**82.** *Free Organic Radicals in the Gaseous State. Part V. The Reaction Products of Free Methyl in Hydrogen and Helium.*

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THE mechanism of the reactions of free methyl and ethyl has already formed the subject of numerous investigations. Paneth and Hofeditz (*Ber.*, 1929, **62**, 1335) first described a method whereby the life period of free methyl could be determined, and made suggestions as to the order of the underlying reaction. In later communications, these investigations were repeated with greater accuracy, and extended to free ethyl (Paneth and Lautsch, *Ber.*, 1931, **64**, 2702, 2708; Paneth and Herzfeld, *Z. Elektrochem.*, 1931, **37**, 577; Hahnfeld, " Ueber das Reagieren freier organischer Radikale im Gaszustand," Diss., Königsberg i. Pr., 1932).

The significant result of the previous investigations was the recognition that the greater proportion of the free radicals disappears by a wall reaction. It was found that, by collision of free radicals with a mirror of a metal which yields a volatile alkyl compound, each encounter leads to adsorption of the alkyl, but that in a glass or quartz tube only $0.1\%$ of the radicals striking the walls remains attached.

The experimental accuracy hitherto attainable has not sufficed to ascertain whether, and under what conditions, the free radicals disappear also by a homogeneous gas reaction. We have therefore introduced various improvements into the experimental arrangements rendering them more precise.

In addition to a more exact dosage of the free radicals and their source, tetramethyl-lead, we have paid special attention to the qualitative and quantitative examination of their reaction products. The free methyl radical was selected as the object of our investigation on the grounds that the reaction products to be expected in this case—methane, ethane, ethylene, hydrogen—are more readily determined qualitatively and quantitatively by the available methods of gas analysis than the less volatile end-products of the transformation of ethylene.

We now find that in hydrogen the free methyl disappears partly according to the equation: $CH_3 + H_2 \longrightarrow CH_4 + H$ (probably in a homogeneous reaction) and partly in the wall reaction : $CH_3 + CH_3 \longrightarrow C_2H_6$. The relative proportion of the two reactions depends on the concentration of the radicals and on the temperature ; low concentration and heating diminishes the formation of ethane and favours that of methane. In helium, instead of hydrogen, the first reaction is excluded, and ethane is the main product; by using helium as carrier gas and maintaining a temperature of $500°$ the half value period of free methyl can be raised to $0.1$ second.

## EXPERIMENTAL.

I. *Improved Experimental Arrangements.*—The apparatus used and the method of measuring the half-life period were the same in principle as were described in Part I (*loc. cit.*). As well as other improvements in the apparatus, however, particular stress was laid upon maintaining the experimental conditions constant and strictly reproducible. The improvements made in accordance with this requirement took the form, first, of the provision of uniform streaming conditions and of uniform conditions of observation of the measurement mirror (variations in lighting could readily introduce errors of over 10% here). Above all, however, attention was paid to the uniform dosage of the tetramethyl-lead vapour, a factor which was a continual source of variation in the experimental results, and of which the control presented the most obstinate difficulties. On account of the importance of this point for the trustworthiness of the entire experimental method, we describe the form of tetramethyl-lead vaporising vessel found most suitable (Fig. 1).

The carrier gas enters through a narrow capillary $K_1$, 10—15 cm. long, placed immediately following the inlet tap 1. The gas streams first through the pre-cooling spiral, which is placed together with the tetramethyl-lead vessel in a cooling bath, and then passes through a layer of copper wool in which the tetramethyl-lead is distributed. Here it is charged with the vapour of the lead alkyl, in amount depending on the temperature of the bath, and finally leaves the vaporising vessel through the capillary $K_2$ and the tap 2.

The capillary $K_2$ is chosen to let through just that quantity of gas corresponding to the conditions of the experiment, while $K_1$ is arranged to pass a trifle more gas. There is thus always maintained in the vaporising vessel the pressure of the main transport gas supply, which is kept constant. The slow passage of the as yet unexpanded gas through the copper wool, which is kept at constant temperature within $0.1°$, together with the pre-cooling of the gas to the temperature of the bath, effects a uniform impregnation with the lead alkyl. The capillaries placed in both the inlet and the outlet tube immediately adjacent to the vaporising vessel prevent the contamination of the grease of the taps with lead alkyl vapour, which had previously been a persistent source of error. Accordingly, the filling of the vaporising vessel with tetramethyl-lead was carried out by distillation in a high vacuum through the side tube $S$, which was afterwards sealed off. Over-night, and during periods of disuse, the inner part of the vaporising vessel was kept at liquid-air temperature (Dewar vessel shown dotted). Variation of the gas stream in the apparatus was achieved by insertion of additional capillaries ($K_3$, $K_4$) connecting the measurement tube directly to the carrier gas lead.

