2. An electrometric study of a number of weak bases and pseudo bases in glacial acetic acid has revealed the large effect of changing ionic strength which was also noted in the spectrophotometric study.

3. The effect of added water on the apparent constants of a number of weak pseudo bases has been investigated and a method outlined for obtaining significant values for the relative basicity of the "halochromic" carbinols.

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

V. THE CONDENSATION OF HYDROCARBONS BY ELECTRICAL DISCHARGE.

COMPARISON WITH CONDENSATION BY ALPHA RAYS¹

By S. C. LIND² AND GEORGE GLOCKLER³ RECEIVED JULY 18, 1930 PUBLISHED NOVEMBER 5, 1930

In a former paper⁴ it has been shown that the condensation of ethane by electrical discharge in an ozonizer is in many ways similar to the same reaction when produced by the ionization due to the alpha particles from radon.⁵ The experiments have now been extended to the gases methane, propane, butane and ethylene. It has been found *that there* exists a similarity in the condensations as produced by the ionization due to α -particles and by electrical discharge in an ozonizer for all the gases studied. It is the object of the present paper to describe these experiments and to discuss certain experimentally determined ratios which support the statement made. The experiments on ethane have been repeated with the new apparatus and confirm the former study. They are included for the sake of completeness and for comparison.

Experimental Procedure

The apparatus used to study these condensations is shown in Fig. 1 and consists of an all-glass pyrex ozonizer, a Liebig condenser and a manometer. The system as a whole is of the circuit type and a slight circulation was probably attained by the thermal siphon principle since the ozonizer would naturally heat up (to about 40°) during a run due to power losses and since the condenser kept the other leg of the system cold, by

¹ This paper includes part of an investigation on "The Effect of Electrical Discharge upon Gaseous Hydrocarbons," Project No. 8 of American Petroleum 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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S. C. Lind and George Glockler, Trans. Am. Electrochem. Soc., 52, 37-46 (1927).

⁵ S. C. Lind and D. C. Bardwell, THIS JOURNAL, 48, 2335-2351 (1926).

having tap water (18°) running through it. The pressure in the ozonizer changes on account of the changes of temperature due to the reaction. A correction of 12 mm. was applied at the maximum pressure, which was determined by noting the pressure drop in the butane reaction that occurred when the reaction had been stopped near the maximum pressure when the system was allowed to cool to room temperature (Fig. 3). The drop in pressure at the end of the experiments due to cooling was noted to be about

10 mm. and these two corrections were applied to the curves shown in Fig. 2. The trap at the bottom of the ozonizer should catch any liquid condensates and was also used in the first step of the fractional distillation of the gases resulting from the condensations. The ozonizer proper was placed into the circulating system by means of two ground seals (stopcock grease and mercury-seals) in such a manner that it could easily be removed for cleaning before each run. The electrical set-up consisted of a Thordarson Transformer which would furnish about 18,000 volts to the ozonizer with 94 volts and 7.4 amperes in its primary. The electrical conditions were kept constant at these values during all the experiments. The first series of experiments consisted of runs of eight and one-half hours' duration. The pressure changes were observed during the whole period and after the conclusion of each experiment the remaining gases were analyzed for hydrogen, methane, ethane, propane, butane and pentane by fractional distillation, beginning at liquid-air temperatures. The hydrogen in the hydrogen-methane mixture was removed by diffusion through a palladium tube. The remaining methane was checked by combustion and a correction applied for any ethane that might have been pumped off with the hydrogen-methane fraction. Ethane was distilled off at -150° , propane at -120° and butane at -90° . The re-





maining gas was taken to be pentane. The liquid composition (empirical formula) could be determined from these gas analyses by constructing an "atomic balance sheet." It is possible to find the number of carbon and hydrogen atoms that must have gone into the liquid condensate from the amount of hydrocarbon used, its composition and the

GAS ANAL	YSIS OF THE	HYDROCARB	ons Used	
CH4	C ₂ H ₆	C ₂ H ₅	C_4H_{10}	C ₂ H ₄
100.0				•••
	98.0	0.5		
	2.0	99.1	1.0	0.3
		0.4	97.2	1.4
				98.5
			1.8	
		<u> </u>		
100.0	100.0	100.0	100.0	100.2
	GAS ANAL CH4 100.0 100.0	GAS ANALYSIS OF THE CH4 C2H4 100.0 98.0 2.0 100.0 100.0 100.0	GAS ANALYSIS OF THE HYDROCARBO CH4 C2H4 C2H3 100.0 98.0 0.5 2.0 99.1 0.4 100.0 100.0 100.0	GAS ANALYSIS OF THE HYDROCARBONS USED CH4 C2H4 C4H3 C4H10 100.0 98.0 0.5 2.0 99.1 1.0 0.4 97.2 100.0 100.0 100.0 100.0

TABLE I

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analyses of the resulting gases. The initial gases were obtained from commercial sources except methane, which was prepared from sodium acetate. They were reasonably pure as the following analysis (by fractionation) shows.

