Summary

A method for the preparation of certain primary amines is described in which monochloro-amine is condensed with an aldehyde and the condensation product in alcoholic solution reduced with sodium amalgam.

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THE THERMAL DECOMPOSITION OF METAL ALKYLS IN HYDROGEN-ETHYLENE MIXTURES

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The reactivity of metal alkyls undergoing decomposition by heat offers many interesting problems of both scientific and practical interest. The production of a reactive fragment of decomposition among inert hydrocarbons might offer a means of bringing these compounds into a state of reactivity with the possible formation of more interesting products. A study of the reactivity of such fragments with hydrogen is of importance also as indicating the direction of chemical change in systems obtaining when hydrocarbons are subjected to processes of thermal degradation or "cracking." To these ends we have investigated the decomposition of several metal alkyls in the presence of various mixtures of hydrogen and ethylene.

When a metal alkyl is decomposed by heat, leaving the free metal as a deposit, it seems an unavoidable assumption that the alkyl group must have existed, at least for a short space of time, as a free radical. If it can then be shown that any resulting reaction could not be attributed to the metal or to the temperature, the postulated mechanism of whatever reaction occurs must be such as to involve the alkyl radical. For this reason mercury diethyl and lead tetraethyl were chosen, since they decompose under temperature conditions which do not of themselves induce reaction of hydrogen and ethylene, and since the metals themselves do not exhibit any marked catalytic effect.

Extensive recent work by Taylor and Marshall,[1] Olson and Meyers,[2] Bates and Taylor,[3] Taylor and Hill,[4] Bonhoeffer and Harteck,[5] von Wartenburg and Schultze,[6] and others demonstrates the interest which atomic

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[1] Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

[2] Olson and Meyers, THIS JOURNAL, **48**, 389 (1926).

[3] Bates and Taylor, *ibid.*, **49**, 2438 (1927).

[4] Taylor and Hill (Taylor, "Nichols Medal Address"), *Ind. Eng. Chem.*, **20**, 439 (1928); THIS JOURNAL, **51**, 2922 (1929).

[5] Bonhoeffer and Harteck, *Z. physik. Chem.*, **139A**, 64 (1928).

[6] Von Wartenburg and Schultze, *ibid.*, **2B**, 1 (1929).

hydrogen and its reaction with hydrocarbons have aroused. Taylor postulated the formation of ethyl radicals by interaction of hydrogen atoms and ethylene, and examined from the energetic standpoint the possible production of ethane from ethyl radicals and hydrogen molecules. The decomposition of mercury diethyl might yield ethyl radicals direct and thus might induce ethane formation in a hydrogen atmosphere. In this paper it is shown that the liberation of ethyl radicals in a mixture of hydrogen and ethylene produces the same results as does the introduction of hydrogen atoms. It will be shown that the product is mainly a polymeric form of ethylene without considerable quantities of saturated hydrocarbons, and that the ultimate products from atomic hydrogen and hydrocarbons are similar. This points to similar stages in the two sets of reactions.

The literature offers only slight data as to the products of thermal decomposition of the metal alkyls.[7] Evidence as to these products may be derived from any reaction they cause in a hydrogen–ethylene mixture, or from a blank run using the metal alkyl alone. Moreover, since mercury diethyl and lead tetra-ethyl were the compounds used, the investigation of their thermal decomposition in hydrocarbon–hydrogen mixtures might serve to throw some light on their anti-knock action in motor fuels, since in that case they are thermally decomposed in a hydrocarbon–air mixture.

