[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

A Study of the Reactions of Free Ethyl Radicals from the Thermal Decomposition of Tetraethyllead[1]

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It has long been assumed that the thermal decomposition of hydrocarbons of the paraffin series takes place first by the scission of a C–C bond with the formation of free alkyl radicals, followed by the reactions of these radicals with each other or with hydrocarbon molecules to produce olefin and smaller paraffin hydrocarbons.[2] Rice, Johnston and Evering have recently demonstrated the existence of free alkyl radicals obtained by decomposing paraffin hydrocarbons and acetone.[3] In view of the importance now being attributed to free radicals, a study of the reaction products of a wide variety of them reacting with each other in the absence of other substances, so far as this is possible, is desirable. For if the thermal decomposition of hydrocarbons consists of splitting into radicals which then react to form the final products, a study of the reactions of the radicals themselves should throw considerable light on the mechanism of hydrocarbon decomposition. Certain of the metal alkyls offer an interesting possibility for such a study. This is especially true of the lead alkyls since Paneth and his co-workers have demonstrated that both tetramethyl- and tetraethyllead break down when heated to produce free radicals.[4] Rice and his co-workers have shown that the free radicals obtained from the lead tetra-alkyls have identical properties with those obtained by the thermal decomposition of hydrocarbons and acetone.[3] A special advantage is obtained by using the lead alkyls to produce the free radicals because they decompose at temperatures considerably lower than those at which hydrocarbons decompose, that is, at which rupture of a C–C bond occurs. Hence by the low temperature decomposition of tetraethyllead, free ethyl radicals may be obtained and their reactions studied without the possibility of decomposition occurring within the radicals themselves.

The thermal decomposition of tetramethyllead has been studied by Simons, McNamee and Hurd, who report that two sets of reactions occur, one set taking place on the walls of the reaction vessel, the other in the homogeneous gas phase.[5] Geddes and Mack studied the thermal decomposition of tetraethylgermanium, their interest being centered upon the rate of the decomposition rather than upon the products formed.[6]

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(1) Part of the material contained in this paper was presented at the Buffalo meeting of the American Chemical Society, Sept., 1931.

(2) See (a) Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., 1929; (b) Rice, THIS JOURNAL, **53**, 1959 (1931).

(3) Rice, Johnston and Evering, *ibid.*, **54**, 3529 (1932).

(4) (a) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929); (b) Paneth and Lautsch, *Nature*, **125**, 564 (1930).

(5) Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 939 (1932).

(6) Geddes and Mack, THIS JOURNAL, **52**, 4372 (1930).

Taylor and Jones decomposed tetramethyllead, tetraethyllead and diethylmercury in the presence of ethylene. They were studying the effect of free ethyl and methyl groups upon ethylene.[7] Ipatjev, Bogdanov and Razuvaev have investigated the action of hydrogen at high pressures upon tetraphenyl-, tetramethyl- and tetraethyllead.[8]

The present work is an attempt to determine how free ethyl radicals, split off from tetraethyllead, react with each other, by a study of the reaction products. The experiments were carried out under a wide variety of conditions. Liquid tetraethyllead was decomposed at its boiling point; the flow method was used at atmospheric pressure and at low pressure; the static method was used at several temperatures and pressures and in the presence of nitrogen and of Pyrex glass packing. Each of these methods has its advantages and disadvantages. The flow method would appear to be the best for our purpose, for under these conditions the concentrations of tetraethyllead and of the hydrocarbon products are uniform throughout the experiment. These conditions give the best chance of studying the reactions of the free radicals without complicating side reactions. However, the very fact that the concentrations of starting material and of products are constant may serve to mask any effect they might have upon the reactions. The static method would probably show whether or not uniform concentration is an important factor in the results obtained by the flow method, for in the former method the conditions are constantly changing. The disadvantage of the static method is that initially the concentration of tetraethyllead is very high compared to that of the free ethyl groups, and at the end of the experiment the concentration of hydrocarbon products is very high, so that the reactions might change considerably in nature and amount during the course of the heating. The results of experiments by the static method must therefore be regarded as the composite results of a series of reactions which may change in rate more or less uniformly during the course of the experiment.

