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THE CHEMICAL ACTION OF GASEOUS IONS PRODUCED BY ALPHA PARTICLES. IX. SATURATED HYDROCARBONS

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RECEIVED JULY 15, 1926 PUBLISHED SEPTEMBER 4, 1926

Preliminary to a study of its oxidation under the influence of alpha particles, the stability of pure methane was first examined. The absence of change of pressure during exposure to radon mixed with methane in a 2cm. bulb led us to conclude that like carbon dioxide[1] methane is stable under these conditions, and that hence its oxidation probably could be carried out without encountering complications. The latter conclusion was found to be true, but not on account of the assumed stability of methane, the assumption of which now seems to be quite erroneous.[2]

Similar exposure of pure ethane to alpha-radiation gave a more readily apparent result.[3] A liquid phase soon appeared, showing some reaction to be taking place. Similar results were even more readily obtained with propane and with butane. This suggested a reëxamination of the behavior of methane. The residual gases after radiation of methane were separated by fractionation at low temperature, and by using a palladium diffusion apparatus[1] to remove hydrogen. It was found that only about one-fourth of the original methane remained unchanged, despite the constancy of pressure observed. This could readily be accounted for by a reaction such as $2CH_4 = H_2 + C_2H_6$. Further study has shown, however, that other simultaneous reactions must be taken into account in explaining the remarkable constancy of total pressure during the methane reaction. This will be referred to later.

In general, the reactions that all of the paraffins from methane to butane undergo are complicated by simultaneous and successive reactions to such a degree that only their broader aspects have been worked out. On this account we forego attempting to apply the usual equation for velocity of reaction except to the oxidations of methane and of ethane. Some changes of experimental procedure were also necessitated.

Owing to the difficulty of interpreting the manometric data, even with the aid of thermal analysis at low temperatures, it was necessary from time to time to lower the system to liquid-air temperature and to pump off hydrogen and methane for analysis. To provide enough material for this purpose, larger reaction vessels had to be used. This involved the obstacle of not being able to calculate α-ray ionization accurately by the

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[1] Lind and Bardwell, THIS JOURNAL, **47**, 2690 (1925).

[2] Lind and Bardwell, *Science*, **62**, 422 (1925).

[3] Lind and Bardwell, *ibid.*, **60**, 364 (1924).

average-path method[4] for spheres of such large size. The first expedient was to run two parallel experiments, one in a small sphere for manometry and the calculation of ionization, another in a larger sphere for chemical analysis. This duplication has been rendered unnecessary by a most valuable contribution of Professor W. Mund[5] of the University of Louvain, who has ingeniously solved the problem of calculating ionization produced by radon in spheres, without imposing the former upper limitations as to diameter. We have used Mund's equation successfully, and incidentally can support its validity by having found agreement with values obtained by the average-path method in an intermediate region where both are applicable.

The different saturated hydrocarbons behave similarly in their ionic reactions, as was pointed out in Part VII. Free hydrogen is always eliminated, free carbon never; condensation products result which may be gaseous, liquid or solid, and the reactions continue under further radiation even in the liquid and solid members. Not only is hydrogen liberated but also hydrocarbons lower than the original one are formed. All of this soon gives a mixture of hydrocarbons still interacting; therefore the sample "cuts" should be taken at the shortest intervals feasible in order to maintain conditions as simple and definite as possible.

The experimental methods are in general identical with those previously employed, though the procedure requires some explanation, and a few new methods of analysis and preparation are described in the following sections.

Preparation of Gases.—Methane was taken from the middle fraction of a large supply of liquid methane that Dr. Frank Porter had purified from natural gas from Petrolia, Texas. The boiling points of the first and last thirds of the liquid phase did not differ by more than 0.01°.

Ethane was taken from a large supply prepared by Dr. A. G. Loomis and Mr. J. E. Walters for vapor-pressure measurements. Its purity was demonstrated by the same test as for methane above.

Propane and butane were purified by fractionating commercial grades (about 90%) of these gases, obtained from Dr. A. B. Lamb of Harvard University. The boiling points of the first and last thirds of purified gas did not differ by more than 0.01°. The vapor-pressure tests of purity were made in the cryostat used by Perry and Bardwell[6] and Perry and Porter[7] with platinum-resistance thermometer No. 4.[8]

Methods of Analysis.—The gaseous hydrocarbons separated as products of radiation were tested for unsaturation (see Part VII). They were then exploded with an excess of oxygen and the contraction was measured. The carbon dioxide formed was determined by absorption with potassium hydroxide (see Part VI). This combustion served as an approximate check on the fractionation.

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[4] Lind, "Chemical Effects of Alpha Particles, etc.," Chemical Catalog Co., New York, **1921**, p. 82.

[5] Mund, *Ann. Soc. Sci. Brux*, **44**, 336 (1925); *J. Phys. Chem.*, **30**, 890 (1926).

[6] Perry and Bardwell, THIS JOURNAL, **47**, 2629 (1925).

[7] Perry and Porter, *ibid.*, **48**, 299 (1926).

[8] Loomis and Walters, *ibid.*, **47**, 2851 (1925).

Experimental Procedure.—Experiments on the oxidations of methane and of ethane and preliminary studies of methane, ethane and propane condensations were conducted in small bulbs (2 cm. diameter). The procedure was that described in Part VI. The experiments reported in Tables I, II, III and IV were conducted as follows.

Radon was introduced in the usual manner[1] and measured by its γ-ray activity four hours after the time of introduction. The pure hydrocarbon was then introduced and its pressure measured. After a suitable period of radiation, the total pressure was again measured at room temperature. The bulb was then immersed in liquid air and the hydrogen and methane produced in the reaction were removed by a Toepler pump.[9] The bulb was then brought quickly to room temperature and the total pressure measured. Following another interval of radiation, the total pressure was measured and the hydrogen and methane produced were removed from the bulb in liquid air. This procedure was repeated for several intervals of radiation. The hydrocarbons that are condensable in liquid air were then separated by fractionation using baths at —150°, —125° and —95° for the removal of ethane, propane and butane, respectively, by means of a Toepler pump.