Experimental Details

Apparatus.—The apparatus was set up as shown in Fig. 1. It was made of soft glass without rubber joints, and all connecting parts were of capillary tubing. The reaction chamber A was of 250 cc. capacity, made of pyrex with capillary side tube and ground joint C for connecting to the remainder of the apparatus. The reaction chamber was closed with a ground-glass stopper B, and an inlet and exit tube were provided for circulating water through the body of the stopper itself. A resistance furnace F, which could be raised and clamped about the reaction chamber, was used to maintain it at 250 to 300°. The furnace was not considerably larger than the reaction vessel. Consequently a certain temperature gradient existed along the tube, hottest in the middle and cooler toward each end. The gradient was, however, always within the limits stated, 250–300°. D is an open-tube mercury manometer, and E is a precision gas buret, water-jacketed and using mercury for the containing liquid. The mercury compensating arm of the buret had platinum leads sealed through, and connection was made through a small lamp to a battery, to give reproducibility in readings. The manometer was similarly arranged. From the other arm of the three-way stopcock on the buret, passage was provided through suitable stopcocks to a pump, to the outer air, and to a gas analysis apparatus. This latter was of the Orsat type, with mercury-filled water-jacketed precision buret similar to E, and connecting by a branching capillary to four liquid absorption pipets of the bubbling type containing, respectively, potassium hydroxide solution, fuming sulfuric acid, alkaline pyrogallol and acid cuprous chloride. The fifth outlet carried a pipet with sealed-in platinum spiral for

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[7] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, **1921**, p. 92.

slow combustion, and the sixth a tube of copper oxide, both using mercury as the containing fluid. The copper oxide tube was constantly maintained at 250–280° by a wrapping of resistance wire connected to a transformer.

Preparation of Materials.—The mercury diethyl and mercury dimethyl were prepared by several methods, the most satisfactory being that of Marvel and Gould.[8] Both were found to boil sharply, after being twice distilled, the diethyl at 97–99° under 125 mm. pressure and the dimethyl at 94° and atmospheric pressure. One sample of mercury diethyl was lost when it decomposed with a slight explosion during distillation, leaving distilling flask, fractionating column and condenser coated with a gray deposit of mercury. One sample of mercury dimethyl was kindly furnished by Professor Marvel, while all of the lead tetra-ethyl used in this work was the product of the E. I. du Pont de Nemours Company. The hydrogen was electrolytic hydrogen taken from cylinders, and was purified by passing first over heated platinized asbestos and then over phosphorus pentoxide. The ethylene was taken from a cylinder of the commercial gas, the quality of which has frequently been tested in this Laboratory for catalytic purposes with completely satisfactory results.[9] It was passed over phosphorus pentoxide before use.

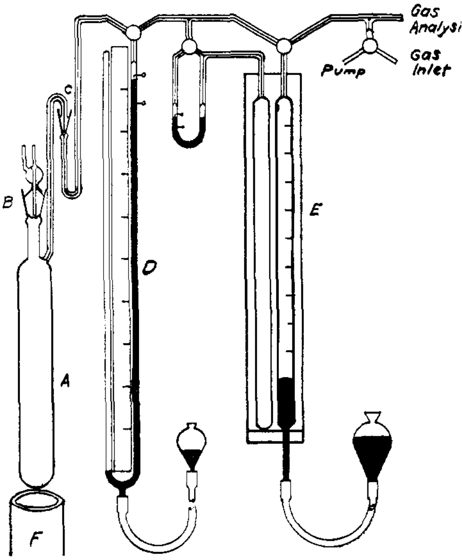

Fig. 1.

Experimental Procedure

In making a run the reaction tube was unsealed at B and C and a small sealed thin-walled bulb containing a known weight of the metal alkyl was introduced. The reaction vessel was then reattached, using de Khotinsky cement on top of the ground-glass joints, which were water-cooled, and the entire apparatus evacuated. The apparatus was always washed out several times by admitting and pumping out one of the gases to be used in the run, usually hydrogen. For the actual run, each portion of gas admitted was measured through the buret and then transferred to the reaction chamber. Finally the manometer was read and the furnace clamped in position and turned on, having previously been adjusted for a temperature of 250–300°. There was, obviously, first of all an increase in pressure due to the rise in temperature, followed by a further sudden increase when the bulb of alkyl burst. A maximum pressure was then developed followed by a reduction in pressure due to reaction. In most cases there was no further volume change after five to seven hours. It is evident that we chose a temperature range in which the decomposition of alkyl was a slow reaction. In this temperature range the rate of decomposition of mercury diethyl was much faster than that of dimethyl, which latter also showed considerable tendency to distillation without decomposition to the cooler parts of the reaction system. It is for this reason

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[8] Marvel and Gould, THIS JOURNAL, **44**, 153 (1922).