Experimental

The tetraethyllead used in these experiments was the commercial grade purified by the method recommended by Calingaert.[9] In the experiments made by the static method and in those using the flow method at low pressure, the purified material was further distilled in high vacuum at room temperature.

The method of gas analysis used was that given by Hurd and Spence.[10] It was found, in agreement with these authors, that butane was absorbed slowly in the fuming sulfuric acid pipet, along with ethylene. To allow for this, the gas was passed into this pipet several times until a constant amount was absorbed in each passage. A correction was then made to the butane and ethylene percentages. This correction was determined separately for each analysis. In the combustion analysis of the hydrocarbons

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(7) Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930).

(8) Ipatjev, Bogdanov and Razuvaev, *J. Russ. Phys.-Chem. Soc.*, **61**, 1791 (1929).

(9) Calingaert, *Chem. Rev.*, **2**, 56 (1925).

(10) Hurd and Spence, THIS JOURNAL, **51**, 3356 (1929).

of the saturated series, it was found that the average number of carbon atoms in the molecule ranged from about 2.5 to 3.5. These gases were calculated as ethane and butane, since it was certain that at the low temperatures used in the experiments the butane formed in the reaction would not decompose to form either propane or methane, neither would these gases be expected to form from the free ethyl radicals. To justify this assumption, several samples of the gaseous reaction products were fractionated by means of liquid air, and an acetone and solid carbon dioxide mixture, into three fractions which were analyzed separately. The combined results of the separate analyses were compared with the analysis of the original sample, and agreed closely in each case. No detectable amounts of methane or propane were found.

Decomposition of Liquid Tetraethyllead at its Boiling Point.—It is reported in the literature by several workers that tetraethyllead boils at about 220° with decomposition. Experiments to determine the products of this decomposition were performed. The apparatus consisted of a 50-cc. round-bottomed flask with a neck 50 cm. long to serve as a reflux column. The apparatus was filled with nitrogen, five cubic centimeters of tetraethyllead introduced, and the system pumped out and then filled with nitrogen several times in order to eliminate oxygen from the apparatus. The flask was then fitted with a delivery tube extending under water into a two-liter bottle which served to collect the gases. The flask was heated gently with a luminous Bunsen flame so that the liquid was kept just at the boiling point, with no visible refluxing. In making the first run, the heating was apparently too rapid, as a mild explosion resulted after about 500 cc. of gas had been collected. With more careful heating, two runs were made in which all of the tetraethyllead was decomposed. A deposit of finely divided lead was left in the flask. This deposit was easily removed with nitric acid; no evidence of the presence of carbon was detected. The data obtained are given in Table I. It is apparent that most of the ethyl groups have reacted to form ethane and ethylene, with only a small amount of butane. This is in marked contrast to the products formed when the decomposition takes place in the vapor phase, as the results below will show.

TABLE I

PRODUCTS OBTAINED FROM THE THERMAL DECOMPOSITION OF LIQUID TETRAETHYLLEAD

	Run 1	Run 2
Time of run, min.	32	40
Grams of $Pb(C_2H_5)_4$ used	8.25	8.25
Cc. of gas obtained	1780	1885
ANALYSIS OF GASES, %		
Ethylene	41.0	40.6
Ethane	52.7	52.5
Butane	3.6	4.9
Hydrogen	0.5	0.2
Butylenes	2.1	1.8
H/C ratio in gases	2.54	2.54

Decomposition of Tetraethyllead by the Flow Method.—The flow method was used to decompose tetraethyllead in the vapor phase, both at atmospheric pressure and at a pressure of one millimeter.

