of k_1 have been interpolated from data previously given (Ref. 1).

TABLE VII

RATE OF DEHYDRATION OF TERTIARY BUTYL ALCOHOL k_2, AT 0.2 N

Run No.	T. °C.	HNO_3 M	KNO_3 M	k_1 hrs.$^{-1}$	K_c $\times 10^{-3}$	k_2 hrs.$^{-1} \times 10^5$
2	25	0.200	...	0.286	7.42	3.85
8	25	.100	0.100	.143	7.41	1.93
10	25	.200	...	.286	7.46	3.835
13	35	.200	...	1.022	3.949	25.88

The temperature coefficient and the heat of activation are shown in Table VIII in which, for comparison, are given also similar data for the hydration reaction. The temperature coefficient of the dehydration rate has the exceedingly high value of 6.73.

TABLE VIII

TEMPERATURE COEFFICIENT AND HEAT OF ACTIVATION

	Temp. coeff., k_{35}/k_{25}	Heat of activation kg. cal./mole
Dehydration of $(CH_3)_3COH$	6.73	34.82
Hydration of $(CH_3)_2C{=}CH_2$	3.57	23.26
ΔH in aqueous solution		11.56

Summary

The equilibrium between isobutene, water and tertiary butyl alcohol has been measured in dilute aqueous solution in the presence of 0.1 and 0.2 N nitric acid, starting from the alcohol side. The equilibrium constant at an ionic strength of 0.2 N has a value of 7.48×10^3 at 25° and 3.94×10^3 at 35°.

The free energy change has been calculated and found to be:

$$C_4H_8(g) + H_2O(l) = C_4H_9OH(l)$$
$$\Delta F^\circ_{298\cdot 1} = -1330 \text{ cal}; \quad \Delta F_{308\cdot 1} = -946 \text{ cal.}$$

When ΔH is calculated by two different methods, *viz.*, from the change in ΔF with temperature and from the relation $\Delta H = \Delta F + T\Delta S$, two values are obtained, *viz.*, −12,800 cal. and −12,900 cal., respectively.

On the assumption that the reverse reaction of dehydration of tertiary butyl alcohol is first order with respect to the alcohol, the dehydration rate was calculated by combining the equilibrium constant with the known rate of hydration of isobutene. It was found that (a) the dehydration rate at an ionic strength of 0.2 N is proportional to the acid concentration, (b) the temperature coefficient of this reaction for the ten-degree interval between 25 and 35° is 6.73, an unusually high value, and (c) the heat of activation is 34.82 kg. cal. per mole.

PASADENA, CALIF. RECEIVED FEBRUARY 15, 1934

[CONTRIBUTION FROM THE GENERAL MOTORS RESEARCH LABORATORIES]

The Decomposition of Tetraethyllead in Ethylene and Hydrogen in Benzene Solution

BY PAUL L. CRAMER

A study of the thermal decomposition of tetraethyllead in various types of hydrocarbons has been made in this Laboratory during the past two years. This work was started with the idea of investigating the possible alkylation of olefins by means of free radicals and the work was later extended to include a study of the possible reactions of free radicals with paraffin and aromatic hydrocarbons. These reactions were carried out in the liquid phase at relatively low temperatures and high pressures. For this study, this method offered several advantages over vapor phase methods; namely, large amounts of reactants could be used without the danger of excessive reaction temperatures, the complete decomposition of tetraethyllead could be effected at reasonably low temperatures, and the reactions would be very much less affected by variations in temperature and pressure as well as by other factors which are known to influence vapor phase reactions.

This first paper presents the results obtained from the thermal decomposition of tetraethyllead in benzene solution and in benzene solution in the presence of varying amounts of ethylene and hydrogen. No previous work has been reported concerning the decomposition of tetraethyllead in solution in the presence of ethylene. Taylor and Jones[1] have investigated the decomposition of tetraethyllead in the presence of ethylene and hydrogen by vapor phase methods. The thermal

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[1] Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930).

decomposition of tetraethyllead under a variety of conditions has been studied by Meinert.[2] Ipatiev and co-workers[3] have decomposed tetraethyllead in benzene solution but no attempt was made to determine the reaction products. The same authors presented evidence to show that alkyl and aryl lead compounds are reduced by molecular hydrogen under similar conditions and for this reason the experiments with hydrogen presented in this paper were carried out in order to determine whether ethane might possibly be formed from this source as well as by the hydrogenation of ethylene.

The results presented in this paper, which under certain conditions closely resemble those reported for similar vapor phase reactions, are discussed from the standpoint of reactions involving free ethyl radicals.