[9] Pease, *ibid.*, **45**, 1196 (1923).

that its use was abandoned. It should be observed that the rates of decomposition of the alkyls under these dilute conditions are radically different from those obtaining during bulk distillations of the material.

On attainment of constant pressure the heat was removed, and when cool a final reading of the pressure and temperature was taken. A sample of the gas was then withdrawn, using the buret E as a pump, and passed directly into the buret of the gas analysis apparatus, where its composition was determined.

In each of the first eight runs the apparatus was immediately evacuated without being disconnected and the experiment was followed by a blank run, using the same gases in approximately the same quantities as before, in order to determine whether the results could in any degree be attributed to catalytic effects of the free metal resulting from the decomposition of the metal alkyl. As every case showed no volume change after prolonged heating, this practice was discontinued.

Experimental Results

The results of the runs made are presented in the two tables herewith shown. No run using a metal alkyl alone, or with hydrogen or ethylene, or both, has been omitted. Table I presents in columns two and three the volumes of reacting gases introduced. In the fourth column the weight and nature of the metal alkyl is given, and this is calculated to the number of cubic centimeters of free alkyl radicals that would be liberated on complete decomposition, giving the values recorded in the fifth column. The sixth column shows the volume after reaction, as calculated from the original volume and the original and final manometer readings. The subsequent analysis showed how much of this volume was

TABLE I

EXPERIMENTAL RESULTS

All gas volumes in a given experiment are calculated to the same temperature and pressure.

Expt.	H_2 taken, cc.	C_2H_4 taken, cc.	Metal alkyl, g.	C_2H_5 equiv., cc.	Vol. after reaction	H_2 disappeared, cc.	C_2H_4 disappeared, cc.	C_2 as satd. gas	C_2 as liquid
1	46.6	44.4	0.105^a	19.2	60.4		13		
2	49.2	49.6	.316^a	57.8	89.4		33.9		
3	50.4	50.1	.023^a	4.2	84.7	11.65	19.5		
4	None	95.9	.249^a	45.5	50.0		80.3		
5	51.0	50.4	.209^b	57.8	96.5	13.0	33.8		
6	50.2	50.8	.388^c	79.8	93.9				
7	49.8	50.5	.0301^a	5.5	85.3				
8	53.1	47.9	.0176^a	3.2	98.4				
9	None	None	.0904^c	18.8	2.6				
10	None	None	.2844^c	59.3	10.5				
11	None	None	.4416^c	92.0	38.2				
12	None	None	.3930^a	36.0	24.8	−0.7	−5.2	7.6	23.2
13	None	84.2	.0316^a	5.8	78.7	−1.4	8.4	Lost	Lost
14	None	95.9	.0186^a	3.4	77.4	0.0	22.3	6.4	19.3
15	49.4	49.3	.0359^a	6.6	80.7	5.2	19.1	17.1	8.6
16	56.0	54.8	.0672^a	12.3	88.5	12.1	28.9	6.4	34.8
17	50.5	47.5	.0692^a	12.7	80.4	4.0	24.8	5.6	31.9
18	61.4	64.0	.0480^a	8.8	99.7	5.4	28.3	11.9	25.2

TABLE I (*Concluded*)