Lead mirrors produced under similar conditions and during the same time with the foregoing experimental arrangements show by their appearance alone the serviceability of the method. Objective confirmation must be provided, however, by quantitative determination of the deposited lead. Hahnfeld (*loc. cit.*), in experiments on ethyl, in hard-glass tubes, weighed the mirror directly by cutting it out and determining the loss in weight on dissolution of the lead. Owing to the higher temperature necessary for the decomposition of tetramethyl-lead, however, the use of quartz tubes was necessary, so this method could not be applied.

Of the methods available for the determination of small quantities of lead, the colorimetric determination as sulphide appeared most suitable for our purpose (for details, see Wunsch, Diss., Königsberg, 1933); mean values of several determinations on each solution were used and were accurate within $3\%$.

II. *Influence of Temperature on the Rate of Disappearance of Free Methyl.*— With this apparatus we first accurately determined a half-life curve of free methyl at room temperature, in hydrogen at 1—2 mm. pressure with a streaming velocity of 1035 cm. per sec., using a quartz tube 170 cm. long and 1 cm. in diameter. At the end of the tube, a lead mirror was allowed to deposit for 3 minutes in the usual way (temperature of vaporising vessel, $-52°$). This was then removed, by the action of free radicals from varying distances, the mirror being observed always under the same conditions of illumination. The reciprocal of the duration of the removal process, $1/d$, was used as a relative measure of the activity, $A$, of the radicals.

The streaming velocity was calculated from the volume of hydrogen passing through the apparatus in unit time. The time elapsing between the moment of formation of the free radical and its reaction with the mirror may be calculated from the streaming velocity, allowance being made for the fall of pressure in the measurement tube (cf. Part III, *loc. cit.*, note 4, p. 2709). The results of the measurements are given in Table I (a), where $z$ is the time interval between formation and reaction, and $D$ the distance between the place of formation and that of reaction.

As may be seen by comparison with the earlier measurements of the life period, we have extended the range of our measurements about four-fold (to $106.8 \times 10^{-3}$ sec. as against $26 \times 10^{-3}$ sec.). The fact now emerges that if—as in the former work—log $A$ be plotted against $z$ (Fig. 2, curve I), the plot is no longer a straight line, *i.e.*, the disappearance of free radicals from the
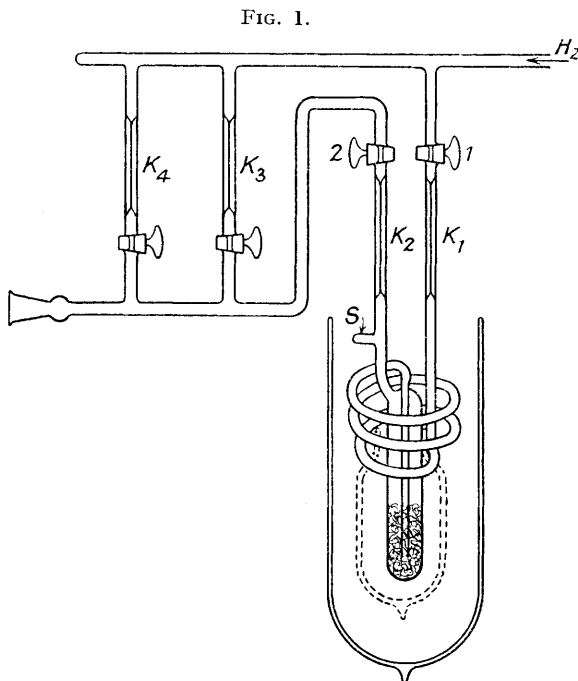
Fig. 1.

