly large amount of liquid condensate from butane gas by electrical means and its fractional distillation*, it was decided to build an all-glass ozonizer apparatus consisting of twelve ozonizers connected in parallel as to gas flow and as to electrical wiring. This apparatus is shown in Fig. 1. It may be said at once that indeed the solid formation just mentioned was quite negligible and only near the upper ends of the ozonizers toward the close of the long experiment was there any solid product formed.

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 cooperation of the Central Petroleum Committee of the National Research Council.

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⁴ Lind and Glockler, *THIS JOURNAL*, 51, 2811-22 (1929).

Experimental Procedure

The ozonizers were supplied with about 20,000 volts from the secondary of a Thor-darson transformer using a primary current of about 12 amperes and a primary voltage of about 110 volts. During the initial stages of the experiment the machine was kept in operation during the daytime only, in order to study its behavior. On account of the possibility of breakdowns and fires resulting therefrom it was necessary to watch the apparatus and when the run was finally made continuous during the twenty-four

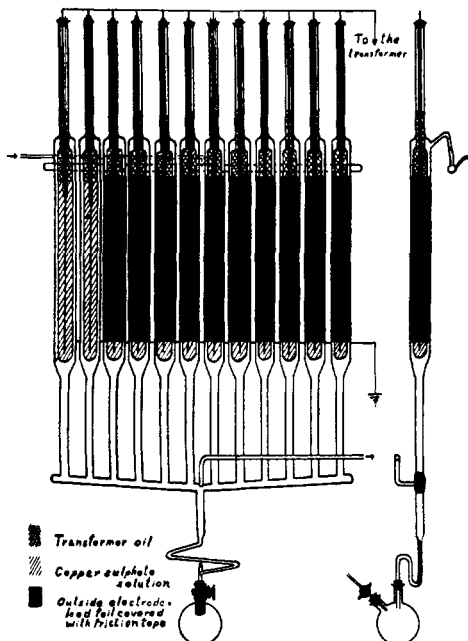


Fig. 1.—Twelve ozonizer tubes in parallel.

hours of a day it was necessary to have a watch maintained at all times. The apparatus was run for 659.2 hours at a gas flow of 3.46 liters of butane (25°, 1 atm.) per hour. There were then used 5420 g. of butane which yielded 1041 cc. of liquid condensate weighing 832.8 g., having a density of 0.804. These figures show that 15.37% by weight of the butane used was converted into liquid condensate. The temperature of the apparatus was about 50° due to the electrical energy consumed (356 k. w. h.), since the twelve ozonizers were protected by asbestos boards (not shown in Fig. 1). This higher temperature was found to aid the run-off of the liquid condensate as previously noted.⁵ The performance of the apparatus was followed by noting daily the amount, color and index of refraction of the liquid product. Its average index of refraction was 1.4600 and its average molecular weight in benzene by the freezing-point method was found to be 178. The color on the arbitrary scale of the Union Oil Co. colorimeter was about 2.75 scale readings. The exit gases have not been analyzed since the primary interest in this present research was concerned with the production and fractionation of the liquid condensate.

Fractionation of the Liquid Condensate.—In order to carry out the fractional distillation of the liquid hydrocarbons obtained from butane, a small chain-still⁶ was built having an 18-inch column filled with iron chain (about 1/8-inch link). With this still the liter of liquid product was distilled at low pressure (using liquid-air traps to avoid loss) and was separated into three main fractions, as shown in Table I.

The Middle Fraction II.—The fractions noted in Table I are still complex mixtures of liquid hydrocarbons and they were in turn subjected

⁵ Lind and Glockler, *THIS JOURNAL*, 50, 1767 (1928).

⁶ This still was built after a drawing obtained from Dr. E. W. Washburn, Bureau of Standards, Washington, D. C. We wish to thank Dr. Washburn for much valuable information regarding distillation problems which was obtained from him during a visit at the Bureau.

TABLE I
 EXPERIMENTAL DATA

No.	Fraction	Vol., cc.	Density	Wt. g.	B. p., °C.	range mm.	Index of refraction
I	Light (liq.-air trap)	450	0.740	335	0-160	740	1.3713-1.4334
II	Middle (cond. at room temp.)	117	.795	93	78-112	5	1.4386-1.4558
III	Heavy (rem. as residue)	465	.872	405	230	10 ⁻⁴	1.4855
		1032	0.804	833			

to further fractional distillation. The middle fraction (II) was thus separated (at 5-mm. pressure) into five sub-fractions boiling between 90 and 98° with a large residue of 38 g. These sub-fractions were again distilled at low pressure in a smaller still of the same design into 14 further small fractions. The range of boiling points now widened to 78-112°. The amounts of the fractions were now rather small and further attempts of separating "middle fraction II" will be made at a later date when more of this material is available for investigation.