In the experiments at atmospheric pressure, the reaction tube was of heavy Pyrex glass, 20 mm. inside diameter and 40 cm. long. This tube was placed in a specially constructed tube furnace at an angle of about 20° to the horizontal. A buret was sealed by means of deKhotinsky cement to a 12-cm. length of 10-mm. tubing sealed to the upper end of the furnace in a vertical position. A trap kept in ice water was sealed onto the lower end of the reaction tube and served to collect any liquids which were carried over by the gases. The side arm of the trap was connected to a manometer and to a 12-liter bottle in which the gases were collected. This bottle had a leveling device so that the pressure inside the system could be kept constant. The temperature of the furnace was measured by a thermocouple placed alongside and in contact with the reaction tube at the center of the furnace.

Before making a run the system was pumped out with an oil pump for half an hour, after which dry nitrogen was admitted. The apparatus was again pumped out and nitrogen admitted, this procedure being carried out several times in order to remove all oxygen. The furnace was heated to the desired temperature and maintained there for half an hour before beginning the run in order to insure a steady thermal state. Lead tetraethyl was dropped slowly into the reaction tube from the buret. The buret reading, the gas volume and the temperature were recorded at five-minute intervals, thus making it possible to keep the rate of the decomposition uniform. The liquid tetraethyllead was quickly vaporized in the hot tube. It was apparent that the substance could be vaporized without decomposition if the amount present at any one time was small and the rate of vaporization rapid. Furthermore, the vapors were found to be far more stable than the substance in the liquid form. This is shown by the fact that even when the furnace temperature was 325°, an appreciable amount of the tetraethyllead vapor passed unchanged through the reaction tube and was condensed in the trap. During the experiment, the decomposition was smooth and uniform. Lead was deposited loosely on the sides of the tube, and small amounts in the form of fine dust were carried over by the gases and settled out in the trap. The results of a number of runs made by this method are given in Table II. Run number 7 was made with the reaction tube packed with small pieces of Pyrex glass so that the surface to volume ratio was increased about tenfold. There were small amounts of liquid products mixed with the undecomposed tetraethyllead found in the trap in runs three, five and one. These liquids were present in amounts too small to identify, but it was observed that a portion of them boiled from 0 to 30° and a portion from 30 to 50°. They had an odor resembling that of petroleum ether. Only traces of these liquids were formed above 375°.

TABLE II

PRODUCTS FROM THE THERMAL DECOMPOSITION OF TETRAETHYLLEAD USING THE FLOW METHOD AT ATMOSPHERIC PRESSURE

Run number	3	5	1	4	2	6	7[a]
Temperature of furnace, °C	300	325	375	425	450	475	425
Time of run, min	105	65	95	70	60	45	23
Grams of $Pb(C_2H_5)_4$ used	24.3	17.3	56.9	49.5	47.4	39.6	18.4
Cc. of gas obtained	1750	2015	9455	9500	9545	8330	3650
ANALYSIS OF GASES, %[b]							
Ethylene	12.0	11.4	24.8	29.4	31.3	31.2	32.3
Ethane	46.1	41.9	26.0	20.5	17.3	19.1	18.2
Butane	34.6	34.9	32.7	35.7	36.8	34.6	35.5
Hydrogen	5.8	8.1	11.4	11.1	12.4	12.1	12.5
Butylenes	1.6	3.7	5.1	3.2	2.2	3.0	1.5
Liquid products, cc	1–2	1–2	trace	trace	trace	trace	trace
% Decomposition, approx	34	55	76	89	93	96	89
H/C ratio in gases	2.66	2.65	2.56	2.53	2.52	2.52	2.53

[a] The tube was packed with Pyrex glass. [b] The system was full of nitrogen at the start of the run and of reaction products at the end of the run. The analyses were calculated on a nitrogen free basis to compensate for the gases remaining in the tube.

The percentage decomposition given in the table is approximate and was calculated from the amount of tetraethyllead used in the run and the carbon and hydrogen content of the gaseous products.

