

molecule. Alternate rotational levels have a weight of one, and the remainder a weight of three, but whether it is the odd or even levels which have the greater weight depends on the symmetry of the oscillational state. It is easily shown, however, that at temperatures high enough so that the rotational sum may be replaced by integrals the expression for Q reduces to the following

$$Q = Q_{\text{rot.}} \cdot Q_{\text{vib.}} \approx \frac{1}{2} \int_0^{\infty} (2j + 1) e^{-j(j+1)\sigma} dj \times Q_{\text{vib.}}$$

$$= \frac{4}{2\sigma} Q_{\text{vib.}}$$

The use of this expression gives us the absolute entropy, including the part due to spin. If the factor 4 is omitted we obtain the "virtual" entropy.

Summary

1. The calculation of the entropies of linear polyatomic molecules from spectroscopic data is shown to be similar to and only slightly more complicated than similar calculations for diatomic molecules.

2. The entropies of carbon dioxide, nitrous oxide, hydrogen cyanide and acetylene at 298.2°A. have been calculated from spectral data. The "virtual" entropies (those to be compared with calorimetric data) are found to be 51.07, 52.58, 48.23 and 48.00 entropy units, respectively. The absolute entropies are 51.07, 56.94, 51.79 and 50.75, respectively.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE THERMAL DECOMPOSITION OF ORGANIC COMPOUNDS FROM THE STANDPOINT OF FREE RADICALS. II. EXPERIMENTAL EVIDENCE OF THE DECOMPOSITION OF ORGANIC COMPOUNDS INTO FREE RADICALS

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In a recent paper² there was proposed an explanation for the decomposition of paraffin hydrocarbons based on the assumption that the unimolecular decomposition consists of the primary rupture of a C-C bond, with the formation of free radicals,³ followed by the decomposition of those

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² Rice, *THIS JOURNAL*, **53**, 1959 (1931).

³ The following is a bibliography of some of the more recent work in which the thermal production and reactions of free radicals are studied: (a) Taylor, *Am. Phil. Soc.*, **65**, 90 (1926); (b) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929); (c) Schultze and Müller, *Z. physik. Chem.*, [B] **6**, 267 (1929); (d) Paneth, *ibid.*, [B] **7**, 155 (1930); (e) Paneth and Lautsch, *Nature*, **125**, 564 (1930); (f) Taylor and Jones, *THIS JOURNAL*, **52**, 1111 (1930); (g) Paneth and Herzfeld, *Z. Elektrochem.*, **8**, 9 (1931); (h) Paneth and Lautsch, *Ber.*, **64**, 2702 (1931); (i) Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 939 (1932).

radicals larger than ethyl into olefins and smaller free radicals, which then react with the surrounding hydrocarbon molecules forming a saturated hydrocarbon and regenerating free radicals. In this way a chain mechanism can be set up which explains in a satisfactory manner the different products formed in the pyrogenic decomposition of hydrocarbons. We have found this scheme highly satisfactory as a means of representing the thermal decomposition of a wide variety of compounds; we have applied it to the thermal decomposition of unsaturated hydrocarbons, ketones, aldehydes, acids and ethers, and it leads to a semi-quantitative prediction of the products formed which is in good agreement with the results of experiment. However, before publishing an account of these formal schemes it seemed desirable to attempt to obtain some evidence that the decomposition of organic compounds really proceeds through a mechanism of free radicals. While we have not been successful in proving beyond doubt that the ordinary thermal decomposition of hydrocarbons proceeds through such a mechanism, we have obtained a sufficient number of interesting experimental results bearing on this question that it seems desirable to publish an account of the work.

The outstanding difficulty in connection with any attempt to establish mechanisms based on free radical formation lies in the recent estimates of the strength of the C-C and C-H bonds; thus Mecke⁴ calculates the energy of a C-H bond in methane to be 115 Cal. and that of C-C bonds in different hydrocarbons to be 110-115 Cal., as compared with the old values of 90 Cal. and 65 Cal., respectively. Since hydrocarbons decompose unimolecularly with an energy of activation of approximately 65 Cal., it is obvious that either hydrocarbons do not decompose through the mechanism of free radical formation, or else that the high values obtained from spectral data are incorrect. If the decomposition of organic compounds proceeds through a mechanism involving the primary rupture of a C-C bond, the strength of this bond cannot be greater than about 80 Cal.⁵ A preliminary account of some experiments designed to demonstrate directly that free radicals are formed when hydrocarbons and other organic compounds are heated, was presented last year.⁶

⁴ Mecke, *Nature*, **125**, 526 (1931). Since this paper was submitted, the authors have had an opportunity of discussing this matter with Professor Mecke. He states that the thermal dissociation of organic compounds into *normal* fragments may certainly be in the range 70-80 Cal., since the high values given in his previous papers are for the adiabatic dissociation into fragments, one or more of which are *excited*. The primary process which actually takes place determines the experimentally found energy of activation. See Mecke, *Z. physik. Chem.*, **B18**, 53 (1932).