Experimental Details

Apparatus.—A steel bomb, fitted with a stainless steel liner and having a volume of 140 cc., was used in these experiments. All connections were made by means of standard high pressure fittings. An exposed iron–constantan thermocouple in conjunction with a Leeds and Northrup potentiometer was used for direct temperature readings.

A standard Burrell gas apparatus was used for the gas analysis and a Podbielniak apparatus was employed to check the analyses of representative runs.

Materials.—Commercial tetraethyllead was purified by washing with 50% sulfuric acid, dilute sodium carbonate solution and finally water. After drying over calcium chloride, it was distilled under reduced pressure in an atmosphere of dry nitrogen.

Commercial ethylene, containing 1% of ethane, and commercial electrolytic hydrogen were used in these experiments.

Procedure.—The tetraethyllead was introduced by means of a buret into the bomb containing the desired amount of benzene. After sealing the bomb, it was cooled to 0° by placing it in a freezing mixture. The outlet to the needle valve was connected to a vacuum pump, a coil glass trap cooled to −78° being placed in the line to collect any benzene or tetraethyllead vapors. After the system had been evacuated to 2–3 mm., dry nitrogen was admitted to the bomb and the system evacuated. This process was repeated three times. No detectable amount of tetraethyllead was collected in the trap and the amount of benzene collected was negligible. After the final evacuation, the needle valve was closed, the bomb was shaken to ensure the complete solution of the tetraethyllead and allowed to come to room temperature. The bomb was introduced into the fusible alloy contained in the furnace which was maintained at 240°. The temperature of the alloy was lowered to 175° by the introduction of the bomb. The temperature of the bomb rose rapidly to that of the alloy and the current was then adjusted so that the temperature of the bomb increased at a rate of 3 to 4° per minute and was finally maintained at 260–275° for two to four hours.

The above procedure was the same for the experiments with hydrogen and ethylene except that the amounts of the gases admitted to the bomb, containing benzene and tetraethyllead, were previously determined for any desired initial pressure at a constant temperature. This was accomplished by admitting the gas from high pressure containers to the bomb, containing the desired amounts of tetraethyllead and benzene, at various gage pressures. After shaking and allowing the pressure to come to equilibrium at a constant temperature, the gas was released, collected and measured over brine as will be described for the collection of the reaction gas. By the use of a suitably graduated pressure gage, it was found that the above method was accurate to within 1%.

For the release and the collection of the gas over brine, the outlet to the needle valve was replaced by a Hoke micro valve equipped with a high pressure fitting. This was connected by means of short rubber tubing through a 25-cc. trap or condenser to the gas holder after first replacing the air in the line by carbon dioxide. After the collection of most of the gas, the bomb was heated sufficiently to distil about 10 cc. of liquid, which was collected in the trap at room temperature. After closing the valve, the liquid in the trap was heated to drive out any dissolved gas and a sufficient amount of the liquid was distilled to ensure the saturation of the gas with liquid vapors.

For the first gas analysis, the liquid vapor was removed from the gas. This was accomplished by connecting the gas holder by short connections through a small spiral condenser to a suitable gas receiver. After the line had been swept out with the gas and connected to the gas receiver, the condenser was cooled to −78°. After approximately 2 liters of the gas had been slowly collected, the small amount of condensate was heated by means of a bath in order to drive over a small amount of dissolved gas. In all of the runs the condensate was practically pure benzene as evidenced by the melting and boiling points of the liquid. Also the corrected volume of the fractionated gas closely agreed with the volume of the original gas after correcting for the vapor pressure of benzene.

For the second gas analysis, a portion of the gas from the first fractionation was collected over brine after passing slowly through an efficient coil condenser at −78°.

To determine the amount of liquid reaction products, the contents of the bomb was drained into a beaker and the lead residue and bomb was washed several times with small amounts of absolute ether. The washings were added to the original liquid and the ether solution was filtered from the suspended lead. The ether and benzene were fractionated from the oily reaction product by means of a small efficient spiral column. Tests were made for any unchanged tetraethyllead by treating the liquid, dissolved in a small amount of ether, with bromine. The lead residue was examined for carbon by dissolving the lead in nitric acid.

Results and Discussion

An outline of the experiments together with the analytical and theoretical data are given in Table I.

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(2) Meinert, THIS JOURNAL, **55**, 979 (1933).

(3) Ipatiev, Razuvaev and Bogdanov, *Ber.*, **63B**, 335 (1930).