Examination of the data in Table II shows that the amount of butane in the gaseous products is very nearly the same at all temperatures, while the ethane and ethylene content changes very markedly. The ratio of ethane to ethylene at the low temperatures is four to one, while at higher temperatures it is about two to three. This increase in the amount of ethylene formed cannot be due to the pyrolysis of ethane or butane since they are both stable at temperatures used in the experiments.[2a] Furthermore, the ratio of ethylene to hydrogen is roughly constant at all temperatures and is 2.5 to 1 rather than 1 to 1. There is therefore a definite tendency to form ethylene rather than ethane at high temperatures, which is in agreement with the relative stabilities of the two gases. The fact that liquid products are more abundant at low than at high temperatures is also significant, for Taylor and Jones have reported that free ethyl groups cause the polymerization of ethylene.[7] These liquid products may be formed by the polymerization of ethylene, induced by the presence of the free ethyl groups. The polymerization evidently occurs more readily at low than at high temperatures. The polymerization of ethylene may account also for the small amounts of butylene found among the gaseous products.

A comparison of runs 4 and 7 shows that increasing the surface area in the reaction tube has practically no effect upon the course of the reaction.

The ratio of hydrogen to carbon atoms in the gaseous products indicates clearly that at low temperatures some of the ethyl radicals abstract hydrogen either from other radicals or from tetraethyllead molecules, consequently producing a large amount of ethane and leaving a deficiency of carbon atoms in the gaseous products. There was some carbon actually deposited in the reaction tube at low temperatures. Above 375°, the H/C ratio is very closely 5 to 2, showing that the reaction proceeds without this effect. These observations are in agreement with the results found by Simons, McNamee and Hurd for tetramethyllead.[5]

Flow Method at Low Pressure.—In order to use the flow method at low pressure it was necessary to pump the vapor of tetraethyllead through a hot tube by means of a high speed pump capable of reaching low pressures and of allowing the gas pumped off to be collected. An automatic Sprengel pump was built but proved to be too slow for the purpose. However, the Sprengel pump, operating to maintain a pressure of less than a millimeter, provided a good fore pump for a mercury vapor pump, which had the necessary speed. The mercury vapor pump operated below 100° so that no decomposition took place in the pump.

The apparatus consisted of several small bulbs sealed onto a manifold of 10-mm. tubing which was connected by means of a 2-cm. length of 1-mm. capillary tubing, which served to minimize backward diffusion of the gases, to a U-tube of 4-mm. tubing. The U-tube was 12 cm. in length and was placed inside a small electric furnace. From the U-tube a connection led to the mercury vapor pump, which in turn was directly connected to the Sprengel pump, where the gases were collected. The apparatus was built entirely of Pyrex glass, and was thoroughly flamed and pumped out to a pressure of 10^{-6} mm. before using.

A seal on the first bulb was opened, a quantity of tetraethyllead introduced, and the seal again closed. The system was then pumped out, keeping the bulb and contents at −78°. The tetraethyllead was then fractionally distilled at room temperature, using the cold bath to condense the vapor in the additional small bulbs. The middle fraction was retained, the other bulbs being sealed off. After the system had been pumped out again, it was ready for a run. The furnace was heated to 500°, the pumps started and the tetraethyllead reservoir warmed up to 30° with a water-bath. The gases were pumped off at the rate of about 5 cc. (0°, 760 mm.) per hour, and calculation showed that the time of passage through the hot tube averaged slightly less than one second. The pressure in the system was 0.5 mm. Examination of the U-tube at the end of the run showed that most of the decomposition took place in the first fourth of the tube, the walls there being covered with a smooth deposit of lead. The free ethyl groups therefore had ample time to react with each other before they left the reaction chamber, for both Paneth and Rice have determined the half-life period of the free groups to be of the order 10^{-3} seconds.[2b,4] The data for the experiments are given in Table III.