⁵ This figure was obtained by taking the sum of the activation energy and the average vibrational energy; Professor D. H. Andrews finds from calculations based on Raman spectra that this latter figure for butane is 16.1 Cal. at 900°K.

⁶ "The Preparation of Free Radicals," F. O. Rice and W. R. Johnston; "The Strength of the C-C Bond," F. O. Rice and B. L. Evering. Papers presented at the Buffalo Meeting of the American Chemical Society, September, 1931.

At that time we used an extremely simple method similar in principle to that of Paneth and Hofeditz,^{3b} we found that when hydrocarbon vapors at pressures of a few mm. were passed through a quartz tube heated in the range of 800–1000°, the gases leaving the furnace rapidly removed mirrors of many different metals, such as lead, zinc and antimony, even at distances of 30 to 40 cm. from the furnace.

The first question which we may consider is whether this high temperature decomposition (in the range 800–1000°) is the same as the ordinary decomposition that occurs in the range 550–650°; a preliminary calculation supports the assumption that the two reactions are the same. Thus, from the results of Pease and Durgan⁷ we find that butane must be heated for 5.2 seconds at 625° to undergo a 10% decomposition; in our own experiments the velocity of flow was of the order of 10⁴ cm. per sec. and since the furnace was 10 cm. long the time of heating was of the order of 10⁻³ sec. By making a simple approximate calculation, using the Arrhenius equation and assuming the energy of activation to be 65,000 Cal., we find that we must heat butane to 900° for 10⁻³ sec. in order to decompose it to the extent of 10%. While we were able to remove mirrors at 800° or even lower, the hydrocarbon was obviously undergoing only a trace of decomposition; when, however, the temperature was in the neighborhood of 900°, a substantial fraction decomposed, as was shown by the amount of gas evolved and the amount of hydrocarbon recovered in the liquid-air trap.

The second question which we must consider is whether the agent that removes the mirrors really consists of free radicals formed by the rupture of a C–C bond, or whether it is perhaps composed of "hot" molecules, as suggested by Burk,⁸ or of alkylidene radicals formed when two hydrogen atoms attached to the same carbon atom split off and form a hydrogen molecule, as suggested by Kassel.⁹ There is also the possibility that in the high temperature decomposition the free radicals are produced at the silica surface; according to this suggestion a hydrogen atom of, for example, a butane molecule would stick to the silica surface, and the butyl radical would fly off and decompose into smaller radicals which are swept out of the furnace. On the basis of this mechanism, the free radicals are produced at the hot walls in the furnace and recombine on the cold walls outside.

One can best decide between these various hypotheses by a chemical analysis of the products formed by the combination of the metal and the active agent. We did not find it convenient to use metals such as lead, antimony or zinc for identification purposes, partly because the alkyl derivatives of these metals are liquids and the small quantities formed

⁷ Pease and Durgan, *THIS JOURNAL*, **52**, 1262 (1930).

⁸ Burk, *J. Phys. Chem.*, **35**, 2446 (1931).

⁹ Kassel, *Chem. Rev.*, **10**, 18 (1932); Kassel, "Kinetics of Homogeneous Gas Reactions," *The Chemical Catalog Co.*, 1932, p. 233.

cannot readily be separated from the excess of hydrocarbon or other organic compound employed, and partly because if two or more radicals were present a large number of different compounds would result, owing to the polyvalent character of these elements. We found that by bringing the active material in contact with a cold surface on which metallic mercury continually condensed, it was possible to obtain mercury dialkyls which react readily and quantitatively with mercuric bromide to form alkyl mercuric bromides. These latter compounds are well-defined crystalline solids with definite melting points. Using this technique we have been able to show that when acetone is decomposed in our apparatus it gives only methyl groups, whereas propane and butane give a mixture of methyl and ethyl groups, the former predominating. It seems reasonably certain from such experiments that the agent that removes the mirror really consists of free alkyl radicals. Further work is necessary in order to determine whether the radicals are produced by a rupture of a C-C bond in the homogeneous gas phase or by the rupture of a C-H bond at a hot silica surface.

We have made some measurements of the life time of the free radicals by following Paneth's plan of noting the time of removal of standard mirrors placed at different distances from the furnace. We found that the rate of disappearance of the radicals at the concentrations produced in our experiment was of about the same order as that obtained by Paneth, namely, a half-life period of 0.006 sec. However, our unimolecular "constants" showed considerable drift and the bimolecular "constants" showed the same effect although not to quite the same extent. Possibly under the conditions of our experiments combination occurs to an appreciable extent both on the wall and in the gas phase. The rate of disappearance of the radicals seemed to be approximately independent of the compound used to produce them.