Methane.—Mund and Koch[10] first exposed methane to α-rays. Using 100 millicuries of radon they found a small reduction of pressure amounting to 10 mm. in three days, from which they concluded that a reaction took place which diminished the number of gaseous molecules present. No mechanism of reaction was proposed nor was any observation of liquid droplets recorded.

The results of the present measurements of the condensation of methane under α-radiation of radon are given in Table I. In the column for total pressure, it is shown that the experiment was conducted in stages. At the end of each stage, the reaction sphere was immersed in liquid air boiling at about 4 cm. pressure and all of the hydrogen produced, together with some of the methane, was pumped off and determined separately. After four such operations, all of the methane was pumped off from liquid air. The residue was then allowed to warm, giving gaseous hydrocarbons, ethane, propane, butane and higher homologs and also some liquid, the total quantities of which are shown in the balance sheet of Table I. The gases were subjected to low-temperature rectification; the fractions were analyzed by combustion methods, including the dry thermal absorption of carbon dioxide as described in Part VI.[1] These fractions examined by the copper catalytic method described in Part VII[11] revealed no unsatura-

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[9] In the methane experiment, the liquid air was boiled at about 4 cm. pressure in order to reduce the temperature to about $-200°$, thus diminishing the loss of methane accompanying the removal of hydrogen.

[10] Mund and Koch, *Bull. soc. chim. Belg.*, **34**, 120 (1924).

[11] Lind, Bardwell and Perry, THIS JOURNAL, **48**, 1557 (1926).

TABLE I

CONDENSATION OF METHANE

Reaction sphere: vol., 32.00 cc.; diam., 3.940 cm. Temp., 25°. E_0 = 0.0671 curie.
Reaction: $2CH_4 \longrightarrow$ (A) $C_2H_6 + H_2$ or (B) $C_2H_4 + 2H_2$.

Time Days	Hours	$e^{-\lambda t}$	P_{total}	Cc. pumped off H_2	CH_4	$\frac{M_{H_2}}{N_{\text{total}}}$	$\frac{-M_{CH_4}}{N_{CH_4}}$
0	0	1.00000	730.2				
0	16.17		729.0				
0	20.75	0.85589	Pumped off H_2 and some CH_4	1.01	2.75	1.62	
0	21.5		640.7				
1	20.5		641.2				
1	21.75	.70955	Pumped off H_2 and some CH_4	0.908	0.470	1.66	
1	22.25		609.6				
3	16.33		610.3				
3	17.75	.51013	Pumped off H_2 and some CH_4	1.173	.693	1.63	
3	18.25		567.8				
6	16.00		570.0				
6	17.5	.29685	Pumped off H_2 and some CH_4	1.135	6.580	1.54	
6	18.0		388.5				
6	19		All methane pumped off from liquid air	Total pumped off in previous steps			
6	19.5		Residual pressure 38.1		10.493	1.61	2.2

Analytical Results in Cc. of Gas

	CH_4	H_2	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
Initial	30.80	...	...	...	...	...
Final	25.24	4.226	0.863	0.296	0.171	0.067

$$\frac{-\Delta CH_4}{\Delta H_2} = \frac{5.56}{4.226} = 1.315$$

Atomic Balance Sheet in Cc.

		C	H
Initial as CH_4		30.80	123.2
Reacted		5.56	22.3
Final in gas phase:			
	as CH_4	25.24	100.96
	C_2H_6	1.726	5.178
	C_3H_8	0.888	2.278
	C_4H_{10}	.684	1.710
	C_5H_{12}	.335	0.804
	H_2		8.452
Total as gases		28.89	119.38
In liquid		1.927	3.84

Emp. formula of liquid $C_nH_{1.98n}$

Over the whole reaction $\frac{N_{\text{total}}}{N_{CH_4}} = 1.05$

$$\frac{-M_{CH_4}}{N_{CH_4}} = \frac{-\Delta CH_4}{\Delta H_2} \times \frac{M_{H_2}}{N_{\text{total}}} \times \frac{N_{\text{total}}}{N_{CH_4}} = 1.32 \times 1.61 \times 1.05 = \mathit{2.2}$$

There was no hydrogenation of the ethane fraction by the copper catalyst, indicating absence of ethylene or other unsaturated hydrocarbons in the gas phase.

tion in the gas phase either from methane or from any of the other saturated hydrocarbons studied, although the liquid residue at room temperature is always unsaturated according to the empirical formula obtained by difference, which in the case of the residual liquid from methane is $C_nH_{1.98n}$. The speedy removal of unsaturated compounds from the gas phase to the liquid will be discussed in connection with the theory of the condensation itself (see also under "Ethane").

Condensation of Ethane.—Ethane was first examined under α-radiation by Lind and Bardwell[4] and independently by Mund and Koch[5] a little later. Mund and Koch put forward the following theory of reaction in two stages: (1) $C_2H_6 \longrightarrow C_2H_4 + H_2$; followed by (2) $xC_2H_{4g} \longrightarrow (C_2H_4)_x l$. Although they state that Reaction 2 takes place almost immediately, yet they seem to believe that the ethylene molecule formed must first be acted on again by radon before it condenses to liquid, in support of which they described an experiment showing direct condensation of ethylene by α-radiation. The two views hardly seem compatible. If the ethylene formed from ethane must be ionized before it condenses, the rate of reaction will be controlled by the partial pressure of ethylene, its specific ionization, and the ratio $-M_{C_2H_4}/N_{C_2H_4}$ (= 5 as shown in Part VIII).[12] Although the $-M/N$ ratio is considerably greater for ethylene than for ethane, nevertheless the low partial pressure of ethylene formed from ethane would entail a slow rate of disappearance if dependent on its ionization. Our continued failure to find unsaturated hydrocarbons in the gas phase (although they are abundantly indicated in the liquid, and although our theory assumes their momentary existence) forces us to conclude that their condensation is really "immediate," by which we mean that they do not behave like ordinary olefins since they require no further action by α-radiation to condense to liquid. Our theory involves the following reactions by Method A and more rarely by B.