The Heavy Fraction III.—This material is the residue which remained in the distilling flask. It is very viscous and has an index of refraction of 1.4855. Beyond the fact that the material is a mixture nothing has been found out about it. It was possible to distil from this heavy oil a much lighter yellow oil at about 230°, using a Nickel-Shot Bath and a very low pressure (10⁻⁴ mm.). It is hoped to study this heavy fraction in greater detail later.

The Light Fraction, I.—This low-boiling section is the material caught in the liquid-air trap and contains, of course, a great deal of dissolved butane. This

gas was removed and collected and its boiling point determined. The total amount of butane (147 g.) was distilled at 0° with exception of a few cubic centimeters which remained as a residue and which must represent slightly higher hydrocarbons. The next material that came over on distilling the "light fraction I" was separated into eleven sub-fractions by making cuts every 10°. The details of this fractionation are shown in Table II; Fig. 2 gives the distillation curve.

It is seen that Fraction I-6 is the largest fraction boiling within a ten-degree interval. This fraction was, therefore, redistilled into five sub-sub-fractions boiling between 105 and 117°.

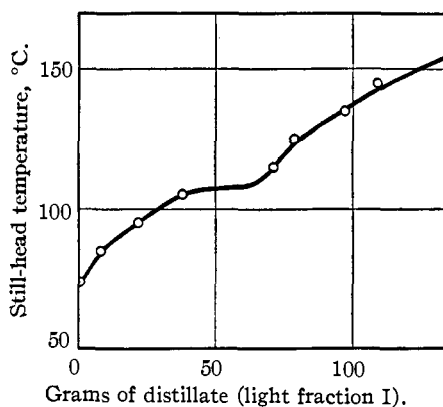


Fig. 2.

TABLE II
FRACTIONATION OF THE "LIGHT FRACTION I" INTO ELEVEN SUB-FRACTIONS (BAROMETER
740 MM.)

No.	Temp. of still-head, °C.	n_{D}^{20} _{sun}	Distillate in grams Each fraction	Total
I-1	26.5-68.0	1.3713	0.2	0.2
I-2	68.0-80.0	1.3843	0.3	0.5
I-3	80.0-90.0	1.3904	7.5	8.0
I-4	90.0-100.0	1.3938	13.5	21.5
I-5	100.0-110.0	1.3997	16.5	38.0
I-6	110.0-120.0	1.4003	33.0	71.0
I-7	120.0-130.0	1.4058	7.5	78.5
I-8	130.0-140.0	1.4110	18.5	97.0
I-9	140.0-150.0	1.4160	12.0	109.0
I-10	150.0-160.0	1.4204	26.0	135.0
I-11	160.0-	1.4334	53.0	188.0
			188.0	

TABLE III
FRACTIONATION OF SUB-FRACTION I-6 INTO FIVE SUB-SUB-FRACTIONS (BAROMETER,
744.2 MM.)

No.	Temp. of still-head, °C.	n_{D}^{20} _{sun}	Distillate, g.
I-6-1	105.0-110.0	1.4004	0.5
I-6-2	110.0-113.0	1.4021	8.0
I-6-3	113.0-115.0	1.4029	6.0
I-6-4	115.0-117.0	1.4036	2.0
I-6-5	117.0-	1.4118	10.0
			26.5

Identification of Fraction I-6-2.—On comparing the boiling point of this fraction and its index of refraction with known hydrocarbons (I. C. T.), it was found that two octanes fit closest in these two properties. They are 2,4-dimethylhexane and 2-methyl-3-ethylpentane. Several properties of this unknown hydrocarbon were therefore determined, such as density, carbon-hydrogen ratio, molecular weight by the freezing-point method in benzene and halogenation number. At the same time these methods were checked on a sample of pure heptane available in the laboratory.

The properties are given in Table IV. The freezing-point determination was checked with pure naphthalene; the combustions were carried out with 0.200-g. samples in an enclosed system;⁷ the halogenations were performed by the iodine-bromide-in-CCl₄ method⁸ and checked against cyclohexene and cymene.⁹

It is at once seen that the unknown material I-6-2 is not a system of

⁷ Geo. Glockler and L. D. Roberts, *THIS JOURNAL*, 50, 828-31 (1928).

⁸ E. M. Johansen, *J. Ind. Eng. Chem.*, 14, 288 (1922).

⁹ The iodine number of cyclohexene was found to be 304 (calcd. 310). By another method Faragher, Gruse and Garner, *J. Ind. Eng. Chem.*, 13, 1044 (1921), found 298. Cymene was also studied and no addition was found, while substitution takes place at a slow rate.