These gases were distilled into the apparatus and any permanent gases were pumped off. The experimental results are shown in Table II, which

TABLE II

	Exper	IMENTAL	DATA			
Gas used	CH_4	C_2H_5	$C_{3}H_{8}$	C_4H_{10}	C_4H_{10}	C_2H_4
Initial volume, cc.	232	229	228	231	231	222
Initial press., mm.	759	754	753	762	756	744
Time of run, min.	510	480	510	80	510	400
Reaction volume, cc.	238	238	238	238	238	234
Final press., mm.	759	754	787	873	808	215
Final H ₂ , cc.	143	147	143	65	148	47
CH4	64	43	36	41	37	8
C_2H_2				1	• • •	
C_2H_4	• • •			5		
C_2H_6	13	28	42	14	38	3
C ₃ H ₈	5	4	16	13	10	1
C ₄ H ₁₀	2	4	2	127	14	2
$C_{\delta}H_{12}$	3	• • •	2	•••	3	
Final gases, cc.	233	226	242	264	247	60

contains the average of at least two experiments carried out with each gas. It was always possible to obtain graphs of the "pressure-time rela-



Fig. 2.—Pressure changes during condensation in an ozonizer.

tion" which checked very satisfactorily indeed, showing that the experiments are entirely reproducible. In Col. 4 of Table II the details of a

short run (eighty minutes) on butane are given, which was stopped at the maximum pressure attained during the longer (510-minute) run. This experiment was performed to find out whether or not unsaturates are formed during the reaction. This point will be discussed later. The detailed runs are shown in Figs. 2 and 3.



Fig. 3.—Pressure changes during a short (80-minute) run with butane, showing temperature effect.

Discussion of Results

1. The Pressure Changes during Reaction.—It is seen that the saturated hydrocarbons all show the same general pressure change as the reaction proceeds in time. They all show a maximum pressure one to two hours after the beginning of the reaction. Especially remarkable is the decrease of pressure during the later stages of the reaction. The one unsaturated hydrocarbon tried (ethylene) shows a decrease in pressure to about one-third of the initial pressure. Since the object of the present research is a comparison of the alpha-ray condensations of the hydrocarbons with the same reactions produced by electrical discharge in an ozonizer, the data of Lind and Bardwell⁶ of the alpha-ray condensations have been recalculated and replotted so as to be easily comparable with the present material.

In the case of the saturated hydrocarbons the α -ray experiments were

⁶ Reference 5 and also THIS JOURNAL, 48, 1556 (1926).

carried out in stages in such a manner that at the end of each period hydrogen and methane were pumped off. When the data are inspected it is seen that in the case of butane a slight increase in pressure is noticeable. In order to compare the pressure data with the present experiments, it was assumed that during each interval the pressure would have increased the same proportionate amount had the methane and hydrogen been present. This assumption may be a drastic one but the object is only to show that there is a slight increase in pressure during the alpha-ray condensations and this is immediately apparent from the data. The essential data are given in Table III and in Fig. 4. For comparison the pressure changes (final/initial press.) for the ozonizer condensations are given for the first ninety minutes of reaction. It should be noted that the abscissas for the radon reaction are "the time" where "ionization produced since the commencement of the reaction" should be taken in order to be comparable to the corresponding curves for the ozonizer reactions. Since in the ozonizer reactions it may be assumed that a constant current was flowing producing a definite ionization the total ionization may be taken proportional to the time. It was not thought necessary to reduce the alpha-ray reactions since this would merely result in a relative shortening of the abscissas. The only thing of interest was the general picture showing the relative pressure