$$C_2H_6 + (\alpha) \longrightarrow C_2H_6^+ + (-);\quad C_2H_6^+ + C_2H_6 \longrightarrow (C_2H_6)_2^+;$$

$$\begin{array}{lll} (A_1) & (C_2H_6)_2^+ + (-) \longrightarrow & \left\{\begin{array}{ll} (1) & C_4H_{10} + H_2 \text{ or} \\ (2) & C_4H_8 + 2H_2 \text{ followed immediately by } xC_4H_{8g} = \\ & (C_4H_8)_x l \end{array}\right. \\ (A_2) & & \\ (B) & (C_2H_6)_2^+ + (-) \longrightarrow CH_4 + C_3H_8 & \end{array}$$

From the ratio $-\Delta C_2H_6/\Delta H_2 = 1.31$, A_1 and A_2 appear to occur about in the ratio 1:1. From analysis of the gases evolved $A_{(1 \text{ or } 2)}$ and B occur in the ratio 5:1.

Our mechanism, based on the assumption of a singly charged, 2-molecule cluster preceding elimination of hydrogen, differs from that of Mund and Koch in certain respects. It predicts the higher gaseous hydrocarbons and more of butane than of propane, as found (Table II). The quantity of any one higher hydrocarbon found in the gas phase is, of course, less than would

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[12] Lind and Bardwell, THIS JOURNAL, **48**, 1575 (1926).

be required by the equations just given, because by further ionization it has in part gone to form yet higher gaseous and liquid members. This

TABLE II

CONDENSATION OF ETHANE

Reaction sphere: vol., 32.92 cc.; diam., 3.977 cm. Temp., 25°. $E_0 = 0.0922$ curie.
Reaction: $2C_2H_6 \longrightarrow$ (A) $C_4H_{10} + H_2$ or (B) $C_4H_8 + 2H_2$.

Time Days	 Hours	$e^{-\lambda t}$	P_{total}	Pumped off H_2, cc.	 CH_4, cc.	 H_2, %	$\frac{M_{H_2}}{N_{\text{total}}}$	$\frac{-M_{C_2H_6}}{N_{C_2H_6}}$
0	0	1.00000	1265.8					
0	3.5		1266.0					
0	5.17	0.96199	Pumped off CH_4 and H_2	0.742	0.216	77.5	1.275	
0	5.5		1244.5					
0	22.0		1243.9					
0	23.7	.84051	Pumped off CH_4 and H_2	2.728	.455	85.6	1.35	
0	23.67		1175.0					
1	22.0		1178.5					
1	23.67	.69943	Pumped off CH_4 and H_2	3.474	.763	82.0	1.57	
2	0.17		1086.9					
2	22.33		1089.3					
2	23.5	.58495	Pumped off CH_4 and H_2	2.733	.582	82.5	1.555	
3	0.17		1019.0					1.7

Analytical Results in Cc. of Gas

	C_2H_6	CH_4	H_2	C_3H_8	C_4H_{10}	C_5H_{12}
Initial	54.75	...	....	...	...	...
Final	40.17	2.268	11.156	0.752	1.61	0.125

$$\frac{-\Delta C_2H_6}{\Delta H_2} = \frac{14.58}{11.16} = 1.31$$

Atomic Balance Sheet in Cc.

		C	H
Initial as C_2H_6		109.50	328.5
Reacted		29.16	87.5
Final in gas phase:			
	as H_2	.....	22.312
	CH_4	2.27	9.072
	C_2H_6	80.34	241.02
	C_3H_8	2.256	6.016
	C_4H_{10}	6.44	16.1
	C_5H_{12}	0.625	1.50
Total		91.931	296.020
As liquid		17.57	32.48
Formula $C_nH_{1.85n}$			

$$\text{Over the whole reaction: } \frac{N_{\text{total}}}{N_{C_2H_6}} = 1.05$$

$$\frac{-M_{C_2H_6}}{N_{C_2H_6}} = \frac{-\Delta C_2H_6}{\Delta(CH_4 + H_2)} \times \frac{M_{(CH_4+H_2)}}{N_{\text{total}}} \times \frac{N_{\text{total}}}{N_{C_2H_6}} = 1.085 \times 1.483 \times 1.05 = \mathit{1.69}$$

There was only 0.5% contraction of "ethane cut" in fuming H_2SO_4 as against about 1% shown by pure C_2H_6 under the same conditions. No hydrogenation of "butane cut" could be effected with copper catalyst.

theory takes into account that $-\Delta C_2H_6/+\Delta H_2$ is not equal to 1 (as required by Mund and Koch) but is between 1 and 2 as we find for methane and also for propane and butane, which again fits with the presence of some higher gaseous saturated hydrocarbons.

To explain the immediate condensation of the unsaturated hydrocarbons, we assume that at least two of the four valences left free by the simultaneous removal of $2H_2$ from a 2-molecule cluster, do not immediately satisfy each other and close up, but remain open and act as centers of attraction for other similar open pairs until a large chain or ring compound is condensed out as liquid, thus preventing the accumulation of any unsaturates in the gas phase. The fact that the unsaturated hydrocarbons do not accumulate in the gas phase is not only shown by failure to find them by the catalytic-hydrogenation method, but also by the constancy of gas pressure during reaction, which requires that all three reactions, A_1, A_2 and B, proceed at constant pressure.

Propane and Butane.—Propane and butane (Tables III and IV) behave much like ethane. Both hydrogen and lower hydrocarbons are eliminated, giving the higher members and an increasing amount of liquid (or solid) the higher the initial member.

With propane, if we use a 2cm. sphere and 100 millicuries, the material becomes entirely solid, passing through a vaseline-like stage and finally becoming sufficiently "dry" to draw away from the wall; but when using a sphere of twice the diameter with the same amount of radon, the product is a clear liquid. The difference appears to be due to the amount of radiation received by the liquid phase which determines secondary reaction and consequently whether condensation may lead to appearance of solid. In the small sphere the formation of liquid is completed while there is still sufficient radon to carry the liquid on into the solid state; furthermore, owing to the smaller area, the wall radiation per unit area is four times greater.