TABLE III

PRODUCTS FROM THE THERMAL DECOMPOSITION OF TETRAETHYLLEAD USING THE FLOW METHOD, PRESSURE 0.5 MM.

Run number	1	2
Time of run, hours	10	12
Furnace temperature, °C.	500	500
Cc. of gas obtained	49.8	54.4
ANALYSIS OF GASES, %		
Ethylene	33.7	32.3
Ethane	17.8	20.7
Butane	34.1	32.3
Hydrogen	14.3	14.3
Butylenes	0.2	0.5
H/C ratio in gases	2.55	2.57

It will be observed that these results are very much the same as those obtained by the flow method at atmospheric pressure when the temperature was above 450°.

Decomposition of Tetraethyllead by the Static Method.—The procedure used was similar to that used by Simons, McNamee and Hurd in decomposing tetramethyllead by the static method.[5] A series of glass bulbs having a thin capillary tube sealed to the bottom were sealed onto a manifold. Several smaller bulbs for the distillation of the sample were sealed to the same manifold, which was then connected by means of a trap to a mercury vapor pump and a McLeod gage. All stopcocks were eliminated by using mercury traps. The system was thoroughly pumped out while being heated, until the pressure remained less than 10^{-5} mm. after standing overnight. A seal was then opened, tetraethyllead introduced into one of the small bulbs and then fractionally distilled at room temperature. The purified sample was distilled into the capillaries of the larger bulbs to a predetermined level and the bulbs were sealed off and heated in a furnace. After the heating, a file mark was made on the thin capillary, which was then sealed into a larger tube, connected with the pumping system in such a way that the tip of the capillary could be broken off by means of a magnetic plunger. The seal was made with deKhotinsky cement. The system having been evacuated, the plunger was allowed to fall and break the capillary, and the gas pumped out and collected by means of an automatic Sprengel pump. The sample of gas was then transferred to the gas analysis apparatus. Experiments were made at several temperatures, and the size of the bulbs was varied from 100 cc. to 500 cc. in order to vary the pressure and still have a sample of gas large enough to analyze. The effects of increased surface in the bulb and of introducing nitrogen were studied. The bulbs were heated in the furnace for different lengths of time, in all cases enough to decompose about 90% of the tetraethyllead in the bulb. The results have been tabulated as far as possible to show the effect of varying the conditions within the bulbs. Table IV shows the effect of temperature and pressure.

The first four columns in the table show the effect of varying temperature. A series of 100-cc. bulbs was heated, each at a different temperature and each long enough

Table IV

Effects of Temperature and Pressure upon the Thermal Decomposition of Tetraethyllead—Static Method

Bulb number	A-1	A-2	A-3	A-4	B-9	C-7	A-3	A-6	A-9
Capacity (cc.)	110	110	110	103	110	108	110	340	550
Temp. of furnace, °C.	150	200	275	350	275	275	275	275	275
Time heated, hrs.	28	6	2	0.5	3	2.5	2	2	2
$Pb(C_2H_5)_4$ used, g.	0.467	0.436	0.426	0.378	0.841	0.498	0.426	0.452	0.459
Pressure of $Pb(C_2H_5)_4$ vapor at furnace temp., mm.	345	360	410	442	807	478	410	141	88
Cc. gas obtained	84.0	43.8	58.7	89.5	118	71.0	58.7	63.4	71.8

Analysis of Gases, %

Ethylene	37.8	9.2	5.9	36.2	6.9	6.8	5.9	11.2	14.2
Ethane	45.8	47.3	44.8	19.4	55.8	44.8	44.8	29.2	24.1
Butane	13.6	38.7	44.2	31.4	32.4	41.8	44.2	51.4	52.2
Hydrogen	1.8	2.7	3.6	10.4	1.7	3.5	3.6	5.9	6.7
Butylenes	1.0	2.2	1.4	2.6	3.3	3.0	1.4	2.2	2.9
H/C ratio in gases	2.54	2.64	2.65	2.50	2.73	2.63	2.65	2.55	2.56