IKLOOUK		IIII ICID	CONDENSITIONS OF	THE OTHE	MIBD
Hy	DROCARBONS, ⁵ F	for Compar	ison with the Ozonizer	REACTION	s
Gas	$1 - e^{-\lambda t}$	Time	Pressure	(Mm. Hg)	P/P_0
CH₄	0	0		730	1.000
	0.144	17 h		729	0.999
	.290	1 d 21 h	729(641/640)	730	1.000
	.490	3 d 16 h	730(610/609)	731	1.001
	.703	6 d 16 h	731(570/568)	732	1.003
C ₂ H ₆	0	0		1266	1.000
	0.038	3.5 h		1266	1.000
	.159	22 h	1266(1244/1245)	1265	0.999
	.301	1 d 22 h	1265(1179/1175)	1269	1.003
	.415	2 d 22 h	1269(1089/1087)	1272	1.006
C₃H8	0	0		830	1.000
	0.134	17 h		830	1.000
	.278	1 d 19 h	830(794/787)	837	1.008
	.393	2 d 18 h	837(740/735)	845	1.018
	. 577	4 d 18 h	845(703/691)	860	1.035
	.752	7 d 17 h	860(644/633)	875	1.053
C ₄ H ₁₀	0	0		826	1.000
	0.152	21.5 h		831	1.007
	.267	1 d 17 h	831(725/717)	838	1.017
	.388	2 d 17 h	838(652/642)	858	1.038
	.489	3 d 17 h	858(591/577)	880	1.066
	.703	6 d 17 h	880(557/529)	928	1.125

TABLE III PRESSURE CHANCES IN THE PADON CONDENSATIONS OF THE SATURATED

changes in the case of the two types of condensation and it is seen that there is a comparable increase in pressure in these two modes of condensation. It is believed then that the curves of pressure increase as a function of time of reaction establish the first point of our thesis: that there is for the saturated hydrocarbons an analogy in their pressure changes during reaction when under the influence of the two activating agents.



Fig. 4.—Comparison pressure changes in the alpha ray and ozonizer condensations for saturated hydrocarbons.

In an entirely similar manner it has been found that the pressure decreases during the condensation of the unsaturated ethylene both when reaction is brought about by the activation due to alpha rays and in electrical discharge in an ozonizer. Here the data of Lind, Bardwell and Perry⁶ were rearranged as shown in Table IV and the comparison is made in Fig. 5 with the data of the present experiments. In the case of the condensation of ethylene it is seen from Fig. 5 that the relation between (P/P_0) and the total ionization is a straight line, showing in a graphical way that the M/Nratio is constant during the reaction. While the two curves show the same general trend (a decrease in pressure to about one-third the initial pressure), they are not of the same shape. This may mean a difference in the detailed mechanism of the two reactions and needs further investigation. For the present purpose only the most obvious features are to be considered.

The main point is: both condensations of ethylene show a pressure decrease to about one-third the initial pressure.

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TABLE IV

	Pressu	JRE CHAI	NGES IN T	he Rai	OON CONDENSATIO	N OF ETI	HYLENE ⁶	
$1 - e^{-\lambda t}$		i P /76 0			$\Delta(1 - e^{-\lambda t})$	$\times \frac{iP}{100}$	Ionizatio	n P/P_0
	$C_{2}H_{4}$	H_2	CH4	Total		760		
0	2.19	0	0	2.19				1.000
0 0996	1 00	0.0069	0 0000	1 01	0.0386×2.05	0.0792	0.0700	0.000
0.0380	1.90	0.0062	0.0029	1.91	$.0114 \times 1.86$.0212	0.0792	0.882
.0500	1.80	.0081	.0038	1.81	10111 / 1100		. 1004	. 850
					$.0697 \times 1.60$.1130		
.1197	1.35	.0196	.0092	1.38	0.917×1.99	0997	.2134	.684
.1414	1.22	.0236	.0109	1.26	.0211 \ 1.52	.0201	. 2421	. 640
					$.0260 \times 1.20$.0312		
.1674	1.10	.0275	.0129	1.14	0014 \ (1 07	0205	.2733	.600
2015	0.95	0320	.0151	1 00	$.0314 \times 1.07$.0365	3098	540
.2010	0.00		. 0101	1.00	$.0632 \times 0.88$.0557		.010
.2647	.70	.0410	.0195	.76			.3655	.470
4099	26	0540	0961	11	$.1381 \times .60$.0830	1195	270
.4020	.50	.0040	.0201	. = 1	$.1791 \times .36$.0620	. 1100	.570
.5747	. 17	.0675	.0318	.27			.5105	.320
71.40		0770	0000	07	$.2345 \times .27$.0646	6761	050
.7142	.15	.0778	.0300	.27	$.2858 \times .25$	0715	.0/01	.350
1.000	.09	.0983	.0420	.23			.6466	.390





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The study relating to pressure changes can be made in another way by comparing the volume changes during the two condensations and the ratios of the final to the initial pressure and the maximum to the initial pressure. The pertinent data are collected in Table V. It is seen that the same general trend exists for both types of reactions (Col. 3 to be compared with Cols. 4 and 5).