TABLE I.

| $D$, cm. | $z \times 10^3$, secs. | $d$, secs. | $A = 10^4/d$. | log $A$. | $D$, cm. | $z \times 10^3$, secs. | $d$, secs. | $A = 10^4/d$. | log $A$. |
|---|---|---|---|---|---|---|---|---|---|
| | | (a) *Tube at* 20°. | | | | | (b) *Tube at* 350°. | | |
| 10 | 6·8 | 190 | 52·63 | 1·721 | 10 | 6·6 | 190 | 52·62 | 1·7212 |
| 25 | 17·5 | 360 | 27·78 | 1·444 | 25 | 18·1 | 200 | 50·00 | 1·6990 |
| 42 | 30·0 | 600 | 16·67 | 1·222 | 42 | 33·1 | 220 | 45·45 | 1·6576 |
| 59 | 43·1 | 900 | 11·11 | 1·046 | 59 | 50·0 | 260 | 38·46 | 1·5850 |
| 78 | 58·4 | 1500 | 6·67 | 0·824 | 78 | 67·0 | 330 | 30·31 | 1·4815 |
| 95 | 72·7 | 2040 | 4·90 | 0·690 | 95 | 85·4 | 420 | 23·81 | 1·3768 |
| 115 | 90·1 | 2820 | 3·55 | 0·550 | 115 | 105·6 | 540 | 18·52 | 1·2676 |
| 133 | 106·8 | 3600 | 2·78 | 0·444 | 133 | 125·6 | 720 | 13·89 | 1·1427 |

gas does not follow the unimolecular law. Owing to the shorter range of measurement and the strong scattering of the individual points in the former work, this was not apparent.

We then determined whether the wall reaction, which is principally responsible for the disappearance of free radicals, could be suppressed. Experience indicates that with increase in the wall temperature of the tube, the accommodation coefficient would decrease, thereby lengthening the life of the free radical. Measurements were carried out exactly as described above, the tube between the point of formation of the radicals (Fig. 3A, *a* and *b*) and the measurement mirror (*e*) being heated electrically (*c*). It was necessary to leave unheated a length of 5 cm., *d*, immediately preceding the mirror.
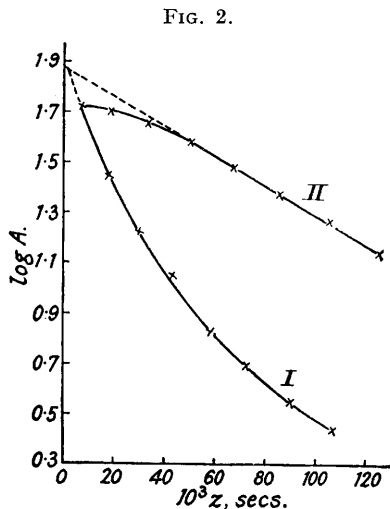
It was established that the life of the radicals did, indeed, increase with rising temperature. Working in a stream of hydrogen, the optimum life period under the experimental conditions used by us was attained with a wall temperature of 350—360°. If the temperature were raised further, the life of the radicals again decreased. It appears that a new reaction assumes prominence, which with rising temperature leads to an ever-increasing destruction of the radicals.

The values obtained under the optimum conditions are collected in Table I (b). In calculating $z$, allowance has been made for the fact that, owing to the thermal expansion of the carrier gas, the pressure and velocity conditions are somewhat different from those obtaining in cold-tube experiments. Accordingly, the values of $z$ differ somewhat from those in Table I (a) despite identical values of $D$.
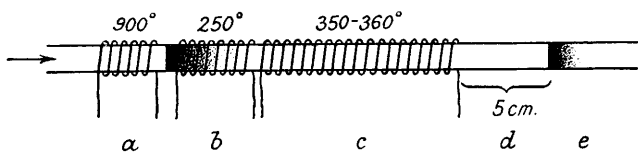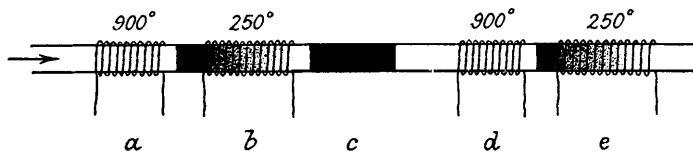


FIG. 2.



FIG. 3A.



FIG. 3B.

The values obtained, plotted in the same way as before (Fig. 2, curve II), form a straight line; only the first three points show an increasing deviation in the direction of the time interval zero. This deviation is to be attributed to the experimental arrangement, since (as stated above) the tube could not be heated right up to the measurement mirror. At this section of the tube, however, as follows from the cold-tube experiments, the radicals are especially rapidly

destroyed. Although the influence of this unheated 5 cm. is inappreciable with great distances between the decomposition point and the measurement mirror, yet, as this distance diminishes, the strong radical-destroying effect of this section of tube becomes increasingly perceptible. The activities fall more and more below the calculated values, and the curve assumes an increasingly downward curvature. The first point is common to both curves, as is to be expected, since this was obtained under the same conditions for both. It is to be anticipated, further, that both curves if extrapolated back to the zero point (as in the broken lines) would again meet in the same value for $A$, since the point $z = 0$ corresponds to the point of decomposition of the tetramethyl-lead. At this point, the extrapolated activities, under otherwise identical conditions of dosage, should be the same. The curve accords with this requirement. From the slope of curve II, the half-value period $T$ of free methyl under the conditions specified is $5 \cdot 2 \times 10^{-3}$ sec.