Expt.	H_2 taken, cc.	C_2H_4 taken, cc.	Metal alkyl, g.	C_2H_5 equiv., cc.	Vol. after reaction	H_2 disappeared, cc.	C_2H_4 disappeared, cc.	C_2 as satd. gas	C_2 as liquid
19	64.1	31.4	0.0615[a]	11.3	81.1	6.7	18.5	Lost	Lost
20	69.2	29.5	.0319[a]	5.8	87.4	6.2	12.6	15.3	3.1
21	68.6	17.9	.0389[a]	7.1	77.3	6.6	13.4	4.3	16.2
22	83.1	None	.0870[a]	15.9	92.2	6.9		17.7	−1.8
23	25.1	69.5	.0212[a]	3.9	79.7	−1.7	17.9	4.0	17.8
24	50.3	49.6	.0427[a]	8.1	83.1	4.8	19.7	6.5	21.3
25[d]	50.5	51.3	.0359[a]	6.9	85.3	3.1	20.3	5.8	21.4
26	92.0	92.0	.1092[a]	20.8	164.7	−8.0	32.7	10.6	42.9
27	95.1	98.1	.0668[a]	12.8	157.7	7.7	38.8	9.6	42.0
28	22.9	24.7	.0393[a]	7.5	42.5	4.0	8.4	6.1	9.8
29	52.8	52.0	.0336[b]	10.3	88.3	7.9	22.1	5.4	27.0
30	92.2	95.4	.0308[b]	9.2	161.1	7.1	30.5	7.0	32.7
31	29.7	29.4	.0174[b]	5.2	50.8	1.5	11.0	4.3	11.9
32	67.9	34.2	.0216[b]	6.7	90.3	10.6	16.6	5.3	18.0
33	32.5	66.1	.0262[b]	8.0	79.3	1.8	23.5	5.9	25.6
34	51.9	52.8	.0348[b]	10.6	93.9	3.6	14.5	5.3	19.8
35	51.0	50.4	.0356[b]	10.9	91.8	1.7	13.6	5.0	19.5

[a] $Hg(C_2H_5)_2$. [b] $Pb(C_2H_5)_4$. [c] $Hg(CH_3)_2$. [d] Run No. 25 was made using the reaction chamber filled with glass wool.

TABLE II

EXPERIMENTAL RESULTS

	Before reaction			After reaction				
	Gas, cc.		Liquid	Gas, cc.			Liquid, cc.	
Run	H_2	C_2H_4	C_2H_5, cc.	H_2	C_2H_4	Saturated	H_2	C_2
12	..	..	36.0	0.7	5.2	18.9$C_{0.8}$[a]	44.9	23.2
14	..	95.9	3.4	None	73.6	3.7$C_{3.46}$	36.6	19.3
15	49.4	49.3	6.6	44.2	30.2	6.3$C_{5.43}$	19.4	8.6
16	56.0	54.8	12.3	43.9	25.9	18.7$C_{0.68}$[a]	69.15	34.8
17	50.5	47.5	12.7	46.5	22.7	11.2C_1	62.95	31.9
18	61.4	64.0	8.8	56.0	35.7	8$C_{2.97}$	52.2	25.2
20	69.2	29.5	5.8	63.0	16.9	7.5C_4	7.8	3.1
21	68.6	17.9	7.1	62.0	4.5	10.8$C_{0.8}$[a]	31.8	16.2
23	25.1	69.5	3.9	26.8	51.6	1.3C_6	34.7	17.8
24	50.3	49.6	8.1	45.5	29.9	7.7$C_{1.69}$	43.7	21.3
25	50.5	51.3	6.9	47.4	31.0	6.9$C_{1.7}$	42.3	21.4
26	92.0	92.0	20.8	100.0	59.3	5.4C_4	82.9	42.9
27	95.1	98.1	12.8	87.4	59.3	11.0$C_{1.75}$	87.0	42.0
28	22.9	24.7	7.5	18.9	16.3	7.3$C_{1.67}$	20.0	9.8
29	52.8	52.0	10.3	44.9	29.9	13.5$C_{0.3}$[a]	53.5	27.0
30	92.2	95.4	9.2	85.1	64.9	11.1$C_{1.26}$	66.0	32.7
31	29.7	29.4	5.2	28.2	18.4	4.3C_2	23.6	11.9
32	67.9	34.2	6.7	57.3	17.6	15.4$C_{0.7}$[a]	34.3	18.0
33	32.5	66.1	8.0	30.7	42.6	6.0$C_{1.97}$	51.0	25.6
34	51.9	52.8	10.6	48.3	38.3	7.3$C_{1.44}$	41.2	19.8
35	51.0	50.4	10.9	49.3	36.8	5.7$C_{1.76}$	40.4	19.5

[a] The low values for carbon content are undoubtedly due to imperfect removal of hydrogen in the copper oxide. We have satisfied ourselves that this in no way affects the validity of our conclusions concerning the carbon–hydrogen balance.

ethylene (or other unsaturated gases) and how much hydrogen, and these values subtracted from the volumes introduced give the values which comprise the seventh and eighth columns.