TABLE V PRESSURE RELATIONS. COMPARISON OF RADON AND OZONIZER CONDENSATIONS OF

		HYDROCA	RBONS		
Gas	V Final other gases, cc. (I)	olume relations Hydrocarbon used, cc. (II)	Ratio <u>Col. I</u> Col. II (III)	$\frac{P_{\text{final}}}{P_{\text{initial}}}$ (IV)	$\begin{array}{c} \text{relations} \\ \hline P_{\text{max.}} \\ \hline P_{\text{initial}} \\ (\text{V}) \end{array}$
		Radon Cond	lensation		
CH₄	5.63	5.56	1.01		
C_2H_6	15.92	14.58	1.09		
C ₂ H ₈	19.50	17.07	1.14	• • •	
C_4H_{10}	2 8.09	24.69	1.13		••
C_2H_4			•••	0.323	••
		Ozonizer R	leaction		
CH4	169	168	0.998	1.00	1.03
C_2H_6	198	201	.985	0.99	1.07
C ₈ H ₈	226	212	1.060	1.05	1.14
C_4H_{10}	233	217	1.07	1.07	1.16
C_2H_4	60	222	0.27	0.29	••

2. Free Hydrogen Production.—A further point of comparison between the alpha ray and the ozonizer condensations is the "free hydrogen production" as related to the amount of initial hydrocaron reacted. This quantity may also be expressed as the ratio $(-\Delta H.C./\Delta H_2)$ "hydrocarbon disappearing to hydrogen appearing." The necessary data for its calculation are given in Table VI and for the alpha-ray reactions the figures are taken from the work of Lind and Bardwell.⁵ It should be

TABLE VI

FREE HYDROGEN PRODUCTION

Analysis of free hydrogen production of saturated hydrocarbons by electrical discharge (ozonizer) and comparison with alpha-ray reaction.⁵

	CH4	C_2H_6	C ₃ H ₈	C4H10	C ₂ H ₄
Initial gas (cc. N. T. P.) taken	231.5	229.4	228.1	231.0	222.2
% of gas reacted	72.7	87.6	93.0	94.5	100.0
H ₂ of init. gas reacted (cc. N. T. P.)	167 imes 2	201 imes 3	212 imes 4	218 imes 5	222.2 imes 2
Free hydrogen (ozonizer)	143	147	143	148	47
From ozonizer reaction					
% = (Free H ₂ × 100)/(H of					
init. H. C. reacted)	42.8	24.4	16.8	13.6	10.6
The same $\%$ (α -reaction)	37.8	25.5	16.1	13.9	11.9
$-\Delta HC \int \alpha$	1.32	1.31	1.54	1.44	4.18
ΔH_2) oz.	1.17	1.37	1.44	1.50	4.70

noted that the two modes of expressing the "free hydrogen appearing during the reaction" are related as follows:

 $-\Delta H.C./\Delta H_2 = 1/(\text{free } H \times n)$, where n = 2,3,4,5 for CH_4 , C_2H_6 C_3H_8 and C_4H_{10} , respectively.

By comparing lines five and six and lines seven and eight of Table VI it is seen that these ratios are the same for both types of condensations.

The second point in our argument that the condensations of hydrocarbons by alpha rays and by electrical discharge are similar reactions is then: "the amount of free hydrogen produced is of the same order in both types of condensations." The ratio in question changes to a larger value (about 4) for the unsaturated ethylene.

3. The Percentage of Hydrogen in the Hydrogen-Methane Fraction.—The ratio $\Delta H_2/\Delta(H_2 + CH_4)$ was calculated from the data on gas analysis of the gases after the condensation. It is seen (Table VIII) that the percentage of hydrogen in the hydrogen-methane mixture is about 80%for the reactions of the saturated hydrocarbons and a little greater (86%) for the unsaturated ethylene. The comparison with the similar data on the alpha-ray reaction shows that *in both types of condensation hydrogen and methane appear in the same relative amounts*.

4. Percentage of Liquid Conversion.—The fraction of the hydrocarbon that has undergone reaction which appears as liquid product is seen to be greater in the order: methane, ethane, propane, butane and ethylene. Again this behavior is the same for both kinds of reaction and it may be said that it appears to be easier to convert these hydrocarbons into liquid in the order given.