Consideration of the curves I and II suggests that the deactivation of the free radicals proceeds by two distinct reactions. The first, preponderant at room temperature, decreases with rising temperature and *vice versa*, since experiment shows that no free radicals pass if a point on the tube is chilled with liquid air. The vapour pressure of the methyl radical (which presumably does not differ much from that of methane) is far too high at liquid-air temperature for this to be due entirely to a freezing out of the radicals. The other, as yet hypothetical, reaction by which the free radicals disappear, increases with rise in temperature. Up to 350°, the decrease in the first reaction outweighs the increase in the second, so that the life of the methyl radical shows a net increase. Above 350°, the disappearance of radicals by the second reaction becomes so great that the life decreases again.

III. *The Reaction Products of Free Methyl in Hydrogen.*—An investigation of the reaction products under various conditions was undertaken to ascertain the nature of the reactions, and to what extent they are responsible for the disappearance of the free radicals.

For this purpose we developed a technique which enabled the reaction products to be collected quantitatively during continuous running, without altering any of the foregoing conditions of experiment (cf. the collection of products during intermittent running, Simons, McNamee, and Hurd, *J. Physical Chem.*, 1932, **36**, 939). On the supposition that the recombination products would be principally gases of low b. p., no success could be anticipated from a simple condensation in liquid-air-cooled traps. Filling the condensation tubes with adsorbent charcoal was not practicable, since the streaming velocity must be maintained at its former rate. We accordingly constructed tubular copper-gauze cylinders, packed with active charcoal, which were so arranged in wash-bottle-like traps that the gas stream could flow over both their inner and outer surfaces (Fig. 4). We established that a measured volume of methane, added to the hydrogen, was removed quantitatively from the gas by the traps, which were cooled externally by liquid air. After replacing the cooling bath by boiling water, the gas could be quantitatively extracted by means of a Töpler pump, and estimated. As a result of this test, we could safely assume the complete absorption of the expected gaseous products.

With this experimental arrangement, we first carried out four runs during which the vaporising vessel was kept at − 31°, and the tetramethyl-lead quantitatively decomposed (cf. Part I, *loc. cit.*, p. 1340). The pressure at the decomposition point was 1·6 mm. throughout. The analyses of the gas mixtures so obtained are set out in Table II. By comparison of the quan-



Fig. 4.
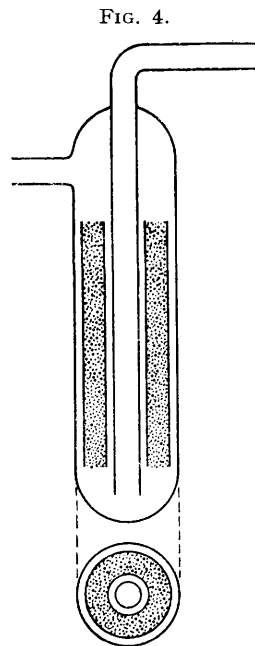
TABLE II.

| Duration of expt., hrs. | Pb deposited, mg. | Gas obtained, c.c. | $C_2H_4$, %. | $C_2H_6$, %. | $CH_4$, %. | $CH_3$, c.c., calc. from amount of Pb | $CH_3$ found, c.c. |
|---|---|---|---|---|---|---|---|
| 8½ | 278·7 | 78·6 | 0·5 | 40·9 | 58·6 | 121·0 | 111·0 |
| 8 | — | — | 0·9 | 42·8 | 56·3 | — | — |
| 7½ | 256·6 | 68·1 | 0·9 | 42·5 | 56·7 | 111·0 | 97·6 |
| 8 | 265·3 | 70·0 | 0·6 | 42·3 | 57·1 | 114·8 | 100·0 |

tities of gas found (converted into its equivalent amount of free methyl) with those calculated from the simultaneously determined weights of deposited lead, it may be seen that about 10% of the expected gases escape measurement. The origin of this loss we take to be, on the one hand, a complete disruption of the methyl, recognisable by the deposition of carbon in the decomposition zone, and on the other hand, the invariable formation of perceptible amounts of oily products which cannot afterwards be recovered from the adsorbent charcoal. The average composition of the gases we found to be : $C_2H_4$, 0·7; $C_2H_6$, 42·1; $CH_4$, 57·2%. Taking into account that for the formation of each molecule of ethylene or ethane, two methyl radicals have disappeared, while for methane only one is required, the above figures can be so converted as to show what percentage of the radicals present is used up in forming each of the three gases named. The proportions are $C_2H_4$, 1; $C_2H_6$, 59; $CH_4$, 40%, so a high proportion of methyl is used up at room temperature in the formation of methane.