General Discussion of the Action of Alpha Particles on Saturated Hydrocarbons

The most striking characteristic of these reactions is the fact that beginning with any pure member of the series, exposure to α-radiation results in the elimination of hydrogen or lower saturated hydrocarbons, thus building up higher members by addition or condensation as a result of valences freed in the process. Soon a mixture of gaseous and later of liquid or eventually of solid phases is present which may contain all members of saturated and unsaturated series up to the highest product attained. To produce by this means sufficient quantities of the liquid or solid phases to permit their separation and identification appears to be a difficult task which has not been attempted in the present work. However, the

TABLE III

CONDENSATION OF PROPANE

Reaction sphere: vol., 34.79 cc.; diam., 4.051 cm. Temp., 25°. $E_0 = 0.0737$ curie.
Reaction: $2C_3H_8 \longrightarrow$ (A) $C_6H_{14} + H_2$ or (B) $C_6H_{12} + 2H_2$.

Time				Pumped off				
Days	Hrs.	$e^{-\lambda t}$	P_{total}	H_2, cc.	CH_4, cc.	H_2, %	$\frac{M_{H_2}}{N_{\text{total}}}$	$\frac{-M_{C_3H_8}}{N_{C_3H_8}}$
0	0	1.00000	830.1					
0	17		829.9					
0	19.25	0.86557	Pumped off CH_4 and H_2	2.01	0.423	82.6	1.150	
0	19.5		786.8					
1	19.0		794.1					
1	19.5	.72163	Pumped off CH_4 and H_2	2.16	.724	74.8	1.30	
1	19.75		734.5					
2	17.75		740.3					
2	18.5	.60730	Pumped off CH_4 and H_2	1.78	.554	76.2	1.365	
2	19.0		690.8					
4	17.5		703.4					
4	18.75	.42292	Pumped off CH_4 and H_2	2.685	.655	80.3	1.27	
4	19.0		632.5				Wtd.	
7	17.0		643.9				Av. 1.263	
7	18.0		Pumped off from liq. air	2.37	.665	78.1		
7	18.25		576.8	11.005	3.021			1.74

Analytical Results in Cc. of Gas

	C_3H_8	CH_4	H_2	C_2H_6	C_4H_{10}	C_5H_{12}
Initial	38.0	...	....	...	...	..
Final	20.93	3.021	11.005	1.763	2.120	1.59

$$\frac{-\Delta C_3H_8}{\Delta(H_2)} = \frac{17.07}{11.01} = 1.54$$

Atomic Balance Sheet in Cc.

	C	H
Initial as C_3H_8	114.00	304.00
Reacted	51.2	136.6
Final as gases:		
as H_2	.....	22.01
CH_4	3.021	12.084
C_2H_6	3.526	10.578
C_3H_8	62.79	167.44
C_4H_{10}	8.48	21.20
C_5H_{12}	7.95	19.08
Total	85.76	252.39
As liquid	28.23	51.61
Formula of liq. $C_nH_{1.83n}$		

Over the whole reaction: $\frac{N_{\text{total}}}{N_{C_3H_8}} = 1.137$

$$\frac{-M_{C_3H_8}}{N_{C_3H_8}} = \frac{\Delta C_3H_8}{\Delta(CH_4 + H_2)} \times \frac{M_{(CH_4+H_2)}}{N_{\text{total}}} \times \frac{N_{\text{total}}}{N_{C_3H_8}} = 1.216 \times 1.263 \times 1.137 = \mathit{1.74}$$

No hydrogenation of the butane cut could be effected with copper catalyst.

TABLE IV

CONDENSATION OF BUTANE

Reaction sphere: vol., 33.21 cc.: diam., 3.988 cm. Temp., 25°. $E_0 = 0.1216$ curie.
Reaction: $2C_4H_{10} \longrightarrow$ (A) $C_8H_{18} + H_2$ or (B) $C_8H_{16} + 2H_2$.

Time Days	Hrs.	$e^{-\lambda t}$	P_{total}	Pumped off H_2, cc.	Pumped off CH_4, cc.	H_2, %	$\frac{M_{H_2}}{N_{\text{total}}}$	$\frac{-M_{C_4H_{10}}}{N_{C_4H_{10}}}$
0	0	1.00000	825.5					
0	21.5		830.5					
0	22.0	0.84789	Pumped off CH_4 and H_2	4.391	0.769	85	1.163	
0	22.25		717.1					
1	16.75		724.7					
1	17.75	.73253	Pumped off CH_4 and H_2	3.160	.550	85.1	1.195	
1	18		642.1					
2	17.25		656.4					
2	17.75	.61187	Pumped off CH_4 and H_2	2.955	.565	84	1.21	
2	18.0		576.6					
3	17.0		591.2					
3	17.5	.51109	Pumped off CH_4 and H_2	2.301	.439	84	1.245	
3	18.0		528.8					
6	16.75		557.3					
6	17.5	.29685	Pumped off CH_4 and H_2	4.268	.812	84	1.263	
6	17.75		441.0	17.075	3.135	Wtd.		
						Av.	1.21	1.8

Analytical Results in Cc. of Gas

	C_4H_{10}	CH_4	H_2	C_2H_6	C_3H_8	C_5H_{12} and higher
Initial	36.10	...	....	..	..	...
Final	11.41	3.135	17.075	3.42	2.83	1.615

$$\frac{-\Delta C_4H_{10}}{\Delta H_2} = 1.44$$

Atomic Balance Sheet in Cc.