This method of production of free radicals from organic compounds suggests several ways for measuring directly the strength of the C-C bond. The first method permits us to make a direct measurement of the decomposition into free radicals. The time intervals required for the removal of a standard mirror at different distances from the furnace give us an arbitrary measure of the concentration of the radicals at these points, and by extrapolating we can obtain the concentration of the radicals as they leave the furnace. If we do this for two temperatures, both in the range in which the fractional decomposition is small, the ratio of the two concentrations so obtained is the ratio of the two velocity constants, and a simple calculation gives us at once the energy of activation of the decomposition into free radicals. If this energy of activation should be about 65,000 Cal. we would have strong evidence that the ordinary thermal decomposition of hydrocarbons consists of a primary dissociation into

radicals. Some preliminary experiments with acetone have indicated a value of 67,000 Cal. for the activation energy of the dissociation into free radicals, as compared with the accepted value of 68,500 Cal. for the ordinary thermal decomposition.¹⁰

The second method consists of an analysis of the products of the decomposition; thus if all the C-C bonds in butane have the same strength, the ratio of methyl and propyl to ethyl groups should be 2:1. It appears, however, that under the conditions of our experiment, in which there was considerable decomposition of the butane, the propyl groups are unstable and decompose, probably into ethylene and methyl groups. Under these conditions we should expect the decomposition to yield methyl and ethyl groups in the ratio of 2:1. Actually an experiment yielded a mixture of methyl mercuric bromide and ethyl mercuric bromide in the ratio of approximately 2.3:1. This method is subject to serious limitations because the decomposition in the furnace may not consist of a homogeneous dissociation through rupture of a C-C bond, and because the ethyl groups probably decompose to some extent into ethylene and hydrogen atoms or into methyl and methylene groups. The third way consists of a direct measurement of the heat of combination of two methyl groups, by passing the gases from the furnace into a calorimeter and noting the rise in temperature and the amount of ethane formed. We have not as yet made any measurements along these lines.

Experimental

Original Paneth Experiment.—We first built an apparatus in all respects practically identical with that of Paneth and Hofeditz,^{3b} using hydrogen as the gas for carrying the lead tetramethyl. Our results completely confirmed those obtained in the original experiment. Following this we carried out a few simple experiments with the free methyl groups which were formed, according to the original method, in a current of hydrogen.

A platinum-rhodium thermocouple, sensitive to 0.5°, showed no rise in temperature when placed in the current of hydrogen containing the free methyl groups; that these were present in abundance could easily be shown by the fact that a lead mirror was readily removed after the gas had passed over the thermocouple.

In our next experiment we inserted a coil of copper wire consisting of about twenty turns of wire of 0.2 mm. diameter between the furnace and the mirror. A qualitative test showed that this had no effect on the methyl groups, since lead mirrors were removed apparently just as easily whether the coil was there or not. Heating the copper wire up to about 300° was also without effect. This experiment was repeated, using both iron and nickel in place of the copper, in each case with identical results. None of these metals, either hot or cold, had any perceptible effect on the methyl groups.

In another experiment a heavy lead mirror was formed for about 3 cm. along the tube; free methyl groups could not pass through this in the cold, since they combine

¹⁰ Hinshelwood and Hutchinson, *Proc. Roy. Soc. (London)*, A111, 245 (1926).

with it to form lead tetramethyl, but on heating the mirror to about 200° the free methyl groups apparently passed through unchanged, since they readily removed cold lead mirrors further down the tube.

Use of Condensable Gases.—In order to detect the free methyl radicals formed in the decomposition of lead tetramethyl, it is necessary to have a very rapid stream of gas in order to sweep the radicals away quickly from the heated zone in which they are formed. The use of a permanent gas such as hydrogen or nitrogen necessitates an elaborate pumping system, since all of the gas must be pumped out of the apparatus. If, however, one could use a substance which is frozen out by liquid air and which is not attacked by the free radicals, the experiment would be very much simplified, since an

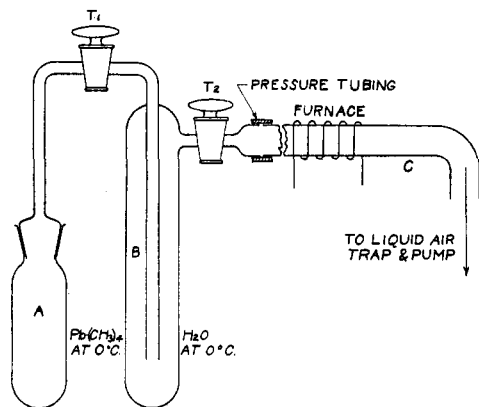


Fig. 1.—Apparatus for preparing free methyl groups using lead tetramethyl in a current of water vapor.

The pressure in B is kept at about 4 mm.; by opening the stopcock T_1 the lead tetramethyl vapor bubbles through the water, and the rate can be easily regulated. When stopcock T_1 is shut, and T_2 is open, so that only water vapor passes over the metallic mirror, even the strongest heating of the quartz tube has no effect on either a lead or antimony mirror.

Carbon dioxide may also be used to carry the lead tetramethyl, but in this case the latter is kept in the trap B, in which a temperature about -80° is maintained and solid carbon dioxide is kept in trap A which is also maintained at -80° . The tubing joining A and B should have 50–100 cm. of 1 mm. capillary for convenience in regulating the flow of the carbon dioxide.