Having obtained the above concordant results, we investigated the manner in which the relative proportion of the reaction products was dependent upon the concentration of the radicals. The temperature of the vaporising vessel was varied from $- 1°$ to $- 50°$, other conditions being maintained constant. The pressure was 1·4—1·6 mm., and the streaming velocity 1140 cm. per sec., $821 \times 10^{-7}$ g.-mol. of hydrogen flowing through the apparatus per sec. The results are collected in Table III (a). It will be seen that, on using low concentrations of tetramethyl-

TABLE III.

| Temp. of bath. | Duration of expt., hrs. | Pb deposited, mg. | Gas obtained, c.c. | PbMe$_4$ decomp. per sec. mols. $\times 10^9$. | $\dfrac{10^5 PbMe_4}{H_2}$. | Gas analysis, %. | | | Per cent. of CH$_3$ disappearing as | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $C_2H_4$. | $C_2H_6$. | $CH_4$. | $C_2H_4$. | $C_2H_6$. | $CH_4$. |
| | | | | *(a) Tube at 20°.* | | | | | | | |
| $- 1°$ | 1 | 271·6 | 71·0 | 364·0 | 444·0 | 2·4 | 49·5 | 48·0 | 3·1 | 65·3 | 31·6 |
| $-15$ | 3 | 382·8 | 100·5 | 171·0 | 208·0 | 1·7 | 50·0 | 49·3 | 2·3 | 65·8 | 31·9 |
| $-25$ | 6½ | 296·4 | 80·4 | 61·3 | 74·6 | 1·0 | 48·1 | 50·9 | 1·4 | 64·4 | 34·2 |
| $-31$ * | 8 | 266·9 | 72·2 | 45·0 | 54·8 | 0·7 | 41·9 | 57·5 | 1·0 | 59·0 | 40·0 |
| $-45$ | 12½ | 102·5 | 24·7 | 11·0 | 13·4 | 0·0 | 37·5 | 62·5 | 0·0 | 54·5 | 45·5 |
| $-48$ | 20 | 133·4 | 35·2 | 8·9 | 10·9 | 0·0 | 32·1 | 67·9 | 0·0 | 48·6 | 51·4 |
| $-50$ | 24 | 125·2 | — | 7·0 | 8·5 | 0·0 | 28·9 | 71·7 | 0·0 | 44·8 | 55·2 |
| | | | | *(b) Tube at 350°.* | | | | | | | |
| $- 1$ | ⅔ | 190·0 | 54·3 | 392·0 | 466·0 | 2·2 | 43·8 | 54·0 | 3·0 | 60·0 | 37·0 |
| $-19$ | 1½ | 153·3 | 44·4 | 138·0 | 168·0 | 1·5 | 35·2 | 63·3 | 2·2 | 51·5 | 46·3 |
| $-31$ | 5¾ | — | — | — | — | 0·8 | 26·9 | 72·3 | 1·2 | 42·1 | 56·7 |
| $-31$ | 5 | 178·0 | 58·1 | 47·5 | 58·0 | 0·8 | 27·4 | 71·8 | 1·2 | 42·7 | 56·1 |
| $-48$ | 20 | 126·0 | 37·0 | 8·5 | 10·3 | 0·2 | 10·2 | 89·6 | 0·3 | 18·9 | 81·2 |

* The value for $-31°$ is the mean of the values in Table II.

lead ($PbMe_4 : H_2 = 8·5 \times 10^{-5}$), 45% of the radicals disappear as ethane and 55% as methane. With higher concentrations ($444 \times 10^{-5}$), these values are 65% and 32% respectively. The amounts of ethylene (3%) also formed at the higher concentrations are of secondary importance. In view of the considerable amount of energy required to form ethylene and hydrogen from two methyl radicals (cf. Simons, McNamee, Hurd, *loc. cit.*, p. 945), their origin may be attributed to the hot (*ca.* 900°) decomposition zone.

