[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

The Decomposition of Alkyllead Compounds*

BY GEORGE CALINGAERT, HYMIN SHAPIRO, F. J. DYKSTRA AND LEWIS HESS

The literature contains comparatively few data on alkyllead halides, carbonates and hydroxides, beyond their preparation, analysis, approximate melting or decomposition points, and approximate solubilities in a number of common solvents. It is known[1,2,3] that most of the compounds are unstable to light and heat, inorganic lead salt being produced under the latter condition, together with lead-free organic decomposition products. In 1925, Calingaert[1] suggested that triethyllead halides, on heating, disproportionate to tetraethyllead and diethyllead dihalide, since the yield of tetraethyllead was quantitative for this type of reaction. In 1938, Evans[4] described briefly the thermal decomposition of dibutyllead dichloride, showing that butyl chloride, tributyllead chloride and lead chloride are produced. Gilman and Apperson[5] indicated that the decomposition of diethyllead dichloride in petroleum ether probably follows a similar course. They also studied the related reaction of tetraethyllead with aluminum chloride, and stated that under the prevailing conditions, the diethyllead dichloride initially formed probably decomposed in accordance with the equations

$$2Et_2PbCl_2 \longrightarrow Et_3PbCl + PbCl_2 + EtCl,$$

and

$$Et_2PbCl_2 \longrightarrow PbCl_2 + C_4H_{10}$$

with the former reaction predominating. Still earlier, Austin[6] claimed to have established the reversibility of the disproportionation of triphenyllead chloride and triethyllead chloride in boiling organic solvents.

In order to elucidate the mechanism of the decomposition of the alkyllead compounds, triethyllead and diethyllead chlorides, bromides, hydroxides and carbonates have been prepared, their solubilities measured in several solvents, and observations made on their stabilities on steam distillation. The triethyllead bromide was also observed under conditions of spontaneous decomposition at room temperature. In each instance an effort was made to collect quantitatively the products of decomposition and identify them.

Results

The results of the present work showed that the alkyllead compounds vary considerably in stability and also in their mode of decomposition. Although the salts readily undergo the redistribution reaction,[7] this transfer-type reaction has no effect on the composition unless more than one kind of alkyl group is present. In general, when trialkyllead halides decompose during steam distillation, they disproportionate in accordance with the equation

$$2R_3PbX = R_2PbX_2 + R_4Pb \qquad (1)$$

In the case of the dialkyllead salts, a similar disproportionation is believed to take place in accordance with the equation

$$2R_2PbX_2 = (RPbX_3) + R_3PbX \qquad (2)$$

in addition, these salts undergo direct decomposition as follows

$$R_2PbX_2 = PbX_2 + R{-}R \qquad (3)$$

In the experimental work, no $RPbX_3$ compounds were isolated. These are certainly very unstable; only the iodides have been reported and, at best, they were imperfectly characterized.[8,9] However, the decomposition products actually isolated, PbX_2 and RX, are the compounds to be expected from the breakdown of $RPbX_3$ intermediates.

As may be seen from the general decomposition equations given, the end products of the decomposition of R_3PbX and R_2PbX_2 salts are the same, owing to the partial interconversion of the dialkyl and trialkyl salts, but the proportions of the end products would be expected to vary with the relative stabilities of the two types of compounds; thus the net result for the decomposition of trialkyllead halides is given by the equations

$$3R_3PbX = 2R_4Pb + PbX_2 + RX \qquad (4)$$

and

$$2R_3PbX = R_4Pb + PbX_2 + R{-}R \qquad (5)$$

The extent of the direct decomposition of the dialkyllead salts to inorganic lead halides and hydrocarbons also varies from one alkyl compound to another.

When the dihalides are steam distilled, they decompose with extreme rapidity, the bromide in a few seconds and the chloride in two minutes. The subsequent decomposition of the triethyllead halide is rather slow even at 100°; that of the chloride is about 74% complete in 7.6 hours, while that of the bromide is 72% complete in 2.7 hours. The

---

* Presented at the American Chemical Society Meeting, Chicago, Ill., April, 1948.

[1] Calingaert, *Chem. Revs.*, **2**, 43 (1925).

[2] Grüttner and Krause, *Ber.*, **49**, 1415 (1936).

[3] Krause and von Grosse, "Die Chemie der metallorganischen Verbindungen," Borntraeger, Berlin, 1937, pp. 396 ff.

[4] Evans, *J. Chem. Soc.*, 1466 (1938).

[5] Gilman and Apperson, *J. Org. Chem.*, **4**, 162–168 (1939).

[6] Austin, THIS JOURNAL, **54**, 3287 (1932).

[7] (a) Calingaert, Beatty and Hess, *ibid.*, **61**, 3300 (1939); (b) Calingaert, Soroos and Shapiro, *ibid.*, **62**, 1104 (1940); (c) Calingaert, Dykstra and Shapiro, *ibid.*, **67**, 190 (1945).

[8] Lesbre, *Compt. rend.*, **200**, 559 (1935); **204**, 1822 (1937).

[9] Mr. J. V. Capinjola of this Laboratory recently attempted, without success, to repeat Lesbre's work. This instability contrasts sharply with the relatively high stability of the corresponding $RSnX_3$ types.[10]

[10] (a) Pope and Peachey, *Chem. News*, **87**, 254 (1903); (b) Pfeiffer and Lehnhardt, *Ber.*, **36**, 3028 (1903); (c) Pfeiffer and Halperin, *Z. anorg. Chem.*, **87**, 348 (1914).