to decompose most of the tetraethyllead. In the case of the first bulb, heated to only 150°, the amount of tetraethyllead in the bulb was so great that it could not all vaporize, since the vapor pressure of $Pb(C_2H_5)_4$ at 150° is only approximately 140 mm., and there was sufficient present in the bulb to give a pressure of 345 mm. at 150° if it were all vaporized. A comparison of the products obtained in this run with the results in Table I indicates that most of the decomposition has taken place in the liquid phase, which is to be expected. In all of the other runs the temperature was high enough to ensure that all of the tetraethyllead would vaporize before the final temperature was reached. It is

Table V

Effects of Increased Surface and of Nitrogen upon the Thermal Decomposition of Tetraethyllead—Static Method

Bulb number	C-7	C-8	C-5	C-1	C-3	C-4
Capacity of bulb, cc.	105	60	315	220	105	105
Bulb packed	No	Yes	No	Yes	No	No
Pressure of N_2, mm. at 20°	...	...	...	...	251	283
Temp. of furnace, °C.	275	275	275	275	275	275
Time of heating, hours	2.5	2.5	2.5	2.5	2.5	2.5
$Pb(C_2H_5)_4$ used, g.	0.498	0.373	0.574	0.479	0.403	0.393
Pressure of $Pb(C_2H_5)_4$ vapor at furnace temp., mm.	500	661	192	230	407	397
Cc. gas obtained	71	57	80	70	90	91

Analysis of Gases, %[a]

Ethylene	6.8	5.7	8.1	5.5	7.2	5.8
Ethane	44.8	55.1	36.7	44.4	51.9	48.8
Butane	41.8	32.3	46.8	41.7	35.2	39.3
Hydrogen	3.5	4.3	4.8	5.2	2.2	3.1
Butylenes	3.0	2.5	3.6	3.2	3.4	3.1
H/C ratio in gases	2.63	2.70	2.61	2.65	2.66	2.65

[a] The analyses of runs C-3 and C-4 have been calculated on a nitrogen free basis for comparison with the others.

interesting to note that as the temperature increases, the ethylene content of the gases decreases, and the butane content increases until 350°, at which point the ethylene becomes very abundant, the hydrogen increases and the ethane decreases markedly in amount. This will be discussed more fully in a later section. The last five columns of Table IV show the effect of pressure upon the decomposition. High tetraethyllead pressure favors the formation of ethane; as the pressure is lowered, butane becomes the most abundant product. This fact, together with the hydrogen–carbon ratios, shows that at the high pressures some of the ethyl groups form ethane at the expense of the hydrogen atoms of other ethyl groups. This was confirmed by the fact that slight amounts of carbon were formed on the walls of the bulb where the H/C ratio in the gases was high.

A series of runs was made with half the bulbs packed with small pieces of Pyrex glass, the others unpacked. Two runs were made with nitrogen at a pressure of approximately one-third of an atmosphere (at 20°) in the bulb. The results of these runs are given in Table V.

Due to the smaller volume in the packed bulbs, the pressure is slightly greater than in the corresponding unpacked bulbs, but a comparison with the results in Table IV will show that the small increase in pressure is not enough to account for the increased amount of ethane formed and the corresponding decrease in the amount of butane. It is evident that one of the reactions responsible for the ethane formation is a wall reaction. Nitrogen as an inert diluent has nearly the same effect as increased surface.

Discussion

In discussing a possible mechanism for the thermal decomposition of tetraethyllead, we shall consider that the molecule first breaks up into a lead atom and free ethyl radicals. This has been assumed by all previous workers in the field and is in complete accord with the experimental results. The discussion therefore resolves itself into an effort to determine what happens to the ethyl groups which are released.

An examination of the products formed under varying conditions indicates four reactions which are involved. We shall state these reactions and proceed to discuss them in the light of the data obtained.