We have also found that the apparatus may be simplified still further by making a solution of lead tetramethyl in an organic solvent such as heptane or acetone. In this case no other transport gas is needed and only reservoir B is required; the temperature of this is adjusted so that the vapor pressure of the organic compound is 1 to 2 mm. as it enters the furnace. By using capillary tubing between trap B and the quartz tube the vapor pressure of the organic compound in B may be comparatively high. We found that a 1% solution of lead tetramethyl in heptane or acetone is quite satisfactory.

In removing mirrors by any of the methods described in this section, the first step is to open stopcocks T_1 and T_2 and evacuate the apparatus. This automatically removes all dissolved oxygen and makes unnecessary the elaborate purification train in the original Paneth experiment. The furnace is then heated to $500\text{--}600^{\circ}$ and a metal-

ordinary oil pump could then be used to maintain a vacuum in the apparatus. It occurred to us that water vapor had all of the characteristics that we required since it can be completely frozen out, is very stable and is easily purified. Our experiments with water vapor were successful and we found that metallic mirrors could be readily removed by the simple apparatus shown in Fig. 1.

The quartz tube C can conveniently be about 50 cm. long and 0.4 cm. internal diameter, and contains a small piece of metal at the low pressure end which can be used to form mirrors. We have found that thick-walled rubber tubing is quite satisfactory for joining the ends of this quartz tube to the rest of the apparatus.

lic mirror is formed by heating the piece of metal in the quartz tube. The mirror is then cooled with water, the stopcocks T_1 and T_2 are opened, and the current of gas containing the free methyl groups is allowed to pass over the mirror. Frequently the first mirror is either not removed or removed with difficulty because of surface impurities, and it is best to heat this while the current of gas is flowing and drive it down the tube. The stopcocks may then be turned off and a new clean mirror formed.

Life of Free Methyl Groups.—We next attempted to determine the life time of the free methyl groups produced by heating lead tetramethyl in a current of acetone. We followed the method developed by Paneth and his co-workers exactly, using a standard metallic mirror, which is distilled onto a quartz tube, and measuring the time of removal by the free radicals. The reciprocal of this time is assumed to be proportional to the concentration of the radicals. By taking measurements of the times of removal of standard mirrors at different distances from the furnace we found that the concentration of free methyl groups diminished rapidly as they passed down the tube. We measured the acetone pressures at the inlet and outlet of the quartz tube and also measured the weight of acetone passing through the apparatus in a known time interval. From this we could determine the time taken for the free methyl groups to pass from the end of the furnace to the standard mirror.

Paneth and his co-workers have investigated very completely the kinetics of the disappearance of the free methyl and free ethyl groups produced by the decomposition of the corresponding lead tetra-alkyl, using hydrogen, nitrogen and neon-helium mixtures as transport gases. They found that the rate of disappearance was approximately independent of the nature and pressure (over a range of a few mm.) of these gases, that the radicals disappeared according to a unimolecular law, and that the half-life was approximately 0.006 sec. in a tube of about 0.4 cm. diameter. Paneth and Herzfeld showed that the radicals combine mainly on the wall and only a small proportion combine in the homogeneous gas phase.

We present in Table I the results of some preliminary measurements in a quartz tube 0.4 cm. diameter, the acetone pressure at the standard mirror

TABLE I

RATE OF DISAPPEARANCE OF FREE METHYL GROUPS FROM LEAD TETRAMETHYL
Using acetone as transport gas. 1% lead tetramethyl in acetone.

d , cm.	34	32	30	28	26	24	22	20
$\Delta t \times 10^4$, sec.	74.6	68.5	63.0	57.3	52.0	47.0	42.2	37.6
t_m , sec.	183	163	132	88	86	68	47	32

d is distance from furnace to standard mirror; Δt , time taken to travel from furnace to standard mirror; t_m , time required to remove standard mirror.

being 0.22 mm. mercury; the standard mirror was kept at one point and the furnace was moved along the tube to different distances from the mirror. The fall in pressure down the tube was 0.007 mm. per cm. length.

The constants calculated according to a first order equation show considerable drift so that the half-life varies from $1-2 \times 10^{-3}$ sec. as compared with 6×10^{-3} sec. obtained by Paneth and Hofeditz. There is somewhat better, but still not very good, agreement with a second order equation.