We investigated also the products resulting from the disappearance of free radicals under the same conditions, but in a tube heated to 350—360°. For this purpose, the quartz tube was furnished for its entire length with a furnace winding, so that the radicals must decay over a length of 130 cm. according to the reaction scheme valid under hot-wall conditions. This displacement of the results as compared with decomposition in the cold tube may be seen from Table III (b).

In this instance, with low tetramethyl-lead concentrations ($10·3 \times 10^{-5}$), 18·9% disappears in the form of ethane and 81·2% as methane, while with higher concentrations ($466 \times 10^{-5}$) the proportions are 60% and 37% respectively : heating of the tube evidently favours the formation of methane both at low and at high concentrations. Moreover, only a small proportion of the radicals had the opportunity to decompose according to the hot-wall scheme, while the greater part underwent decomposition in the further part of the apparatus by the reactions obtaining in the cold tube. To secure complete decomposition in a hot tube it would have been necessary either to employ a disproportionately long tube, since the life in a hot tube

is longer (Fig. 2), or else to lower the streaming velocity. The latter was not possible if other conditions were to remain constant.

To form some conception of the reactions occurring under the conditions employed in the life-period determinations given in Table I and Fig. 2, the values for the percentage of methyl forming methane (from Table III) were plotted against the concentrations of tetramethyl-lead employed, and extrapolated to a lead alkyl concentration of $2 \times 10^{-5}$. (With the minute lead alkyl concentrations employed in these determinations, the collection of the quantity of gas required for analysis would have occupied too long.) Fig. 5 shows the curves obtained—I and II being derived from Table III a and b respectively.

FIG. 5.
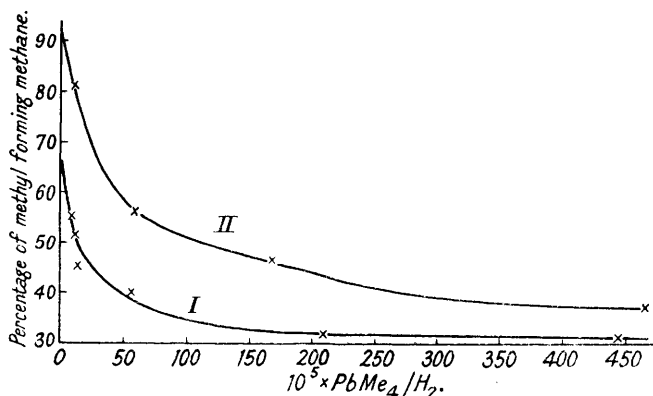


The extrapolated values indicate that, under the conditions obtaining during the determination of the half-value curve in the cold tube, 60% of the radicals disappeared as methane and 40% as ethane. In the hot tube, however, 90% formed methane and 10% ethane.

IV. *Influence of Concentration on the Yield of Free Methyl.*—The effect of temperature on the course of the reaction having been ascertained, it was important to investigate whether an appreciable fraction of the radicals was already destroyed in the hot decomposition zone.

In order to ascertain the maximum yield of free radicals resulting from the decomposition of tetramethyl-lead, a mirror of lead at least 3 cm. long was produced on the wall of the tube by distillation of the metal (Fig. 3B). Directly in front of this mirror ($c$) tetramethyl-lead was decomposed by a spiral ($a$) combined with a " quantitative decomposition spiral " ($b$). The resulting radicals reacted with the lead mirror ($c$) and the newly formed lead alkyl was again quantitatively decomposed by spirals $d$ and $e$.

If the tetramethyl-lead were to split off 100% of its methyl content in the form of free radicals, one would anticipate that the lead deposited at the point of origin of the radicals would be equal in amount to that, derived from the mirror ($c$), which separates upon the second pair of spirals. Comparison of the amount of primary lead, originating from the decomposition of the lead alkyl, with the secondary deposit on the second pair of spirals, which has been transported by the free radicals, enables the yield of free radicals actually obtained to be estimated. The lead was determined colorimetrically as before.

TABLE IV.

| $10^5 PbMe_4/H_2$. | Lead I, mg. | Lead II, mg. | Yield of radicals, %. | $10^5 PbMe_4/H_2$. | Lead I, mg. | Lead II, mg. | Yield of radicals, %. |
|---|---|---|---|---|---|---|---|
| 21·4 | 7·330 | 3·500 | 48 | 2·0 | 0·686 | 0·530 | 77 |
| 9·1 | 3·110 | 1·806 | 58 | 1·5 | 0·510 | 0·396 | 78 |
| 5·7 | 1·949 | 1·349 | 69 | 1·5 | 0·508 | 0·419 | 82 |
| 2·6 | 0·882 | 0·648 | 74 | | | | |

The results are collected in Table IV. Lead I represents the amount of lead deposited in the formation of the radicals, and Lead II that transported by the radicals.