TABLE IV
 PROPERTIES OF PURE HEPTANE, THE UNKNOWN HYDROCARBON I-6-2 AND TWO KNOWN OCTANES

Property	Heptane		Octanes	
	"I. C. T."	Obs.	2,4-Dimethylhexane and 2-methyl 3-ethyl-pentane ("I. C. T.")	Unknown I-6-2
Boiling point, °C.	98.0	97-98	110.0-114.0	110.0-113.0
Density	0.684	0.681	0.708	0.708
Index of refr.	1.3850	1.3855	1.4016-26	1.4021
Carbon, %	83.90	83.79	84.11	84.55
Hydrogen, %	16.10	16.21	15.89	15.45
freezing point	100.12	102.0	114.1	114.7
Mol. wt. {	combustion	113.5
	halogenation	113.7
	Empirical formula by combustion	C ₇ H ₁₆	...	C ₈ H ₁₈
Unsaturation {	combustion, %	30.0
	halogenation, %	22.5

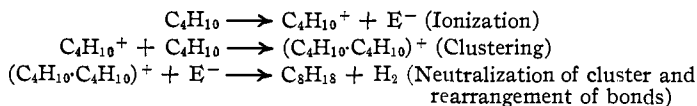
saturated octanes but the halogenation and combustion data show the presence of unsaturated substances. Since the molecular weight, density and index of refraction are very closely those of octanes, it may be assumed that the unsaturation found is due to octylenes.

Discussion of Results.—It is believed that in this work the largest quantity of liquid condensate ever produced from a gaseous hydrocarbon by electrical means has been made. Furthermore, the fractional distillation of this material has been carried to a more detailed extent than has been accomplished by previous investigators. For instance, Pryanishnikow¹⁰ has studied the liquid condensation products obtained from ethylene by electrical discharge, but his fractionation involves cuts covering much larger temperature intervals than is the case in the work reported here. Of course, the identification presented here has therefore a better basis. It would require a still larger amount of liquid condensate to push the separation still further. This would involve the identification of isomeric octanes and octylenes and this problem has not been solved completely even with ordinary hydrocarbon materials.

The distillation curve of the "light fraction I" (Fig. 2) shows that the Fraction I-6 (33 g.) is the largest fraction obtained. From the range of boiling points of this fraction obtained upon further fractionation and from the detailed study of Sub-Fraction I-6-2 it appears that these materials are octanes. Octanes or at least 8-carbon atom materials of molecular weights near octanes are then relatively most abundant in this final liquid product. This result seems to follow quite simply from the cluster theory of ionic gas reactions as proposed by one of us.¹¹ On this theory the reactions leading to condensation by doubling are as follows.

¹⁰ D. N. Pryanishnikow, *Ber.*, **61B**, 1358-1363 (1928).

¹¹ S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., Inc., New York, 2d ed., 1928, p. 100.



Since any butane ions formed would meet with neutral butane molecules most frequently because of the greater concentration of butane, it is to be expected that octanes would be formed relatively in greatest amount. Of course, other possible hydrocarbons would be built by continued and successive actions of the type referred to and since decomposition would also take place it is readily understood that probably all possible combinations of radicals take place in such a manner as to produce a most complex mixture of hydrocarbons.

Just which of the isomeric octanes would be produced in greatest amount would depend upon the reactivity of the various carbon-hydrogen bonds of the butane molecule, and, since it has not been possible to identify the isomers of octane formed, this question must await further experimentation. The octylenes found can be thought to be formed by splitting off two hydrogen molecules upon reaction and rearrangement as typified in Equation 3 above.

In future work it is hoped to carry on the study and identification of some of the other larger fractions as obtained from the present series of distillations and to produce still greater quantities of the original mixture for a more detailed fractionation.

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

Summary

A quantity of liquid hydrocarbons (1041 cc.) has been prepared from gaseous butane by condensation in an electrical discharge. A system of twelve all-glass ozonizers was used for the purpose. The liquid product obtained was separated into 40 fractions by fractional distillation at various pressures. These fractions consist of very light, medium and also very viscous oils. One of the light fractions was studied in detail and found to have the following properties: b. p. 110–114.0°; index of refraction, 1.4021; density, 0.708; molecular weight, 114.7; percentage of carbon, 84.55; percentage of hydrogen, 15.45; empirical formula, $\text{C}_8\text{H}_{17.4}$; unsaturation by halogenation, 22.5 mole per cent. These properties serve to identify this material as a mixture of octanes and octylenes. It is interesting to note that this largest fraction of the lighter oils consists of eight-carbon-atom molecules which can be produced from butane by simple doubling according to theory.

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