Reaction (1): an ethyl radical may, when the concentration of tetraethyllead is high, extract hydrogen from the tetraethyllead molecule and form ethane. We shall indicate the reaction thus: $C_2H_5 + [H] \longrightarrow C_2H_6$. Reaction (2): two ethyl groups may combine to form butane: $2\ C_2H_5 \longrightarrow C_4H_{10}$. Reaction (3): two ethyl groups may react to form ethylene and hydrogen: $2\ C_2H_5 \longrightarrow 2C_2H_4 + H_2$. Reaction (4): two ethyl groups may react by disproportionation: $2\ C_2H_5 \longrightarrow C_2H_6 + C_2H_4$.

Reaction (1) is of primary importance at high pressures and low temperatures. The percentage of ethane was always very high under such conditions. The ethane percentage in the gaseous products was in some cases four times as great as the ethylene percentage, hence the ethane could not all have been formed by reaction (4), which would produce ethane and ethylene in equal amounts. The reaction is a wall reaction, for the results in Table V show a marked increase in the ethane percentage without a corresponding increase in ethylene when the bulbs were packed so as to increase the surface. The conditions best suited to this reaction are a high concentration of tetraethyllead molecules and a slow rate of decomposition, so that there is a greater chance for an ethyl group to collide with a tetraethyllead molecule than with another ethyl radical. These conditions occur in runs 3 and 5 made by the flow method and in most of the runs made by the static method, particularly in run B-9 where the initial pressure of tetraethyllead vapor was highest. In run A-4, Table IV, the temperature was high, hence the rate of decomposition was rapid and the concentration of ethyl groups high. Consequently the influence of reaction (1) on the products from this run was small, and the percentage of ethane is very low. In runs A-6 and A-9, the initial pressure of tetraethyllead vapor was low, which also inhibited reaction (1). That this reaction is due to the extraction of hydrogen from a tetraethyllead molecule rather than from one of the hydrocarbon products is made evident by the conditions under which the reaction occurs. Simons, McNamee and Hurd found that a similar reaction occurred with tetramethyllead.[5] They assume that this reaction takes place to a greater extent at low temperatures than at high, because the methyl radicals are released on the wall in the condensed phase when the temperature is low and hence can react easily with adjacent tetramethyllead molecules, while at high temperatures the methyl groups are released mostly in the gas phase and hence can react readily with each other, less readily with other molecules of tetramethyllead. There seems to be no evidence that most of the decomposition occurs on the walls at low temperatures and in the gas phase at higher temperatures. Geddes and Mack have found, on the contrary, that at least in the cases of tetraethyllead and tetraethylgermanium, the decomposition is 98% homogeneous in the gas phase.[6] Of course this tells us nothing about the reactions of the free groups after the decomposition. The difference in the relative importance of this reaction at different temperatures can be satisfactorily explained on the basis of the relative concentrations of the ethyl radicals and tetraethyllead molecules.

Reaction (2) is of interest because it shows definitely that two free ethyl groups can combine to form butane, probably by a wall reaction or by a three-body collision. Paneth, without making a complete analysis of the products of the decomposition, reported that a large fraction of the ethyl radicals was recovered as butane. A similar reaction has been found by Simons, McNamee and Hurd to take place with methyl radicals. The percentages of butane in the products from runs made by the flow method are fairly constant. This is not the case when the reaction is carried out in a sealed bulb, in which case the most apparent fact is that reaction (2) becomes more effective as the initial pressure of tetraethyllead is lowered, and less effective when the surface in the bulb is increased. But these are precisely the conditions which either hinder or favor reaction (1), and an inspection of the data shows that as the butane content of the gaseous products increases, the ethane content decreases, and vice versa. This explains the apparent change in the relative rate of reaction (2) with changes in temperature or pressure when the static method was used. Any factors which cause an increase in the yield by reaction (1) will cause a decrease in the products of reaction (2), due to the depletion of the ethyl radicals. When the flow method was used, the temperature was high, and the concentration of ethyl groups was also high, due to the more rapid decomposition of the tetraethyllead, and the data show very little change in the effectiveness of reaction (2) in determining the end products of the decomposition.