In the first nine runs the analysis was made by cooling the tip of the reaction tube in liquid air, and assuming that the uncondensed gas was hydrogen. It was then warmed to room temperature and a part drawn off into a bromine pipet to determine the percentage of unsaturated hydrocarbons. In Runs 9, 10 and 11 the volume of gas after reaction was too small to be so analyzed. Since it was necessary to know more about the residual gas, the Orsat gas apparatus was sealed on at this time and used in all subsequent runs. The accuracy thus achieved permitted the calculation of the last two columns. Since it was not known what molecular formula could be assigned to the saturated hydrocarbons remaining after the removal of all other constituents, they are reported in the eighth column as cubic centimeters of C_2, that is, half the volume of carbon dioxide formed on combustion. Knowing then the amount of C_2 introduced and the amount appearing in the gas phase after the reaction, the difference gives the amount of C_2 transformed into liquid, that is, the volume of ethylene converted into liquid products.

It remained to be shown, however, what was the nature of the liquid. For this purpose the second table was compiled. In it the first six columns are derived from the corresponding columns of Table I. The seventh column gives the number of cubic centimeters of saturated hydrocarbon present after the reaction (residual volume less the volumes of ethylene and hydrogen found) and its mean carbon content. The calculation of this latter can best be shown by an example. In Run 14 the volume of saturated gas was 3.7 cc., which when burned gave 12.8 cc. of carbon dioxide (twice the value in column ten of Table I). It must then consist of a mixture of hydrocarbons, and the mean carbon content of the mixture must be 12.8/3.7, or $C_{3.46}$. Since the general formula is $C_nH_{2n} + 2$ and in this case $n = 3.46$, the H_2 content of the 3.7 cc. of saturated hydrocarbon is 16.4 cc. Knowing this, the difference between the volume of H_2 introduced (in all forms) and the volume of H_2 in the gas phase after the reaction

$$(H_2 + 2C_2H_4 + 2^1/_2C_2H_5) \longrightarrow (H_2 + 2C_2H_4 + H_2 \text{ as satd.})$$

gives the H_2 content of the liquid, which is shown in column eight. Column ten of Table I, the C content of the liquid, is brought down as column nine of Table II, this giving the H_2 and C_2 content of the liquid in adjacent columns. From comparison of these values, it is at once evident that within the experimental error the formula for the liquid is C_nH_{2n}, that is, it is a polymer of ethylene.

Dynamic Run.—Since it was evident that a considerable portion of the products of reaction were liquids, an apparatus was set up for a dynamic run. In this apparatus

(Fig. 2) hydrogen, having passed through platinized asbestos and phosphorus pentoxide, joined a stream of ethylene dried by phosphorus pentoxide. Each gas was measured through a calibrated flowmeter and the combined stream could then pass directly into the furnace or could be forced through a by-pass where it bubbled through a triple-effect wash bottle containing lead tetra-ethyl. The reaction chamber consisted of a piece of forty-millimeter tubing in the line, about which was a resistance furnace for maintaining a working temperature of 310–350°. The reaction tube was filled with glass wool to break up the stream of gas and produce more uniform heating. The gas leaving the furnace passed through two traps cooled by carbon dioxide-ether mixture for removing condensable products.

Two runs, each preceded by a blank, were made using this apparatus. The first blank was made by passing ethylene through the furnace at 325°, which gave no condensable product. The first run was then made by turning the stopcock to force the gas to pass through the lead tetra-ethyl before entering the furnace. In this case a liquid collected in the trap. The trap was then cut off and allowed to warm to room temperature. As it warmed, the gas it gave off between 12 and 30° was passed into a gas buret. Its volume was 83.5 cc., and the bromine pipet showed it to be 80% unsaturated. This could not have been mainly ethylene or propylene, since the gas analyzed was caught only above −12°.