Free Radicals from Organic Compounds.—It seemed from the fore-

going experiments that it should be possible to decompose organic compounds, such as hydrocarbons or ketones, according to these methods but using the vapor of the material itself as transport gas. The apparatus shown in Fig. 2 was made for this purpose. It consists of a conical Pyrex flask A of about 50 cc. capacity, fitted with a well ground joint connected with 10–15 cm. of Pyrex tubing about 1 mm. internal diameter; this tube is fitted with the stopcock T_1 and is connected by pressure tubing to the quartz tube B, which is about 0.4 cm. in diameter and 50 cm. long. This

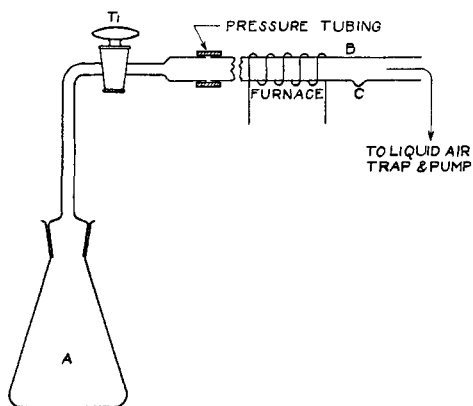


Fig. 2.—Apparatus for preparing free radicals from organic compounds.

tube in turn is connected by pressure tubing with a liquid-air trap and the pumping system. Tube B is also fitted with an electric furnace capable of sliding along the tube and has a groove at C for holding small pieces of different metals.

When using this apparatus, about 20 cc. of an organic compound is placed in A and the apparatus is evacuated for a few minutes with stopcock T_1 open and flask A kept at a temperature about 50–100° below the boiling point of the organic compound. Any good oil pump capable of giving a vacuum of 0.05 mm. will do, although we found it practical to use an auxiliary mercury vapor pump on account of the greater speed of evacuation. When all the dissolved air has been displaced from the liquid and swept out of the apparatus, stopcock T_1 is closed and the apparatus is ready for use.

We found that a great variety of organic compounds, such as hydrocarbons, alcohols, ketones, acids, ethers and aldehydes, when passed through the furnace at 800–1000°, readily removed mirrors of many different metals, such as lead, antimony or zinc. The metal alkyls formed were caught in the liquid-air trap, together with the excess of the organic compound. Thus, when the fragments from acetone were used to remove antimony mirrors, the trap contained a colorless antimony compound, presumably antimony trimethyl, and a yellow oil insoluble in acetone, which on cooling in liquid air changed to a deep red solid. This oxidizes spontaneously in the air and is presumably the same compound that has been described by Paneth and Hofeditz.^{3b}

It is very inconvenient to attempt to identify the free radicals in these compounds directly partly because of the difficulty of separating the small quantity formed from the excess of the original organic compound used as

the source of the free radicals and partly because of the large number of different compounds formed when we have a polyvalent metal and two or more free radicals present. We shall describe our final method of identification in a succeeding section.

It is particularly important in connection with this work not to permit any trace of oxygen to come in contact with the metallic mirror, since this prevents attack by the free radicals, presumably by coating the surface with a film of oxide.¹¹ However, after the furnace has been heated and the stream of organic compound is passing through, it is perfectly possible to admit oxygen on the side of the furnace away from the mirror; in fact we have removed lead and antimony mirrors by bubbling oxygen through the heptane in flask A. The limit to the amount of oxygen that can be used is fixed by the capacity of the furnace to bring about complete removal of free oxygen so that none reaches the mirror.

Surface impurities also may prevent attack by the free radicals. Preliminary heating in a current of pure hydrogen or other reducing gas frequently cleans up the metal so that the first mirror is readily removed.

Life of Free Radicals from Organic Compounds.—This can be determined, using the apparatus shown in Fig. 2, in a manner exactly similar to that described in the previous section, in which the life of free methyl groups obtained from lead tetramethyl was measured. The results, using acetone and heptane, are given in Table II. As before, the unimolecular velocity constants show a considerable drift and the half-life for the methyl groups from acetone varies from 0.55×10^{-3} to 2.8×10^{-3} sec. and the half-

TABLE II
RATE OF DISAPPEARANCE OF FREE RADICALS FROM HEPTANE AND ACETONE

<i>d</i> , cm.	Heptane $\Delta t \times 10^4$, sec.	<i>t_m</i> , sec.	<i>d</i> , cm.	Acetone $\Delta t \times 10^4$, sec.	<i>t_m</i> , sec.
20	39.2	48	20	37.6	95
10	17.2	11	20	37.6	80
30	66.0	64	13	22.4	58
15	27.6	25	10	16.5	21
21	41.5	47	16	28.5	77
14	25.5	18	20	37.6	100
28	60.1	64	15	26.4	56
24	49.4	48	10	16.5	24
16	29.8	35			
12	22.3	19			

d is distance from furnace to standard mirror; Δt , time taken to travel from furnace to standard mirror; *t_m*, time required to remove standard mirror. Cross section of tube 0.4 cm. Pressure of heptane at mirror 0.24 mm.; fall in pressure, 0.0077 mm. per cm. length. Pressure of acetone at mirror 0.24 mm.; fall in pressure of acetone 0.007 mm. per cm. length.

¹¹ Paneth and Lautsch have recently reported^{3b} that mirrors of tellurium are not subject to this inactivation.

life of the fragments from heptane varies from 0.84×10^{-3} to 2.2×10^{-3} sec. The observations do not give a very satisfactory constant when substituted in a second order equation.