5. The Liquid Composition.—As has been noted above, it is possible to calculate the average empirical composition of the liquid product from the gas analysis of the reaction products. This calculation has been carried out from the data of Table II and the results are given in Table VIII. It is seen that the average composition of the liquid mixture cor-

III OMIC DIIDIII (D OIIDI	I FOR CONDENDITION OF	
gas volume (N. T. P.)	$= V_0 = V$ (reaction vesse	$1) \times \frac{273}{298} \times \frac{P}{760} = K \times P$
	Carbon	Hydrogen
H_2		K imes 218 imes 2
CH4	K imes 24.2 imes 1	K imes 24.2 imes 4
C_2H_4	$K \times 80.0 \times 2$	$K \times 80.0 \times 4$
	$\overline{K \times 184.2}$	$\overline{K \times 852.8}$
Initial gas	$K \times 1992.0$	$K \times 3984.0$
Liquid phase	$\overline{K \times 1907.8}$	$\overline{K \times 3131.2}$
Liquid com	position $= \frac{3131.2}{1907.8} = 1.65$	or $C_n H_{1.65n}$

TABLE VII Atomic Balance Sheet for Condensation of Ethylene⁶ by Radon

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TABLE VIII

Condensation of Five Hydrocarbons in Electrical Discharge: (Summary of Results and Comparison with Alpha-Ray Condensations⁵

	CH4	C_2H_8	C ₃ H ₈	C_4H_{10}	C_2H_6
(1)	Pressure	Changes			
Final press./initial press. (ozonizer)	1.00	0.99	1.05	1.07	0.29
Final vol./H. C. used (ozonizer)	1.00	0.99	1.06	1.07	.27
Max. press./init. press. (ozonizer)	1.03	1.07	1.14	1.16	••
Final vol./vol. H. C. used (alpha rays)	1.01	1.09	1.14	1.13	.32
(2)	Free Hy	drogen			
$\Delta(\Delta H.C./\Delta H_2)$ (ozonizer)	1.17	1.37	1.44	1.50	4.70
$\Delta(\Delta H.C./\Delta H_2)$ (alpha rays)	1.32	1.31	1.54	1.44	4.18
(3) Hyd:	rogen-M	ethane Rat	tio		
$\Delta H_2 / \Delta (H_2 + CH_4)$ (ozonizer)		0.77	0.80	0.80	0.86
$\Delta H_2 / \Delta (H_2 + CH_4)$ (alpha rays)		.83	.79	.84	.90
(4) I	lquid Co	nversion			
Per cent. (ozonizer)	54	77	74	77	93
Per cent. (alpha rays)	30	56	52	71	96
(5) L	iquid Co	mposition			
Empirical formula (ozonizer)	C_nH_{2n}	C_nH_{2n}	C_nH_{2n}	$C_n H_{2n}$	$C_nH_{1.7n}$
Empirical formula (alpha rays)	$C_n H_{2n}$	$C_nH_{1.9n}$	$C_nH_{1.5n}$	$C_nH_{1.9n}$	$C_nH_{1.7n}$
(6) H	ydrocarb	on Reacte	đ		
Per cent. (ozonizer)	73	88	93	95	100
Per cent. (alpha rays)	18	27	45	68	92

responds to an empirical formula C_nH_{2n} for the saturated hydrocarbons and to $C_nH_{1.7n}$ for the unsaturated ethylene. Similar results have been obtained for the alpha-ray reactions, as is shown in Table VIII. The composition of the liquid condensate derived from ethylene by alpha-ray condensation has been calculated as shown in Table VIII. Another point of similarity has thus been established: The empirical composition of the liquid mixtures derived from both types of condensations is the same.

6. Total Hydrocarbon Reacted.—The percentage of the total hydrocarbon reacted in a given interval of time under similar conditions is greater in the order given above. The same order is found in the alpha-ray reactions. However, these factors are not comparable since the radon reactions were not carried so far toward completion as the ozonizer reactions; but the data do fit into the general picture very well and again it can be said that both reactions show the same general trend.