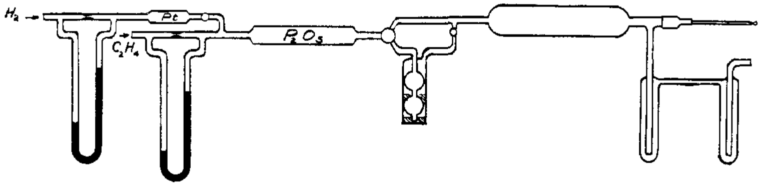

Fig. 2.

The trap containing the liquid was then transferred to a sulfuric acid bath and heated in an effort to determine the boiling point of the liquid. At 150° no boiling occurred, though the liquid was vaporizing rather rapidly at that temperature, as could be seen by the presence of a condensation zone about two centimeters above the surface of the acid, where the vapors condensed and flowed back in a film on the wall.

A second dynamic run was made using hydrogen and ethylene. In a preliminary blank run these gases were passed through the furnace at 310–250° without metal alkyl, and gave no product condensable by carbon dioxide–ether. The by-pass through the lead tetra-ethyl was then used, and the products began to collect in the trap. The flowmeters indicated that the entering gas was 42% ethylene when a sample of the gas issuing from the final trap was passed into the gas buret. A bromination on this sample showed it to consist of 36% of unsaturates. The liquid collecting in the trap was seen to contain suspended flakes of a white solid. If the cooling liquid was removed for a short time, the solid dissolved in the liquid, and was reprecipitated when the trap was again cooled. When the run was stopped, the trap was cut off and placed in a sulfuric acid bath. Its contents were found to boil when the thermometer in the acid read 75°.

Discussion of Results

Decomposition Products from Alkyl Alone.—In Run 12, the first using the Orsat apparatus, a bulb containing 0.3930 g. of mercury diethyl—enough to furnish 36 cc. of ethyl groups at room temperature and pressure—was introduced and the contents decomposed by heat in the absence of other gases. When the decomposition products were analyzed and the composition of the liquid was calculated, it was found that 80% of the carbon and hydrogen appearing in the end-products did so as unsaturated substances. This confirms the statement[7] that the reaction is not the simple formation of butane which one might first expect according to the equation

$$Hg(C_2H_5)_2 = Hg + C_4H_{10}$$

but is rather a complicated one resulting in a mixture of hydrocarbons, both liquid and gas. In the gas phase saturated compounds predominate, while the liquid is a polymer of ethylene, since the calculation of the composition of the latter shows it to be C_nH_{2n} within the limits of experimental error, any deviation from this ratio being rather on the side of the acetylene than of the methane series.

Induced Polymerization.—If we assume that the original decomposition products are ethyl groups, it is evident that their liberation into an atmosphere of ethylene alone induces the latter to polymerize, as is demonstrated by all of the experiments and by Expt. 14 in particular. Here 0.0186 g. of mercury diethyl was used, representing only 3.4 cc. of ethyl radicals. At the end of the run, however, 19.3 cubic centimeters of ethylene was shown to be in the form of a liquid polymer. This shows conclusively that the ethyl groups have brought about an amount of polymerization disproportionate to their own volume. Nor does the presence of hydrogen prevent this from being the case, for in Expt. 33 it is shown that 6.7 cc. of ethyl radicals caused the polymerization of 18.0 cc. of ethylene, despite the fact that there was twice as much hydrogen as ethylene in the original mixture.

Extent of Hydrogenation.—*It is evident that hydrogenation of the* ethylene does not occur to a major extent, but the amount of hydrogenation does increase with the ratio of hydrogen admixed. To demonstrate this, runs were made with varying ratios of hydrogen and ethylene. In Expt. 33, for instance, hydrogen was present in half as great volume as ethylene, in Expt. 35 the volumes were equal, and in Expt. 32 there was twice as much hydrogen as ethylene, the total volume in each case being approximately 100 cc. The results show that the amount of liquid polymer formed increases with the volume of ethylene in the original mixture, though the relation is not at all linear.