Identification of Free Radicals.—We have found mercury alkyls most convenient for identification purposes, since they react quickly and quantitatively at ordinary temperatures with mercuric halides to give alkyl mercuric halides,¹² which are well-defined crystalline compounds. The

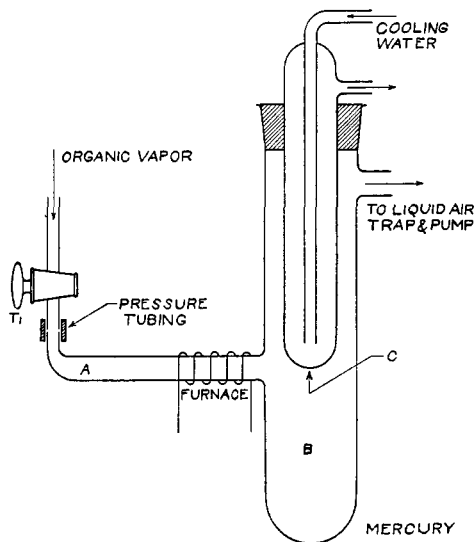


Fig. 3.—Apparatus for the preparation of organo-metallic compounds.

apparatus shown in Fig. 3 was used for preparing the mercury alkyls from the free radicals.

The organic compound is kept in a conical flask (not shown in the sketch) which is connected with the quartz sidearm A by means of pressure tubing. The temperature of the conical flask and the tubing from it are so arranged that a pressure of about 1 mm. is maintained at the entrance to sidearm A, which can be heated by means of an electric furnace to 800–1000°. The quartz tube B contains a few cc. of mercury; this is heated and distils and condenses on the water-cooled Pyrex tube C. The outer walls of B may be

cooled either by air or water so that an additional pumping action is obtained.¹³ Before starting a run a few cc. of saturated alcoholic mercuric bromide is placed in the liquid-air trap. This apparatus can be run continuously for several hours and requires no attention beyond renewing the liquid air occasionally. In one experiment we obtained almost a gram of alkyl mercuric bromides in a three-hour run, and it seems probable that by using a larger apparatus we could obtain 10-g. lots in a day's run. At the end of a run the contents of the liquid-air trap were allowed to warm up to room temperature¹⁴ and filtered from the suspended mercury. A few

¹² Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., New York, 1921, p. 65.

¹³ See Newman, "Production and Measurement of Low Pressures," D. Van Nostrand Co., New York, 1925, p. 75.

¹⁴ Organic solvents containing mercuric bromides or finely suspended mercury were never allowed to warm to higher than room temperature since there is the possibility of formation of organometallic compounds. Frequent tests showed that mercuric bromide does not react with organic substances under the conditions of our experiment.

cc. of hot alcohol was poured over the residue to dissolve any precipitated alkyl mercuric bromides, since these are not very soluble in cold ethyl alcohol. The filtrate containing the alkyl mercuric bromides was then evaporated to dryness at room temperature in a vacuum, and the solid residue sublimed by heating below 50° for an hour or two. In this way all the alkyl mercuric bromide can be separated from the excess of mercuric bromide, since the latter does not start to sublime at an appreciable rate below 70° .

In an experiment (No. 105) using acetone as the source of the free radicals and mercuric chloride¹⁵ in the liquid-air trap, we obtained 0.5 g. of material from the first sublimation (carried out at 90°). This material melted at 140° , and a test with ammonium sulfide showed the presence of a large proportion of mercuric chloride. A second sublimation at 55° gave 0.22 g. of material which melted at 170° ; this is the melting point given in the literature for methyl mercuric chloride.¹⁶ A test with ammonium sulfide proved the second sublimate to be entirely free from mercuric chloride. A few grams of methyl mercuric chloride were prepared through the Grignard reaction¹⁶ and a small quantity of this product was mixed with an approximately equal quantity of our material obtained from free radicals. The mixture melted at 170° and on cooling and solidifying it again melted at 170° . A mixture of equal parts of methyl mercuric chloride and mercuric chloride was ground up together in a mortar and the mixture was found to melt at 140 – 145° .

A similar experiment (No. 111) was performed using butane¹⁷ as the source of the free radicals and having mercuric bromide in the liquid-air trap. The results of the sublimation are given in Table III.

TABLE III
FREE RADICALS FROM BUTANE
M. p. of CH_3HgBr , 160° ; m. p. of $\text{C}_2\text{H}_5\text{HgBr}$, 193.5°

Fraction	Time of sublimation, hours	Temp. of sublimation, $^{\circ}\text{C}$.	Yield, g.	M. p., $^{\circ}\text{C}$.
1	1.0	40	0.217	157
2	1.0	50	.161	160.5
3	1.5	50	.110	172
4	1.5	50	.048	181.5
5	1.0	60	Trace	...

We have carried out a number of experiments in which we examined the alkyl mercuric bromides obtained from butane without finding any indication of the presence of propyl mercuric bromide. The product appears to

¹⁵ Mercuric bromide is preferable to mercuric chloride because there is a greater difference in volatility between it and its alkyl derivatives than in the case of the chloride.