	C	H
Initial as C_4H_{10}	144.4	361.0
Reacted	98.8	246.9
Final as gases:		
as H_2	.....	34.150
CH_4	3.135	12.440
C_2H_6	6.84	20.52
C_3H_8	8.49	22.64
C_4H_{10}	45.64	114.10
C_5H_{12}	8.075	18.38
Total	72.180	222.23
As liquid	72.22	138.77
Formula of liq. $C_nH_{1.9n}$		

$$\text{Over the whole reaction: } \frac{N_{\text{total}}}{N_{C_4H_{10}}} = 1.205$$

$$\frac{-M_{C_4H_{10}}}{N_{C_4H_{10}}} = \frac{-\Delta C_4H_{10}}{\Delta(CH_4 + H_2)} \times \frac{M_{(CH_4+H_2)}}{N_{\text{total}}} \times \frac{N_{\text{total}}}{N_{C_4H_{10}}} = 1.222 \times 1.21 \times 1.205 = 1.78$$

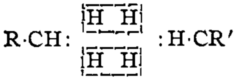
No hydrogenation of the C_8H_8 cut could be effected with copper catalyst at 170°.

residual and in most cases the intermediate fractions of *gas* have been carefully analyzed and support the statements just made. The absence of unsaturated hydrocarbons in the gas phase has been discussed. The empirical formula of the liquid phase indicates unsaturation in all cases.

Geologically it is interesting that this furnishes a method by which the higher hydrocarbons may be built from the lower in nature. The α-radiation in the earth's crust is of very low intensity, yet continued over long geological periods it produces large total effects. *The almost complete absence of hydrogen in most natural gases*, while well recognized, is difficult to explain on this basis unless it be removed by some selective action like the reduction of metallic oxides, which action may also be enhanced by contact catalysis.

The constancy of the ratio in which hydrogen and methane are eliminated from the different members above methane is notable. The following general methods of linkage are suggested.

(1) $R\cdot CH_2\cdot \boxed{H\ \ H}\ .H_2\ C\cdot R'$

(2) 

$R\cdot CH: \begin{matrix}\boxed{H\ \ H}\\ \boxed{H\ \ H}\end{matrix} :H\cdot CR'$

(3) $R\cdot \boxed{CH_3\ \ H}\ .H_2\ C\cdot R'$

(4) $R\cdot \boxed{CH_3\ \ CH_3}\cdot R'$

Just why the ratio should be nearly $5H_2$:$1CH_4$ is not evident. Methane may result from the removal of one of the electrons constituting the carbon-to-carbon bond. On a simple basis of numerical probability the ratio would be $3H_2$:$1CH_4$ but it is quite conceivable that other considerations, possibly steric ones, may cause the rupture to occur in the ratio $5H_2$:$1CH_4$.

The assumption that we make of a 2-molecule cluster being formed before reaction takes place is supported by the M/N ratio of 2, and is in agreement with the same kind of indirect evidence from many other reactions.[13] The further assumption, however, that the 2-molecule cluster is formed on the *positive* ion is based on the evidence that free electrons have little affinity for hydrocarbon molecules.[14]

Summary of Results for Hydrocarbons

Table V contains a summary of results, some of which deserve special attention.

The second column, $-M_{\text{H.C.}}/N_{\text{H.C.}}$[15] designates the number of molecules of original hydrocarbon (of the kind indicated by Col. 1) reacting per ion pair produced on that hydrocarbon. The value 2 conforms with our general theory as already explained, and is seen to be independent of the nature of the hydrocarbon and of all other variables.

Col. 3, $-\Delta\text{H.C.}/\Delta H_2$, shows the ratio of disappearance of H.C. mole-

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[13] Lind, *Science*, **64**, 1 (1926).

[14] Loeb, *Phil. Mag.*. [6] **43**, 229 (1922).

[15] In the following, "H. C." is used as a general abbreviation for hydrocarbon.

TABLE V

CONDENSATION OF SATURATED HYDROCARBONS BY α-RADIATION. SUMMARY OF RESULTS FOR CH_4, C_2H_6, C_3H_8 AND C_4H_{10}

Initial H.C.	$\frac{-M_{H.C.}}{N_{H.C.}}$	$\frac{-\Delta_{H.C.}}{\Delta_{H_2}}$	$\frac{\Delta_{H_2}}{\Delta(H_2 + CH_4)}$	H.C. reacted, %	In liquid phase Atoms reacting, % C	H	Formula
CH_4	2.2	1.32	..	18.1	34.7	17.2	$C_nH_{1.98n}$
C_2H_6	1.7	1.31	0.83	26.7	60.0	37.2	$C_nH_{1.85n}$
C_3H_8	1.7	1.54	.79	44.8	55.0	37.8	$C_nH_{1.83n}$
C_4H_{10}	1.8	1.44	.84	68.4	73.2	56.2	$C_nH_{1.90n}$
		Av.	.82				

Initial H.C.	In gas phase (% of total C atoms reacted) CH_4	C_2H_8	C_3H_8	C_4H_{10}	C_5H_{12} or higher	Found	% H free, calcd. for H_2	$(5H_2 + 1CH_4)$
CH_4	...	31.0	16.0	12.3	6.0	37.8	37.5	..
C_2H_6	7.8	...	7.8	22.1	2.2	25.5	25.0	20.8
C_3H_8	5.9	6.9	...	16.6	15.5	16.1	18.75	15.6
C_4H_{10}	3.1	6.9	8.6	..	8.1	13.9	15.00	12.5

cules per hydrogen molecules generated. A value *1.33* corresponds to a 50:50 split of two double clusters, $2(H.C.)_2$, one breaking to eliminate one and the other, two hydrogen molecules per cluster, thus giving three molecules of hydrogen from four molecules of the hydrocarbon. Propane and butane depart slightly in the direction of too little hydrogen or less unsaturation of products. This will be more clearly brought out below.

Col. 4, $\Delta H_2/\Delta(H_2 + CH_4)$, shows the portion of hydrogen in the hydrogen and methane mixture liberated from the hydrocarbons above methane. The ratio is approximately 5:1 and fairly constant for the different members. Elimination of methane to provide linkage seems to be required theoretically to obtain odd members from even, because mere doubling or cross reactions could not produce any odd members. Ethane is probably produced by direct elimination, according to Method 4 above but is also the result of the condensation of secondary methane.

Col. 5 showing the per cent. of reaction is, of course, dependent on many circumstances capable of arbitrary control and of no fundamental importance, but it will be observed how much more reaction is obtained with the higher members, other things being equal. This is due to their superior stopping power giving more ionization, not to any greater efficiency of the ionization once produced (see Col. 2).