TABLE I

DATA ON THE DECOMPOSITION OF TETRAETHYLLEAD IN BENZENE,[a] HYDROGEN AND ETHYLENE

Runs	1	2	3	4	5	6	7	8	9	10	11	12	13	14
							Outline of Experiments							
$Pb(C_2H_5)_4$, cc.	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5	9.75	2.45	0.1
H_2, cc.	...	...	...	1580	2240	2950	...	...	...	...	...	...	...	...
C_2H_4, cc.	...	...	...	...	...	...	2550	2550	6280	6280	8800	8800	8800	15300
T. and P. for main reaction:														
°C.	185–220	196–242	196–250	185–236	196–231	200–245	202–232	209–238	180–215	178–221	178–235	...	...	...
Atm.	13.6–35.4	17.0–47.6	17.0–48.6	26.5–52.8	44.9–64.0	50.4–77.5	26.5–41.5	26.2–42.8	47.6–41.2	47.3–41.5	58.2–52.7	...	...	...
Final °C.	263	261	258	270	273	273	265	270	267	270	268	270	275	275
T. and P., atm.	71.7	70.0	69.5	91.5	110	113	69.7	70.5	69.7	70.0	68.7	56.5	52.5	83.0
Time of heat, hours	2.0	4.0	4.0	2.5	3.0	2.5	2.5	3.0	3.0	3.0	3.5	3.0	3.0	4.0
							Reaction Products Found							
Gas, cc.	4000	4100	4180	5820	6360	6880	5000	5115	4920	4960	4965	3350	2030	5600
H_2SO_4 sol. olefins, cc.	16	41	46	70	26	34	65	97	98	94	95	70	69	157
C_2H_4, cc.	120	115	163	105	76	48	1205	1105	1300	1165	1328	1478	1623	5280
H_2, cc.	56	41	50	1590	2220	2760	130	107	123	100	100	37	22	nil
C_4H_{10}, cc.	114	234	314	365	388	388	360	457	526	451	448	220	nil	nil
C_2H_6, cc. (a)	3694	3669	3607	3690	3650	3650	3215	3324	2810	3087	2906	1457	220	nil
Liquid, g.	5.5	5.0	6.5	5.2	6.2	5.5	6.9	7.0	10.7	11.0	13.0	6.7	5.9	10.5
							Reaction Products Calcd.							
C_2H_6, cc.	4310	4205	4116	4115	4092	4092	3990	3916	3831	3929	3932	1983	538	22
Liquid, g.	6.2	5.8	5.6	5.3	5.8	5.6	7.9	7.6	12.4	12.3	15.5	12.1	9.8	12.0
							Differences in the Theoretical and Determined Values for Ethane and Liquid							
C_2H_6, cc.	−616	−536	−509	−425	−442	−442	−775	−592	−1021	−842	−1026	−526	−318	−22
Liquid, g.	0.7	0.8	0.9	0.1	0.4	0.1	1.0	0.6	1.7	1.3	2.5	5.4	3.9	1.5
							Amount of Polymerized Ethylene to the Theoretical Amount of Ethyl Radical							
C_2H_4/C_2H_5-							0.15	0.16	0.53	0.57	0.83	1.63	6.4	225

[a] Fifty cc. of benzene was used in all runs. (a) Runs 7–14 are corrected for 1% ethane contained in original charge of ethylene.

Due to the fast reaction rates for runs 1 to 11 inclusive, the temperatures and pressures for the main portion of the reaction can be considered as only approximate values. The rate of reaction, representative of these runs, is shown in Fig. 1.

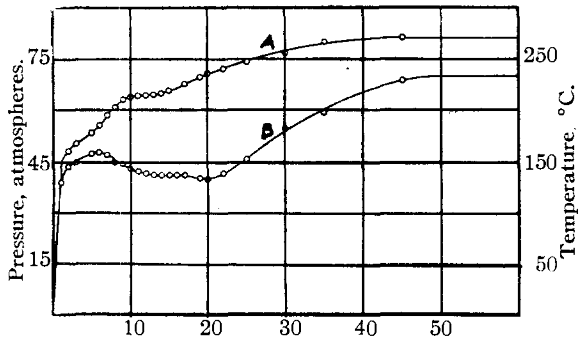

Fig. 1.—Temperature–pressure–time curves for run 10 Table I; A, temperature; B, pressure.

Due to the slow reaction rates, no initial temperatures and pressures could be observed for runs 12, 13 and 14. Approximately two hours of heating time was required to complete the reactions; however, this time was increased in nearly all of the runs to ensure the complete decomposition of the tetraethyllead.