¹⁶ Marvel, Gauerke and Hill, *THIS JOURNAL*, **47**, 3009 (1925).

¹⁷ 99% butane supplied by the Ohio Chemical and Manufacturing Co.

consist entirely of a mixture of methyl and ethyl mercuric bromides, although we were not able to isolate pure ethyl mercuric bromide and obtain a mixed melting point owing to the small quantities available.¹⁸ By comparing the melting points of the fractions obtained in the butane decomposition with the melting points of known mixtures, we obtained a rough estimate of the composition of the four fractions, which contained approximately 10, 20, 62 and 80% of the ethyl compound, respectively. This estimate was further checked by measuring the lowering of the melting point of the pure substances caused by measured small additions of the different fractions. From these estimates we can conclude that under the conditions of our experiment, butane decomposes to give methyl and ethyl radicals in the proportion 7:3.

Propane¹⁹ was also decomposed in the same apparatus (Experiment No. 112) using mercuric bromide in the liquid-air trap; a total of 0.906 g. of alkyl mercuric bromides was obtained from a preliminary sublimation at 60°. The results of a further sublimation into fractions are given in Table IV.

TABLE IV
FREE RADICALS FROM PROPANE

Fraction	Time of sublimation, hours	Temp. of sublimation, °C.	Yield	M. p., °C.
1	0.25	20	Trace	154.5
2	1	30	0.03	157
3	1	40	.03	157.5
4	1	50	.07	157
5	1	55	.18	157
6	2	55	.37	159.5
7	1	60	.04	175-177

We estimate, using the same method as described above for butane, that propane gives methyl and ethyl groups in the proportion 4:1.

Temperature Coefficient of Dissociation into Free Radicals.—An approximate estimate was obtained for acetone by using the apparatus shown in Fig. 2. A standard mirror of antimony was formed at a measured distance from the end of the furnace and the time of removal was noted with the temperature of the furnace at 746°; the experiment was then repeated with the furnace at 820°. Measurements were made with mirrors at different distances from the furnace and a series of ratios of the times of disappearance of such standard mirrors was thus obtained. The following are some of the measurements for acetone

¹⁸ Further confirmation of these views has been obtained by comparing the x-ray spectra of methyl, ethyl and propyl mercuric bromides with the spectra of our fractions. This study was made by Dr. F. R. Whaley and will be described in a separate communication.

¹⁹ We wish to thank the Carbide and Carbon Chemical Co. for supplying us with a cylinder of pure propane.

Distance from end of furnace, cm.	3.6	1.9	1.6
Time of disappearance, 746°C., sec.	235.5	186	168
Time of disappearance, 820°C., sec.	40	26.5	22
Ratio, t_{820}/t_{746}	5.9	7.0	7.6

We then deposited a series of standard mirrors perhaps 1–2 mm. beyond the edge of the furnace and kept them cool by a jet of air; we obtained the value 9.1 for the ratio, t_{820}/t_{746} . The values of the energy of activation Q for different ratios are

Q	60,000	65,000	70,000	75,000	80,000
k_{820}/k_{746}	7.43	8.79	10.41	12.3	14.52

Although our measurements are very crude, we have convinced ourselves that the ratio of the velocity constants at the two temperatures is less than 10.4 at the end of the furnace and therefore the energy of activation for the reaction producing the free radicals must be about 67,000 cal. per mole as compared with 68,500 obtained by Hinshelwood and Hutchinson for the ordinary thermal decomposition. This very close agreement is somewhat fortuitous because our measurements are probably in error to the extent of ± 5000 cal.

Experiments at Higher Pressures.—It seemed desirable to see whether we could obtain any evidence of the existence of free radicals when a hydrocarbon was heated at higher pressures (40–70 mm.) in the temperature range 550–650°; to this end we constructed the apparatus shown in Fig. 4. It consists of a quartz tube A connected with a butane reservoir through a quartz to Pyrex seal and stopcock T_1 . A mercury pressure gage P enables us to determine the pressure in A, which can be allowed to come to any desired point by regulating stopcock T_2 which is connected with the pumping system. Tube A is fitted with an inner tube D through which a stream of cooling water circulates; tube A also contains a small piece of antimony with an iron core which can be moved from point B to point C and back by means of a magnet.

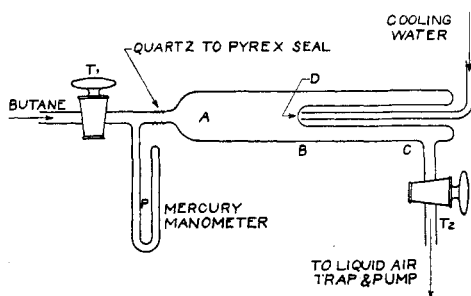


Fig. 4.—Apparatus for testing for the presence of free radicals at higher pressures.