Effect of Pressure.—A series of runs was also made to investigate the effect of pressure. In these runs the hydrogen and ethylene were introduced in nearly equal quantities, but the total volume was about 50 cc. in Expt. 28, about 100 cc. in Expt. 35, and about 185 cc. in Expt. 26. When the amounts of ethylene polymerized in each case are considered, the degree of polymerization is found to be roughly proportional to the pressure, since the value for each in the last column of either table is 9.8, 19.5 and 43.0 cc., respectively.

Effect of Alkyl Concentration and Nature of the Metal.—A comparison of values of ethylene polymerized and ethyl radicals taken will also show that when more ethyl groups are used, more polymerization is accomplished, other things being equal. When mercury diethyl was replaced by lead tetra-ethyl, no change was observed that could be attributed to the difference in the metallic element of the compound.

Wall Effect.—Experiment 25 was made with the reaction chamber filled with glass wool. When it is compared with others, as for example Expt. 24, it is seen that the results are in close agreement. This indicates that a wall effect is not involved to any important extent; the reaction appears to occur in the gas phase. Certain recent considerations of Bonhoeffer and Harteck[5] indicate that the addition of hydrogen atoms to ethylene may possibly be a wall reaction. There is no evidence of such in our work but this may be because we are dealing essentially with a polymerization process. Some recent work of Pease and Chesebro[10] shows that the thermal polymerizations of ethylene and acetylene in glass vessels are essentially homogeneous gaseous reactions.

Discussion of Mechanism

The outstanding result experimentally is the induced polymerization of ethylene by the decomposition of the metal alkyl under conditions of temperature at which ethylene will not polymerize of itself. Any proposed mechanism must suggest a method whereby this may be accomplished. At the same time, it is to be noted that a certain amount of saturated hydrocarbons is produced even in the absence of hydrogen initially. With two exceptions (Expts. 15 and 20), in all experiments in which hydrogen and ethylene are initially present, the polymerized product is greatly in excess of the saturated product. In Expt. 20 the reason for the exception apparently lies in the excess of initial hydrogen, since in Expt. 22 where no ethylene was initially present practically the whole of the alkyl decomposition product appears as saturated hydrocarbon in contrast to the relatively large amounts of unsaturated product in Expts. 12, 13 and 14, where there was no hydrogen originally present. This indicates that the reactivity of the decomposition product of metal alkyl with ethylene is much more pronounced than with hydrogen. Our experiments with several ratios of the gases confirm this.

We shall assume that the decomposition of the ethyl compounds yields initially free ethyl radicals, whether from mercury or lead

$$Hg(C_2H_5)_2 = Hg + 2C_2H_5 \qquad (1)$$

Since, according to modern concepts, the direct addition of two mole-

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[10] Pease and Chesebro, *Proc. Nat. Acad. Sci.*, **14**, 472 (1928).

cules to form a single molecule in the gas phase is an improbable event, we must assume that the process building up hydrocarbon chains does not proceed by a bimolecular reaction of the type

$$C_2H_5 + C_2H_4 = C_4H_9$$

but rather as a three-body collision

$$C_2H_5 + C_2H_4 + C_2H_4 = C_4H_9 + C_2H_4 \qquad (2)$$

an addition of ethylene which may repeat itself, also by a three-body collision

$$C_4H_9 + C_2H_4 + C_2H_4 = C_6H_{13} + C_2H_4 \qquad (3)$$

All such reactions, however, result in free radicals, whereas we have to account for the production of unsaturated polymer $(CH_2)_n$ and saturated product of varying complexity. We can offer several alternative methods whereby these may be produced. Thus, the collision of two radicals may produce one saturated and one unsaturated hydrocarbon, for example

$$C_6H_{13} + C_2H_5 = C_2H_6 + C_6H_{12} + 54 \text{ Cal.} \qquad (4)$$

Since, in general, the C_2 appearing as unsaturated is upward of three times the C_2 appearing as saturated, it is evident that Reaction 4 would represent the simplest process yielding the ratio of $3C_2$ unsaturated to C_2 saturated. Greater ratios would demand further reactions of the type in (2) and (3) prior to the reaction typified by (4). One objection to such a sequence is that reactions of the type in (2) and (3) ought to be greatly in excess of that in (4) since this latter involves reaction between two radicals present only in minute quantities.