7. Statement of Results.—The factors studied have been collected in Table VIII and it is believed that the data shown there support the thesis which it is expected to prove: "for all of the hydrocarbons studied the condensations by alpha rays and in electrical discharge have many points in common, which lead to the belief that they both are brought about by the same agency." 8. Mechanism of Reaction.—The question which remains to be answered is: What is the mechanism of these condensations? On the ion-cluster theory the following steps should be taking place: (1) the formation of an ion; (2) the formation of a cluster; (3) the formation of a larger hydrocarbon molecule with elimination of hydrogen and methane; (4) the ionization of the larger molecule by direct electron impact; (5) the formation of an ion of the larger molecule by electron transfer. This mode of ionization is important because it favors the larger molecules for reaction.

On the basis of these reaction steps it is possible to construct many reaction schemes which will conform to the data of Table VIII. It is easily seen that the possibilities for splitting, rebuilding and rearrangements under the above reaction plan are enormous for any of the hydrocarbons investigated and no satisfactory reaction mechanism can be given unless all of the reaction products have been determined. This would mean that not only must the gaseous reaction products be completely analyzed but also the liquid condensation products. As is well known, the analytical difficulties in the separation of the hydrocarbons are considerable. Even if such analyses were made it must be realized that all of the products of the initial reaction except hydrogen condense in a similar manner and in some cases even more readily than does the initial hydrocarbon. This makes the whole problem one of great complexity and while it has been possible to derive a series of reaction schemes which have the advantage of simplicity, uniformity, compliance with the empirical reaction rules laid down above, we prefer to postpone the discussion to a later date when more analytical data have been procured and shorter runs have been studied. The mechanism of these condensations may be studied by shortening the reaction period, so that the initial reaction products are obtained before they have been changed. This method was employed with butane and it appears that unsaturates are formed during the reaction. However, we have only initiated this study and much more work needs to be done.

9. Unsaturates in the Gas Phase.—While it has been found that the average composition of the liquid condensates corresponds to an olefin, no indication has been found that there existed unsaturates in the gas phase at the end of the eight and one-half hour runs. The fractionations carried out on the gaseous reaction products always showed fractions of hydrocarbons which corresponded closely in vapor pressure to the saturated hydrocarbons. However, *one* experiment on butane was stopped with eighty minutes' duration (Fig. 3) and the pressure had then reached the maximum pressure recorded in the former experiment. The analysis by fractionation showed at once that fractions were now present of different vapor pressures from those obtained previously. Ethylene and acetylene thus appear to exist in the gas phase. The disappearance of these unsaturates during the later stages of the reaction may be the cause of the pressure drop observed. In our further work it is expected to study the composition of the reaction products obtained in runs of short duration where the total pressure has reached the maximum pressure of the longer runs. It is hoped that information from these and even shorter runs may help in the derivation of a possible reaction scheme for these condensations.

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

Summary

The condensation of methane, ethane, propane, butane and ethylene has been studied in electrical discharge. It has been found that these reactions are quite similar to the condensations caused by alpha rays. The following factors give evidence of this similarity of reaction: (1) the pressure changes as a function of the time; (2) the free hydrogen produced during the reaction; (3) the relative amount of hydrogen and methane in the hydrogen-methane fraction of the resultant gases; (4) the percentage of liquid conversion; (5) the average composition of liquid condensate; (6) the percentage of the hydrocarbons reacted. All of these factors are quite similar for both types of condensation and it is argued that both types of reaction must be caused by the same mechanism. A reaction scheme is discussed on the basis of the ion cluster theory. The usual ideas are amplified in one respect in that it is assumed that the larger molecules are ionized not only by electron impact but also by electron exchange.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARIZONA] THE COMPOSITION AND STRUCTURE OF MESQUITE GUM¹

> By Ernest Anderson and Louise Otis Received July 18, 1930 Published November 5, 1930

Previous investigations² have shown that mesquite gum yields l-arabinose and d-galactose on hydrolysis and that it contains a hexose uronic acid. When the work described in this article was begun, the gum was assumed to be the salt of a complex organic acid composed of the above substances. This investigation has established the presence of methanol and d-glucuronic acid as constituents of the gum and has shown conclusively that it

¹ The material in this article is extracted from a thesis submitted by Louise Otis in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Northwestern University.

² C. Morfit, Am. J. Sci., 19, 264 (1855); R. H. Forbes, "The Mesquite Tree: Its Products and Uses," Arizona Agricultural Experiment Station, Bulletin No. 13 (1895); E. Anderson, L. Sands and N. Sturgis, Am. J. Pharm., 97, 589 (1925); E. Anderson and L. Sands, Ind. Eng. Chem., 17, 1257 (1925); THIS JOURNAL, 48, 3172 (1926).