From the analyses of the two gaseous fractions, it was definitely established that methane was not present in the reaction gas and also the analyses indicated that the paraffin fraction consisted largely of ethane together with small amounts of butane. The analytical results were confirmed by the fractionation of the reaction gas from representative runs by means of a Podbielniak apparatus.

Practically all of the benzene was accounted for in all of the runs; thus, the liquid reaction products, light colored oils, were formed from the tetraethyllead, and in the experiments with ethylene from both the tetraethyllead and ethylene. With a few exceptions, there is a close agreement between the determined and calculated values for the liquid reaction products. In calculating the weight of the gaseous reaction products, the weight of the small amount of sulfuric acid soluble olefins was calculated for butylene. There was no evidence of the formation of carbon in any of the runs.

As evidenced by the negligible amounts of lead deposited on the wall of the bomb above the liquid surface, all of the experiments were liquid phase reactions. This evidence is supported by the analytical results; namely, as evidenced by the results in runs 1 to 6 inclusive, the reactions were largely independent of wide variations in pressure as well as relatively small temperature differences, and also, in runs 7 to 13 inclusive, practically the same amounts of unreacted ethylene were obtained from widely varying amounts of tetraethyllead and ethylene. Attempts to decompose any quantity of tetraethyllead in the absence of a solvent gave very inconsistent results.

The gaseous products formed in runs 1, 2 and 3 are somewhat similar to those obtained in the decomposition of pure tetraethyllead in the condensed or liquid phase as reported by Meinert.[2] This similarity is that in both cases the products consist largely of ethane.

As evidenced by the analytical results obtained in runs 4, 5 and 6, molecular hydrogen, under the conditions used in these experiments, takes part in this type of reaction to only a small extent, if any. The reaction products are quite similar to those in runs 1, 2 and 3.

As previously shown for similar gas phase reactions,[1] ethylene is readily polymerized by the simultaneous decomposition of tetraethyllead in solution. This is very well shown in Fig. 1. For runs 7 to 11 inclusive, the amounts of ethane formed in the reactions are consistently less than for runs 1 to 6 inclusive. Experiments carried out with benzene and ethylene alone and under severer conditions of temperature and pressure, showed that the polymerization of ethylene was not the result of temperature and pressure alone. Also, by admitting a large amount of ethylene to the bomb containing freshly decomposed tetraethyllead, it was demonstrated that the above reactions were not promoted by lead under comparable conditions of temperature and pressure.

Concerning the possible mechanism of similar gas phase reactions, two types of primary reactions have been proposed for the reaction of alkyl radicals with olefin and paraffin hydrocarbons. Taylor and Jones[1] have proposed type (1) as the primary reaction of ethyl radicals with ethylene and Rice[4] has proposed type (2) as the primary reaction of free radicals with paraffin hydrocarbons. In order to account for the high percentages of ethane formed when tetraethyllead is decomposed in a static system, Meinert[2] has postulated the extraction of hydrogen from adjacent molecules by ethyl radicals. The same assumption has been made by other investigators[5] for similar reactions with tetramethyllead.

$$C_2H_5— + 2C_2H_4 \longrightarrow C_4H_9— + C_2H_4 \qquad (1)$$
$$C_2H_5— + R—H \longrightarrow R— + C_2H_6 \qquad (2)$$

If in the thermal decomposition of tetraethyllead in the presence of hydrocarbons it is assumed that ethyl radicals so formed react only with each other, then reactions (3), (4) and (5) would determine the maximum amount of ethane that could be formed from a given amount of tetraethyllead.

$$2C_2H_5— \longrightarrow 2C_2H_4 + H_2 \qquad (3)$$
$$2C_2H_5— \longrightarrow C_4H_{10} \qquad (4)$$
$$2C_2H_5— \longrightarrow C_2H_6 + C_2H_4 \qquad (5)$$

If ethyl radicals react with hydrocarbons according to types (1) and (2), it might be possible to determine which of the two reactions is the predominating reaction with certain hydrocarbons by a comparison of the determined amount of ethane with the amount of ethane as calculated from reactions (3), (4) and (5), the amount of ethyl radicals involved in reactions (3) and (4) being calculated from the amounts of hydrogen and butane found in the gaseous products.