Reaction (3) accounts for a large fraction of the gaseous products particularly when the flow method was used. At the higher temperatures, it accounts for most of the ethylene. The ethylene content is about two and one-half times the hydrogen content—hence reaction (3) produces about 80% of the ethylene. It is probable that this reaction takes place in more than one step. Rice, in discussing the part played by free radicals in the decomposition of hydrocarbons, shows from energy calculations that it is possible for an ethyl group to lose a hydrogen atom thus: $C_2H_5 \longrightarrow C_2H_4 + H$.[11] The hydrogen atom and another ethyl radical could then combine to form a hydrogen molecule and another molecule of ethylene. Both of these reactions might occur when two ethyl groups meet in a collision on the wall.

Reaction (4) occurs to a lesser extent than the others, for most of the ethane can be accounted for by reaction (1) and most of the ethylene by reaction (3). Furthermore, there is no relation between the percentages of these gases such as would be demanded if reaction (4) were the main one. This reaction is prominent in only one case, when the temperature was 350° and the decomposition was rapid and the concentration of ethyl groups at any one instant was high (Run A-4, Table IV). It seems probable therefore that this reaction occurs in the gas phase rather than on the walls. This statement is borne out by Rice's conclusions in his paper on free radicals in thermal decomposition.[11] Rice concludes from a study of the decomposition products of hydrocarbons under various conditions, that a reaction between two ethyl groups to produce ethane and ethylene occurs in a ternary collision, and not to any great extent on the walls. The fact that this disproportionation reaction plays such a small part in the reactions of free radicals throws doubt on some of the mechanisms which have been proposed for hydrocarbon decompositions, which assume that practically all of the radicals formed by the breaking of a C–C bond react by disproportionation to produce an olefin and a paraffin hydro-

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(11) Rice, THIS JOURNAL, **53**, 1962 (1931).

carbon. The facts agree rather with Rice's assumption of a chain reaction which is terminated by a ternary collision resulting in disproportionation.

When tetraethyllead is decomposed in the liquid phase, an apparent disproportionation accounts for more than 90% of the total products; but the conditions are very different from those in the vapor phase reaction. The reactions in the liquid phase are undoubtedly more complex than the results indicate, and comparisons with the results of the vapor phase decomposition would be meaningless.

The fact that increasing the surface to volume ratio shows no effect upon the products when the flow method is used and the temperature is above 400° indicates either that the reactions are nearly all homogeneous or nearly all wall reactions. If the latter is true, increasing the surface area would have an effect only on the rate of reaction of the free radicals, not on the products formed. Paneth and Herzfeld, from a study of the kinetics of the reaction, have shown that the radicals react mainly on the walls, and that only a small fraction react in the homogeneous gas phase.[12] It is evident therefore that most of the reactions described above are wall reactions with the exception of reaction (4), which occurs mainly in the gas phase.

Summary

The products formed by the thermal decomposition of tetraethyllead have been studied under a wide variety of conditions with the purpose of securing information about the reactions of free ethyl radicals.

Evidence is presented to show that four reactions are involved. First, a reaction occurring when the concentration of ethyl groups is low and that of tetraethyllead molecules high, is the extraction of hydrogen from a tetraethyllead molecule by an ethyl radical. Second, two ethyl radicals combine in a wall reaction or a three-body collision to form butane. Third, two ethyl groups react on the walls to form a molecule of hydrogen and two of ethylene. Fourth, a reaction in which an ethyl group takes a hydrogen atom from another ethyl group, producing a molecule each of ethane and ethylene. This reaction occurs mostly in the gas phase, and occurs to a less extent than the others.

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(12) Paneth and Herzfeld, *Z. Elektrochem.*, **8**, 9 (1931).