The yield of free radicals is seen to rise to 82% as the concentration of tetramethyl-lead used is decreased. Similar experiments have already been carried out with free ethyl with essentially the same result, *i.e.*, 83% (Hahnfeld, *loc cit.*). It is very likely that in both cases

the use of helium instead of hydrogen as carrier gas will permit of an even nearer approach to 100%.

The decrease in the yield of radicals with increasing concentration may be explained primarily as a result of the greater frequency of collisions within the hot decomposition zone, whereby the radicals are more rapidly transformed into stable products which do not react with lead. The formation of ethylene at higher concentrations, previously detected, confirms this view. More-over, the tarry products then resulting in greater amount protect the lead from attack by the radicals, and indicate falsely a lower yield of free radicals.

An important conclusion drawn from the results collected in Table IV, taken in conjunction with the observations already referred to, is that even at room temperature free methyl is capable of reacting with the carrier gas, hydrogen. We have now established that at a tetra-methyl-lead concentration of $2 \times 10^{-5}$, about 80% of the radicals are still effective behind the decomposition point. Under the same experimental conditions, it appears from curve I (Fig. 5) that at room temperature, 60% of the resulting radicals produce methane and 40% ethane. Even if it be assumed that the 20% of the radicals destroyed within the decomposition zone had given rise to the quantitative formation of methane, there still remains 40% of methane which must necessarily have been formed from methyl and hydrogen in the remainder of the apparatus almost at room temperature, although the gas may be slightly hotter than the walls of the tube.

Our experiments scarcely admit of any interpretation other than that the greater proportion of the methyl radicals disappear at room temperature in the reaction $CH_3 + H_2 \longrightarrow CH_4 + H$. We will not here discuss certain theoretical objections arising from other work. We may point out, however, that the straight line in curve II (Fig. 2) can easily be explained, since in the hot tube the above unimolecular reaction predominates. On the other hand, in the cold tube the order of the wall reaction must depend on the concentration of the already adsorbed radicals, and may therefore deviate from the unimolecular (curve I).

V. *The Reaction Products of Free Methyl in the Absence of a Carrier Gas.*—From the facts thus far ascertained, it follows that, in the absence of hydrogen as carrier, ethane should pre-dominate as the product of reaction. To investigate this, the vapour of tetramethyl-lead was admitted directly to the apparatus. The pressure and velocity of the gases passing through the quartz tube were in this case less than in the previous experiments. Thermal decom-position was effected in one series quantitatively (Expt. A, Table V), and in another series (B, Table V) without using a quantitative decomposition spiral, in order to ascertain whether any reaction could be detected between free methyl and the regenerated lead alkyl produced by its attack on its own lead mirror.

TABLE V.

| Group. | Duration of expt., hrs. | Press., mm. Hg. | Pb de-posited, mg. | Gas ob-tained, c.c. | PbMe$_4$ decomp. per sec., mols. $\times 10^9$. | Gas analysis, %. C$_2$H$_4$. | C$_2$H$_6$. | CH$_4$. | Per cent. of radicals disappearing as C$_2$H$_4$. | C$_2$H$_6$. | CH$_4$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 10 | 0·017 | 214·6 | 50·0 | 28·8 | 2·7 | 89·1 | 8·2 | 2·8 | 93·0 | 4·2 |
| B | 10 | 0·017 | — | — | 28·8 | 2·1 | 91·0 | 6·9 | 2·2 | 94·2 | 3·6 |
| A | ½ | 0·112 | 280·6 | 60·3 | 754·0 | 5·4 | 78·8 | 15·8 | 5·9 | 85·5 | 8·6 |
| B | ½ | 0·112 | — | — | 754·0 | 4·1 | 80·4 | 15·5 | 4·5 | 87·2 | 8·3 |

Analysis showed ethane to be the chief product. Ethylene was present in rather larger amount than in experiments with hydrogen as carrier, which may have been due to the lower streaming velocity. The radicals remain longer in the heated zone, and so have more oppor-tunity to form ethylene, as already mentioned. The origin of the methane also is to be sought in the hot decomposition zone. It is conceivable that the free methyls, by dehydrogenation, reduce other methyl radicals to methane.* A complete dehydrogenation of the radicals, for instance, is shown by the considerable deposition of carbon. For the same reason, the per-centage of methane formed rises with the amount of tetramethyl-lead decomposed in unit time, since—owing to the higher pressure—the free path of the radicals is smaller, and the time spent in the hot part of the tube greater.†

VI. *The Reaction Products of Free Methyl in Helium.*—It was to be anticipated from the

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* Such a process is called in German chemical literature " Disproportionierung."