From the results presented in this paper and also from unpublished data from this Laboratory, it appeared that the mechanism of the reactions could be best interpreted from the standpoint of the above theoretical considerations. The calculated ethane values and the differences in the determined and calculated values are given in Table I. In view of the fact that ethylene is eliminated in this type of reaction, and that benzene acted only as a solvent for the reactions, and also that the complete decomposition of tetraethyllead was effected without evidence of carbon formation, it would seem reasonable to assume that the predominating reaction of ethyl radicals was that of disproportionation and that the ethylene so formed was converted to higher hydrocarbons as induced by reaction (1). It is also reasonable to assume that the negative ethane values given in Table I represent the elimination of ethyl radicals as initiated by reaction (1). This latter assumption is supported by the fact that larger negative ethane values are obtained by the addition of ethylene to the same system. These ethane values appear more significant when compared with those obtained in the decomposition of tetraethyllead in various other hydrocarbons, in which very large negative as well as large positive ethane values were obtained, indi-

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[4] Rice, THIS JOURNAL, **53**, 1959 (1931); **55**, 3035 (1933).

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

cating in one case a high percentage of alkylation and in the other a large amount of extraction of hydrogen to form ethane, the reactions in both cases being accompanied by the conversion of very large percentages of the original hydrocarbons to both higher olefin and paraffin compounds.

In order to give some idea of the possible length of the reaction chains, the relation of the amount of polymerized ethylene to the theoretical amount of ethyl radicals is presented in Table I. This is very well shown in run 14, in which the amount of ethylene in respect to the amount of tetraethyllead was quite large. This fact as well as the apparent molecular size of the liquid reaction products supports the assumption that large radicals are formed as postulated by Taylor and Jones.[1]

In conclusion the writer wishes to thank T. A. Boyd for his interest in this work and for his aid in the preparation of the manuscript.

Summary

A study has been made of the thermal decomposition of tetraethyllead in solution in benzene and also in benzene with varying amounts of ethylene and hydrogen.

Evidence has been presented in favor of the assumption that the predominating reaction of ethyl radicals in solution is that of disproportionation and that the ethylene so formed is converted to higher hydrocarbons as induced by ethyl radicals.

Evidence has been presented to show that molecular hydrogen takes part in this type of reaction to only a small extent, if any.

Large amounts of ethylene are converted to light colored oils by the simultaneous decomposition of tetraethyllead. Evidence has been presented in support of the assumptions, made by previous investigators, that these reactions are induced by ethyl radicals.

DETROIT, MICHIGAN RECEIVED FEBRUARY 15, 1934

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Occurrence of Citral in Florida Valencia Orange Oil[1]

BY E. K. NELSON AND H. H. MOTTERN

Florida Valencia orange oil was prepared in the United States Citrus Products Laboratory at Winter Haven, Florida, by pressing the peel in a Pipkin oil machine and centrifuging the expressed liquid. The amount of oil available (2710 g.) was insufficient for a complete examination because, after removal of the limonene by direct distillation at 10 mm., and distillation of the residue with steam, but 92 g. of terpene-less oil was obtained.

This oil was examined for aldehydes, particular attention being paid to the possible presence of citral. For the separation of aldehydes, the method of Tiemann[2] was used because by the ordinary method of shaking with a solution of sodium bisulfite the citral may go into solution as the stable dihydrodisulfonic acid derivative, from which it cannot be recovered.

The oil was shaken for six hours with a solution of 26 g. of sodium sulfite and 30 g. of sodium bicarbonate in 350 cc. of water. After standing overnight in the refrigerator, the crystalline bisulfite compound was separated by filtration.

A solution of 15 g. of sodium hydroxide was added to the filtrate, and the separated oil, which had a pronounced odor of citral, was extracted with ether. Careful evaporation of the ether gave 3.8 g. of aldehyde which had gone into solution as the labile dihydrodisulfonic acid derivative.

The semicarbazone was prepared and extracted with ether to remove β-citral semicarbazone. Recrystallized several times it melted at 160–162°, and optical crystallographic comparison[3] with α-citral semicarbazone showed its identity with that substance. The α-cítryl β-naphthocinchoninic acid was also prepared. It melted at 206°, and a mixture with the same derivative prepared from pure citral gave no depression in melting point.

From the crystalline bisulfite compound, 6.1 g. of aldehyde was recovered.

The main fraction of this boiled at 90–92° at 10 mm., melted at 17–18°, and gave an oxime melting at 65–67°. It is therefore decyl aldehyde.

Decyl aldehyde has been found in orange oil

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[1] Food Research Division Contribution No. 212.

[2] Tiemann, *Ber.*, **31**, 3318–3320 (1898).

[3] Optical crystallographic examination was made by G. L. Keenan, Food and Drug Administration.