The columns for liquid phase show the greater tendency for the higher hydrocarbons to give liquid upon reacting. The percentage of liquid referred to the original gases would show a yet greater percentage of condensation by the heavy members, for the three reasons that they have not far to go to become liquid, they absorb more energy to promote the process, and produce more liquid in condensing from the same gas volume.

Among the gas-phase data, those for free hydrogen appear to have especial theoretical significance. Taking them in order, for methane we should predict for the primary liberation of hydrogen, 37.5% of the total hydrogen in the methane reacting, according to the following:

For Methane: 50% A: $2CH_4 = C_2H_6 + H_2$ Free hydrogen, %
50% B: $2CH_4 = C_2H_4 + 2H_2$ Calcd. Found
$\overline{16H}$ $\overline{6H}$ = 37.5 37.8

For Ethane: 50% A: $2C_2H_6 = C_4H_{10} + H_2$
50% B: $2C_2H_6 = C_4H_8 + 2H_2$
$\overline{24H}$ $\overline{6H}$ = 25 25.5
or taking account of CH_4 also[16] 20.8

For Propane: 50% A: $2C_3H_8 = C_6H_{14} + H_2$ Free hydrogen, %
50% B: $2C_3H_8 = C_6H_{12} + 2H_2$ Calcd. Found
$\overline{32H}$ $\overline{6H}$ 18.75 16.1
or taking account of CH_4 15.6

For Butane: 50% A: $2C_4H_{10} = C_8H_{18} + H_2$
50% B: $2C_4H_{10} = C_8H_{16} + 2H_2$
$\overline{40H}$ $\overline{6H}$ = 15 13.9
or taking account of CH_4 12.5

This appears to furnish a striking confirmation of the special condensation theory assuming an equal chance of the formation of saturated and of unsaturated hydrocarbons. In fact, the agreement appears too good since no account has been taken of hydrogen generation nor of hydrocarbon loss through secondary reaction of products and of liquid; also some of the lower hydrocarbons like methane or ethane would be regenerated by elimination from higher products. Evidently these various secondary processes would be in part compensatory. The fact that agreement with the theory of the primary reaction is so good indicates the compensations to be fairly exact.

Although not giving the better direct agreement, the comparison which includes elimination of methane with that of hydrogen as a means of linking two hydrocarbons is the one apparently more closely related to the facts, and also the more logical in that the amount of free hydrogen found is greater than that calculated, thus leaving a margin to account for some additional hydrogen generation by secondary reaction.

The entire ensemble of series and parallel reactions is too complicated to analyze completely, but some of the most prominent characteristics may be mentioned and others can probably be developed by further study of the data. Methane forms less liquid than predicted directly from the unsaturated hypothesis, while ethane, propane and butane all form somewhat more. The latter is to be expected from formation of saturated liquid

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[16] This is done by assuming that for each six linkages five will be provided by eliminating hydrogen and one by the methane route; we therefore deduct $^1/_6$ of the theoretical hydrogen before comparison with that found.

members by further direct doubling with elimination of hydrogen. In the case of methane, on account of the determination of liquid by a difference method, the small amount reported is subject to larger error. When ethane is radiated the quantity of butane formed exceeds all members with an odd number of carbon atoms in the molecule, thus supporting the direct-doubling theory.

Reactions of Oxidation

Methane.—It has been stated already that a study of the oxidation of methane was undertaken on the assumption that methane itself was stable under α-radiation. It was found that the reaction with oxygen proceeds regularly according to the equation $CH_4 + 2O_2 = CO_2 + 2H_2O$. The assumed clusters from one ion pair are $(O_2{\cdot}CH_4{\cdot}O_2)^+ + (O_2^-{\cdot}CH_4{\cdot}O_2) = 2CO_2 + 4H_2O$. Experimentally we find *1.5* CO_2 + *3.0* H_2O per ion pair.

The oxidation is exclusive; no hydrogen is found at the end of the reaction, nor does the kinetics indicate any, since the reaction proceeds at all stages proportionally to the radon present and to the pressure of the reactants. The results are shown in Table VI. The deficiency of carbon dioxide at the end of the reaction is probably due to its having reacted to some extent with methane, which will be discussed later.

Table VI

Oxidation of Methane

Reaction sphere: vol., 4.005 cc.; diam., 1.971 cm. Temp., 25°. E_0 = 0.1026 curie.
Reaction: $CH_4 + 2O_2 = CO_2 + (2H_2O)$. Mixture, $1CH_4{:}2O_2$.
Spec. ionization of mixt. 1.09

Time		Radon	Pressure, mm.		CO_2,	Velocity constant	$\frac{-M(CH_4+O_2)}{N(CH_4+O_2)}$
Days	Hrs.	$e^{-\lambda t}$	Total	$CH_4 + 2O_2$, calcd.	calcd.	$(k\mu/\lambda)'$	
0	0	1.00000	690.2	665.5	24.7	..	...
0	3	0.97775	652.4	608.8	43.6	38.9	4.4
0	6	.95600	619.5	559.5	60.0	38.0	4.3
0	9.5	.93123	586.6	510.1	76.5	36.3	4.1
0	19.5	.86395	507.2	391.0	116.2	38.5	4.4
1	2.0	.82283	469.7	334.8	134.9	36.9	4.2
1	9.0	.78075	434.5	282.0	152.5	39.8	4.5
1	19.5	.72163	394.7	222.3	172.4	39.2	4.4
2	8.5	.65460	358.8	168.4	190.4	40.3	4.6
2	20.0	.60050	336.2	134.5	201.7	40.5	4.6
3	20.0	.50161	308.0	92.2	215.8	37.2	4.2
4	21.0	.41582	290.9	66.5	224.3	37.0	4.2
5	20.0	.34994	281.5	52.5	229.0	35.2	4.0
7	6.5	.27018	273.0	39.7	233.3	34.0	3.8
8	20.0	.20393	268.4	32.8	235.6	(28.2)	(3.1)
17	3.5	.04570	254.8	12.4	242.4	(59.9)	(6.7)
29	13.7	.00488	251.3	7.2	244.1	(131.5)	(14.7)
					Wtd. av.	37.8	4.3
Analysis			252.0	O_2 22.2 CH_4 13.7	216.1		

Experiments were made also with excess of oxygen and with excess of methane which gave values of $-M/N$ between 4.2 and 5.1, or practically the same as for stoichiometric mixture, thus showing that the ions of both methane and of oxygen are effective and about equally so.