† These observations agree with those of Simons, McNamee, and Hurd (*loc. cit.*), who also decom-posed tetramethyl-lead by a streaming method in the absence of a carrier gas, and obtained an even larger methane content, inasmuch as they worked at still higher pressures (1·5—2 mm. Hg).

foregoing results that by choice of an inert carrier gas, ethane would again be found to be the chief reaction product of the free methyl radicals. To this end, we replaced the hydrogen as carrier gas by helium, the streaming velocity being 650 cm. per sec., and the pressure in the measuring tube about 1·3 mm. The results obtained are given in Table VI. The displace-

### TABLE VI.

| Temp. of bath. | $H_2$. | Gas analysis, %. $C_2H_4$. | $C_2H_6$. | $CH_4$. | Per cent. of radicals disappearing as $C_2H_4$. | $C_2H_6$. | $CH_4$. |
|---|---|---|---|---|---|---|---|
| − 1° | 0·9 | 2·8 | 87·0 | 9·3 | 2·9 | 92·1 | 5·0 |
| −25 | 1·0 | 1·7 | 89·5 | 7·8 | 1·9 | 94·1 | 4·0 |

ment of the reaction towards the side of ethane formation is seen. Although the pressure in the decomposition tube was greater than in the experiments without a carrier gas, the yield of methane was smaller, since the helium acted as a diluent in diminishing the interaction of the radicals in the hot section of the tube.

VII. *The Life Period of Free Methyl.*—We have seen that, at room temperature in an atmosphere of hydrogen at 1—2 mm. pressure, free methyl disappears by one reaction leading to ethane, and by another giving methane; also that the proportion of the reaction giving rise to ethane may be diminished by heating the wall of the tube. Further, by the choice of an inert gas as the carrier gas, the reaction yielding methane can be practically inhibited. It follows that by the simultaneous use of an elevated temperature and of an inert carrier gas, a means should be provided of extending the life of free methyl.

As our experiments showed, the concentration of free radicals in a stream of helium does, indeed, decay much more slowly in a hot tube than in a cold; *e.g.*, at a distance of 105 cm. from the point of formation, and with a streaming velocity of 650 cm. per sec., it took 71 mins. for the disappearance of a 3-minute measurement mirror when the tube was cold, as against only 7 mins. with the tube hot. It is remarkable that the life of the free methyl did not attain its maximum at 360° in this case, as happens when hydrogen is the carrier gas, but that the highest temperature used by us, a red heat (*ca.* 500°), was found to be best. The temperature could not be raised higher because of experimental difficulties. It is to be expected, however, that the optimum temperature for the life of free methyl would be attained immediately before the inception of a cracking process.

To determine the half-value period, we carried out a number of activity measurements at different distances in the heated tube. The results given in Table VII were thus obtained.

### TABLE VII.

| D, cm. | z × 10³, sec. | d, secs. | A = 10⁴/d. | log A. | K. | D, cm. | z × 10³, sec. | d, secs. | A = 10⁴/d. | log A. | K. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 21 | 32·8 | 170 | 58·8 | 1·769 | 7·4 | 62 | 97 | 265 | 37·7 | 1·576 | 7·0 |
| 35 | 54·5 | 190 | 52·7 | 1·722 | 6·8 | 104 | 162 | 420 | 23·8 | 1·376 | |

From the mean value of the reaction constant ($K = 7·0$), the half value period for the methyl radical under the conditions specified may be calculated to be 0·1 sec. If the accommodation coefficient α be calculated therefrom by the formula of Paneth and Herzfeld (*loc. cit.*), it is found to be but one-tenth of that obtaining in the cold tube : of 10,000 molecules striking the walls, only one is not reflected.

It was possible, therefore, in a tube 1 cm. in diameter, heated to 500°, and with an inert gas as carrier, to prolong the life of the methyl radical to about the same order of magnitude as that of atomic hydrogen. We have no doubt that under still more favourable conditions, the existence of free methyl might be prolonged still further above the half value period of 0·1 sec. now found.

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