This objection can be avoided if we postulate another method whereby a liquid unsaturated polymer may be produced. After processes of the type indicated in (2) and (3) have proceeded, it is possible that they may be succeeded by a reaction of a new type exemplified by the equation

$$C_6H_{13} + C_2H_4 = C_6H_{12} + C_2H_5 + 0 \text{ Cal.} \qquad (5)$$

There is little objection to such a reaction either on the basis of collision frequency or from the energetic standpoint. The reaction would occur more readily the higher the molecular weight of the radical involved. It will be noted that the reaction involves the reproduction of the ethyl radical and hence the possibility of a chain of reactions. Such a chain of reactions could be stopped in various ways. Reaction 4 represents one method. Clean-up on the walls of the containing vessel followed by reaction there, possibly of Type 4, also would form one other method. Interaction with hydrogen which evidently occurs, as is to be concluded from the hydrogen disappearance, represents another method. The precise mechanism of these latter reactions is somewhat uncertain since, as pointed out by Bonhoeffer and Harteck,[5] the reaction

$$C_2H_5 + H_2 = C_2H_6 + H - 10 \text{ Cal.} \qquad (6)$$

should be endothermic. There is, however, another alternative, namely

$$C_2H_5 + H_2 = CH_4 + CH_3 + 30 \text{ Cal.} \qquad (7)$$

which is energetically possible and would account for the methane which we have found in our saturated gas. The final elimination of free radicals must in these cases also be either by (4) or by wall reactions.

A detailed study of the reaction between excited mercury, hydrogen and ethylene, recently completed by Taylor and Hill,[11] has shown that so far as end-products are concerned there is complete parallelism between the alkyl decomposition reaction and that with excited mercury. We are satisfied also that the reactions discussed above may be harmonized with those possible when the starting point is atomic hydrogen rather than a metal alkyl fragment.

The results are indeed highly reminiscent of those of Lind[12] and his co-workers[13] from the interaction of α-particles with ethylene and saturated hydrocarbons. In all these studies it is evident that a polymer $(CH_2)_n$ is the principal product. In the present experiments, there can be no question of ionization occurring; also the amount polymerized bears somewhat the same ratio to activating agent (about 6:1) that is found by Lind for the M/N ratio in ethylene. The question at once suggests itself as to whether it is necessary in the α-particle experiment to assume clusterings around ions or whether one should not assume the formation of radicals as a resultant of the action of the α-particles followed by a sequence of chemical processes identical with those obtaining as a result of the introduction to such systems of either atomic hydrogen or, as in our experiments, free radicals.

Summary

1. It has been shown that the ultimate products of thermal decomposition of mercury diethyl are both gaseous and liquid, and are for the most part unsaturated in nature.

2. Polymerization of ethylene induced by decomposing mercury diethyl in an atmosphere of ethylene has been observed, and the polyethylenic nature of the polymer demonstrated.

3. The decomposition of mercury diethyl in a mixture of hydrogen and ethylene has been found to produce mainly an ethylene polymer in addition to a small amount of saturated hydrocarbons.

4. The effects of alkyl concentration, gas ratio, pressure, containing wall and nature of the metal alkyl have been studied.

5. Using a flow method a liquid product, $(CH_2)_n$, was collected and some of its properties were observed.

6. A possible mechanism for the formation of higher unsaturated and saturated hydrocarbons involving ethyl radicals has been offered.

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[11] Taylor and Hill, THIS JOURNAL, **51**, 2922 (1929).

[12] Lind, Bardwell and Perry, *ibid.*, **48**, 1556 (1926).

[13] Lind and Bardwell, *ibid.*, **48**, 2335 (1926).