The values of $-M/N$ are lower than that calculated, 6, but the latter is attained in the presence of 1 molar % of selenium diethyl, as will be shown in a later paper.

The theory of the exclusivity of oxidation is the same as that set forth for the oxidation of carbon monoxide.[1]

Oxidation of Ethane.—The results for the oxidation of ethane are entirely similar to those for methane except for a drop in velocity constant which sets in when the reaction is about 50% complete. Oxidation is complete to water and carbon dioxide; no liquid phase except water appears. Results are shown in Table VII. The assumed clustering and resulting reaction are $(O_2\cdot O_2\cdot C_2H_6\cdot O_2\cdot O_2)^+ + (O_2\cdot C_2H_6\cdot O_2\cdot {}^-O_2) = 4CO_2 + 6H_2O$; found per each ion pair: $3CO_2 + 4.5H_2O$.

TABLE VII

OXIDATION OF ETHANE

Reaction sphere: vol., 4.095 cc.; diam., 1.985 cm. diam., 25°. E_0, 0.1551 curie. Reaction: $2C_2H_6 + 7O_2 = 4CO_2 + (6H_2O)$. Mixture, $2C_2H_6$:$7O_2$. Spec. ionization of mixt., 1.286.

Time		Radon	Pressure, mm.			Velocity constant	
Days	Hrs.	$e^{-\lambda t}$	Total	$C_2H_6 + O_2$, calcd.	CO_2, calcd.	$(k\mu/\lambda)'$	$\frac{-M_{(C_2H_6+O_2)}}{N_{(C_2H_6+O_2)}}$
0	0	1.00000	702.6	702.6	0	..	...
0	1.5	0.98882	658.9	623.9	35.0	68.5	6.7
0	3.0	.97775	620.3	554.5	65.8	68.4	6.7
0	4.5	.96682	589.0	498.1	90.9	63.3	6.2
0	8.5	.93824	526.6	385.8	140.8	57.6	5.7
0	10.5	.92428	502.6	342.6	160.0	54.9	5.4
0	21.0	.85428	424.4	201.8	222.6	48.8	4.8
1	3.5	.81363	408.1	172.5	235.6	24.9	2.4
2	1.0	.69246	364.9	94.7	270.2	32.0	3.1
2	21.0	.59603	342.8	55.0	287.8	36.3	3.5
4	2.5	.47773	329.4	30.8	298.6	31.6	3.1
8	2.5	.23256	319.4	12.8	306.6	23.4	2.3
∞	...	.00000	318.1	10.5	307.6	5.5	0.5
Final analysis			315.0	4.0	311.0		

Comparison.—Both for methane and ethane the efficiency of the oxidation reaction is only about 75% of the stoichiometric theory, which requires 6 and 9, respectively, of total molecules reacting per ion pair. Comparison of the $(k\mu/\lambda)'$ values near the beginning of the two reactions shows that the "clean up" of ethane and oxygen is proceeding nearly twice as fast as in the case of methane. Since the specific ionizations of the mixtures are 1.286 and 1.08, respectively, it is evident that the greater rate for ethane is due more to its higher clustering power than to the specific ionization of the mixture, which is greater by only 18%. The velocity of ethane oxidation drops sharply when the reaction is about 70% complete. It is possible that toward the end of the experiment, oxidation is not complete in a single stage (see oxidation of propane and butane below).

Propane and Butane.—The oxidations of propane and of butane do not follow the course of those of methane and ethane. Oxidation is not complete; liquid products other than water appear, indicating partial oxidation. The oxidation of propane can be pushed to completion by prolonged radiation, but the general kinetic equation does not apply and apparently complete oxidation has taken place in successive steps, as contrasted with those of methane and of ethane.

Reaction of Methane with Carbon Dioxide.—In an experiment with excess of methane over oxygen, it was observed that the pressure diminution did not cease upon exhaustion of all the oxygen, but proceeded at a steady, though slower, rate. Since it has already been shown that neither methane nor carbon dioxide alone produces change of pressure, it appeared that the excess of methane must be reacting with the carbon dioxide formed in the reaction, to cause a further lowering of pressure. A new experiment starting with $1CH_4{:}1CO_2$ confirmed this supposition. Liquid droplets that did not appear to be water deposited in regular distribution on the wall and later a wax-like solid appeared. Thénard and Berthelot[17] obtained a similar product on subjecting a mixture of methane and carbon dioxide to the action of a silent discharge ("effluve"). The fact that the partial pressure of the gas, permanent at —150°, diminished at the same rate as that of the condensable gas led us to believe that a direct 1:1 addition product of methane and carbon dioxide was being formed which would be a polymer of formaldehyde. Final analysis, however, showed that the methane had been largely replaced by hydrogen as permanent gas. The entire reaction does not appear, however, to be one between secondary hydrogen and carbon dioxide[1] since this would require an induction period, which does not occur. The ratio $-M_{\text{total}}/N_{\text{total}} = 0.76$ is too low to assume that each positive ion, CH_4^+ or CO_2^+, can add to carbon dioxide or methane, respectively, which would require $-M/N = 2$. There is also no reason to expect any exclusivity of reaction, so that both carbon dioxide and methane can either combine each with the other or undergo their separate actions, depending on whether their positive ions react with their own

Probability	Cluster reaction	Change of press.	$-M_{\text{total}}/N_{\text{total}}$
0.3	$CO_2^+ + CO_2 \longrightarrow 2CO_2$	None	0
.3	$CO_2^+ + CH_4 \longrightarrow (H.CHO)_x$Solid	−2 vols.	2
.2	$CH_4^+ + CO_2 \longrightarrow (H.CHO)_x$Solid	−2 vols.	2
.2	$CH_4^+ + CH_4 \longrightarrow C_2H_6 + H_2$	None	0
	or $(C_2H_4)_x + 2H_2$	None	0

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[17] Berthelot, "Essai de Mécanique Chimique," Dunod, Paris, **1879**, vol. 2, p. 383.

molecules or with the opposite kind. We therefore conclude that the complete reaction may be analyzed into the preceding simultaneous reactions, in which the electron, as in many other similar cases, has no function other than the final neutralization of the cluster.