In a preliminary experiment, stopcock T_2 was kept fully open so that there was a pressure of only 1–2 mm. of butane in tube A. The piece of antimony was drawn to point B and an antimony mirror distilled onto the inner tube at point D. The piece of antimony was then drawn down to point C and the tube A heated in the range 800–1000° with the oxyhydrogen flame; mirrors formed in this way were very readily removed.

A second experiment was then performed; after forming a mirror at D and removing the piece of antimony to C, stopcock T_2 was partly closed, so that the pressure in A rose to 70 mm. The part of the tube at B was then heated strongly by means of an ordinary Bunsen burner for several minutes. A large flame was used and the tube was heated strongly for several cm. on each side of the point B; the temperature was probably in the range 550–650°. However, we did not notice the slightest effect on the mirror. On opening stopcock T_2 and reducing the pressure to 1–2 mm., continued heating with the Bunsen flame likewise had no effect; however, on heating with the oxyhydrogen flame the mirror was rapidly removed. We then repeated this experiment but heated the tube B, which contained the butane at 70 mm., with the oxyhydrogen flame instead of the Bunsen burner. Several minutes heating had no effect whatsoever on the mirror as long as the pressure was in the neighborhood of 70 mm.; however, as soon as we opened the stopcock T_2 and reduced the pressure to 1 to 2 mm., the mirror was rapidly and completely removed. It seems therefore that free radicals must have been produced in this experiment but had all recombined before they could diffuse across the 2 or 3 mm. of gas at 70 mm. to the mirror; presumably recombination of free radicals, probably through primary collisions, occurs very rapidly at higher pressures since several experiments in the range 40–70 mm. gave identical results.

Discussion

It seems well at this point to consider the bearing of these results on the theory proposed in the first paper of this series.² In order to do this we must consider separately the several different possible reactions which may bring about the production of free radicals.

In the first place, the high temperature decomposition may consist of a homogeneous dissociation into free radicals through the rupture of a C–C bond; the radicals thus formed may be swept out of the furnace without undergoing any reaction with the surrounding molecules. On this basis, propane should yield a 1:1 mixture of methyl and ethyl groups, and butane should yield a mixture of methyl and ethyl groups in the ratio of 2:1, assuming that the propyl radicals largely decompose into ethylene and methyl groups and that the three C–C bonds are approximately equal in strength. Acetone, on this basis, might be expected to decompose into methyl groups since the acetyl group formed in the primary decomposition probably goes to pieces at once, forming CO and CH_3 . This scheme is not in very good agreement with our experiments because it calls for a ratio of methyl to ethyl of 1:1 in propane and 2:1 in butane, whereas the experimental results are 4:1 and 2.3:1, respectively. However, we must remember that the free radicals are produced by heating the hydrocarbon vapor to 800–900° and undoubtedly they must undergo many collisions with the surrounding hydrocarbon molecules before leaving the furnace; consequently we may expect a chain mechanism such as was described in the first paper of the series; the free radicals which combine with the metallic mirrors should be the same as the carriers postulated in the previous paper. According to this view ethane should not give metal alkyls because the hydrogen atom is the only carrier, propane should give only methyl groups, and butane should give methyl and ethyl groups in the ratio of 3:2, assuming no decomposition of the ethyl

groups. Our results so far are more in accord with this scheme than with that discussed in the previous paragraph.

Finally it is possible that the hydrocarbon may lose a hydrogen atom at the heated quartz surface of the furnace. This would yield the same products as the suggested chain mechanism since in this case a hydrogen atom is given up to the surface instead of to a free radical.

The experimental work that we have done so far is in very good accord with the views expressed in the first paper of this series, and we believe that further work along these lines will enable us to decide definitely as to whether free radicals play an important part in the decomposition of organic compounds in the range 550–650°.

The authors wish to thank Dr. K. F. Herzfeld and Dr. J. E. Mayer for many suggestions and help during the course of this work. We also wish to thank Mr. C. E. Schildknecht for help in preparing some of the organo-metallic compounds from free radicals.

Conclusions

1. A condensable gas such as water vapor or carbon dioxide can be substituted for the permanent gas used in the experiment of Paneth and Hofeditz for the production of free radicals from lead alkyls. A very simple apparatus can therefore be used for preparing the free radicals.

2. A great variety of organic compounds when heated in the range 800–1000° decompose into free radicals; by removing the products rapidly from the furnace, the free radicals formed can be combined with many different metals.

3. When acetone is decomposed in this way it gives only methyl groups, propane gives 80% methyl and 20% ethyl and butane gives 70% methyl and 30% ethyl.

4. The half-life of the free radicals obtained under these conditions is about $1-2 \times 10^{-3}$ sec. as compared with 6×10^{-3} sec. obtained by Paneth and his co-workers. The rate of disappearance does not follow either a first order or second order equation very well.

5. The temperature coefficient of the decomposition into free radicals has been measured for acetone and has been found to be approximately identical with the temperature coefficient of the ordinary thermal decomposition of acetone.

6. A qualitative experiment proved that free radicals in butane at 40–70 mm. pressure did not show the Paneth effect on a metallic mirror a few mm. away from the point of origin of the free radicals.

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