The net result would be $-M/N_{(\text{total})} = 1$ (compare 0.76 found).

Toward the end of the reaction most of the pressure change is doubtless due to interaction of hydrogen and carbon dioxide.

It is a pleasure to acknowledge the assistance of Dr. A. G. Loomis, Mr. J. E. Walters and Dr. Frank Porter of the Cryogenic Laboratory of the United States Bureau of Mines in furnishing us with pure ethane and methane and in giving us valuable advice concerning the fractionation of propane and of butane, and of Professor A. B. Lamb of Harvard University in kindly giving us commercial grades of the two latter gases.

Summary

Under the action of α-radiation from radon in a gaseous mixture, the following reactions have been observed with saturated hydrocarbons.

1. Ethane, propane or butane each condenses with the elimination of hydrogen and methane (approximately $5H_2{:}1CH_4$) to give higher hydrocarbons, gaseous, liquid or solid, saturated and unsaturated. Methane eliminates hydrogen only.

2. The higher the initial hydrocarbon, the more readily the liquid or solid (if the liquid be sufficiently radiated) phase will be attained.

3. Analysis of the gaseous products shows the presence of all saturated members either higher or lower than the original one. Unsaturated compounds are absent in the gaseous state, which indicates immediate condensation of a freshly formed (nascent) unsaturated hydrocarbon to form liquid; a theory is proposed for this behavior. The resulting liquids contain a large proportion of unsaturated hydrocarbons.

4. The ratio $-M_{\text{H.C.}}/N_{(\text{ions})} = 2$ is interpreted as the clustering of two hydrocarbon molecules per each ion pair. The permanent bond is established by eliminating hydrogen, or 2 hydrogens (formation of unsaturated hydrocarbon) or of methane and probably in other ways.

5. The ratio, $-\Delta_{\text{H.C.}}/\Delta H_2$ = about 1.33, indicates a fairly even division between formation of saturated and unsaturated hydrocarbons.

6. Complete oxidation of methane or ethane by oxygen takes place in one step, indicating the following ion cluster reactions per ion pair:

$$(O_2 \cdot CH_4 \cdot O_2)^+ + (O_2^- \cdot CH_4 \cdot O_2) = 2CO_2 + 4H_2O$$

and

$$(O_2 \cdot O_2 \cdot C_2H_5 \cdot O_2 \cdot O_2)^+ + (O_2^- \cdot C_2H_6 \cdot O_2 \cdot O_2) = 4CO_2 + 6H_2O$$

Experimental values for methane were $1.5CO_2$ and $3H_2O$; for ethane, $3CO_2$ and $4.5H_2O$ per ion pair, or 75% of that calculated in each case.

7. The oxidation of propane and butane is not complete in one step. Liquid partial-oxidation products appear.

8. Addition of methane and carbon dioxide was shown. A caramel- or wax-like solid was deposited on the wall.

9. In the oxidation of methane by oxygen, mixtures with excess of either component gave approximately the same —M/N ratio as the stoichiometric mixture, showing the ions of both components to be equally effective in the chemical reaction.

WASHINGTON, D. C.

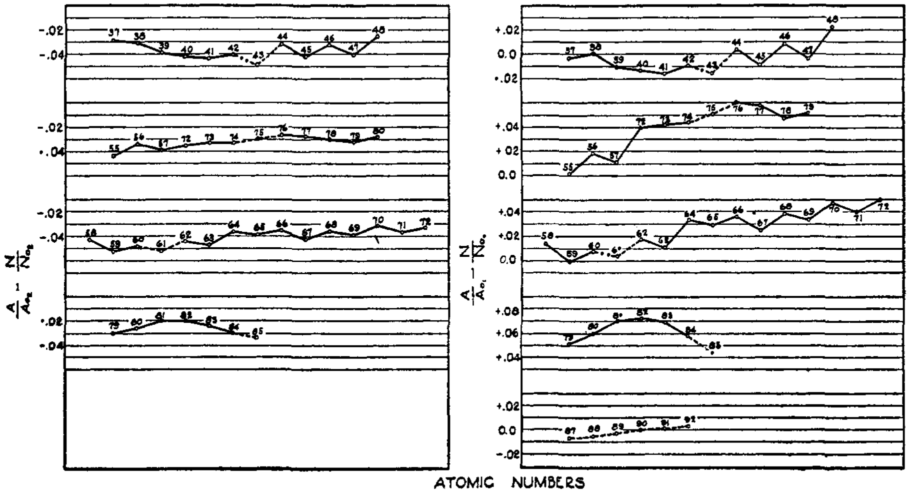
[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

A METHOD OF ESTIMATING ATOMIC WEIGHTS WITH THE AID OF THE PERIODIC LAW

BY EDWARD W. WASHBURN[1]

RECEIVED JULY 23, 1926 PUBLISHED SEPTEMBER 4, 1926

A relationship between atomic weight and atomic number proposed by Harkins and Wilson[2] holds with a fair degree of accuracy for most of the elements in the first three rows of the periodic chart. For the elements beyond nickel, however, the relation fails, probably in part at least because many of these elements are mixtures of several isotopes. All of the elements whose atomic weights have not yet been determined fall in the last five rows of the periodic chart.



The following graphical method, when applied to these elements, exhibits a relation between atomic weight and atomic number which can apparently be applied with considerable confidence to the estimation of most of the missing atomic weights. The method is as follows.

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[1] Chief of the Chemistry Division of the United States Bureau of Standards.

[2] Harkins and Wilson, THIS JOURNAL, **37**, 1386 (1915).