TABLE I

SOLUBILITIES OF LEAD COMPOUNDS AT ROOM TEMPERATURE (G. PER 100 ML. SOLVENT)

	Et_2PbBr_2	Et_3PbBr	Et_2PbCl_2	Et_3PbCl	Et_2PbCO_3	$(Et_3Pb)_2CO_3$	$Et_2Pb(OH)_2$	Et_3PbOH	$PbBr_2$	$PbCl_2$	$PbCO_3$	PbO
Acetone	>5	>5	2.22	>5	0.0016	0.072	...	4.21	0.0010	0.0003	0.0001	0.0000
Ammonium hydroxide (Sp. gr. 0.90)	>5	3.5	>5	>5	224	3.43	...	....	.0076	.0044	....	.0047
Benzene	0.008	70	0.004	80	0.0009	0.0016	...	0.795	.0000	.0000	.0000	.0001
Carbon tetrachloride	.002	>5	.004	>5	.0006	.0017	...	....	.0000	.0000	.0000	.0000
Ether	.009	>5	.003	0.596	.0010	.0023	...	.182	.0000	.0000	.0001	.0000
Mixed hexanes	.000	0.9	.002	.089	.0031	.0018	Insol.	.062	.000	.0000	.0001	.0002
Ethyl acetate	.606[a]	...	...	...	....	....	...	....	<.0004[a]	....	....	....
Water	1.5	1.3	5	2	.0209	.833	>3.4	19.83	.8441	.99	.0001	.002
95% alcohol	1.0	5	2.1	5	.0013	1.75	...	....	.0053	.0015	.0001	.0001

[a] Determined at 0°.

relative extent of the competing reactions in the over-all decomposition of the triethyl- and diethyllead salts is shown

	Cl. %	Br. %
$3Et_3PbX = 2Et_4Pb + PbX_2 + EtX$	66	79
$2Et_3PbX = Et_4Pb + PbX_2 + C_4H_{10}$	34	21
$2Et_2PbX_2 = Et_3PbX + PbX_2 + EtX$	67	63
$Et_2PbX_2 = PbX_2 + C_4H_{10}$	33	37

In contrast to its behavior on steam distillation, diethyllead dibromide decomposes slowly in nitrogen at room temperature, no gas being evolved. Decomposition is virtually complete in fifty hours.

Austin[6] found that triethyllead chloride yielded 64% of tetraethyllead and of lead chloride (from the decomposition of diethyllead dichloride, the disproportionation product) in boiling toluene, while the reaction of tetraethyllead with diethyllead dichloride in boiling benzene gave a 39% yield of triethyllead chloride.

Our failure to find any evidence of reversibility in the steam decomposition runs is no cause for surprise, in view of the difference between Austin's conditions and our own. Presumably, the reaction mechanisms were different in the two cases.

Triethyl- and diethyllead hydroxides differ markedly in the mechanism of their decomposition by steam. The primary reaction of the triethyllead hydroxide is one of disproportionation, resembling the disproportionation of the triethyllead halides. The diethyllead dihydroxide, on the other hand, decomposes directly into lead hydroxide and hydrocarbons. The secondary reaction of the triethyllead hydroxide decomposition is, presumably, identical with that of the diethyllead dihydroxide. The rates of steam decomposition of the hydroxides also differ widely. Triethyllead hydroxide decomposes to the extent of 82% in seven hours, or about as fast as triethylead chloride. Only 10% of the diethyllead dihydroxide decomposes in a period of six hours, a very slow rate compared with the diethyllead dihalides.

The steam decomposition of the carbonates is a combination of disproportionation and hydrolysis. The primary reaction is disproportionation in the case of triethyllead carbonate and hydrolysis in the case of diethyllead carbonate. The decomposition of the triethyl salt is substantially complete in six hours while that of the diethyl salt is less than 15% complete in the same time.

Calculations

The over-all decomposition of the mono-halide salts proceeds as previously indicated in equations (4) and (5).

(a) $3Et_3PbX = 2Et_4Pb + PbX_2 + EtX$

(b) $2Et_3PbX = Et_4Pb + PbX_2 + C_4H_{10}$

If 3a and 2b represent the moles of Et_3PbX decomposed according to the two competing mechanisms, then the following relationships may be used to calculate, by the method of least squares, the per cent. of decomposition by each reaction.

$$Et_3PbX = 3a + 2b$$
$$Et_4Pb = 2a + b$$
$$PbX_2 = a + b$$
$$EtX = a$$
$$C_4H_{10} = b$$

In the same manner, the following over-all reactions and relationships hold for the dihalide salts.

(c) $2Et_2PbX_2 = Et_3PbX + PbX_2 + EtX$

(d) $Et_2PbX_2 = PbX_2 + C_4H_{10}$

(e) $3Et_2PbX_2 = 2PbX_2 + Et_4Pb + 2EtX$

$$Et_2PbX_2 = 2c + d + 3e$$
$$PbX_2 = c + d + 2e$$
$$Et_3PbX = c$$
$$Et_4Pb = e$$
$$EtX = c + 2e$$
$$C_4H_{10} = d$$

It will be observed from Table II that the material balances are in no case perfect, and show in some cases losses of a magnitude which reflects the experimental difficulties involved. These losses were partially compensated in the least squares calculations by attributing the deviations arbitrarily to those measurements which appeared, on the basis of laboratory experience, to involve the greatest probable experimental error.

Experimental

Solubilities.—The decomposition of the lead compounds was followed by making use of differences in the physical and chemical properties of the reactants and products. After they were prepared and purified, the compounds were either used immediately or stored in a Dry Ice-box until just before use. Replicate runs were made on all compounds.

TABLE II

SUMMARY OF EXPERIMENTAL RESULTS

Products (all quantities in millimoles)

Reactants	Et_4Pb	Et_3-$PbCl$	Et_3-$PbBr$	Et_3-$PbOH$	Et_2-$PbBr_2$	Et_2-$Pb(OH)_2$	Et_2-$PbCO_3$	C_4H_{10}	EtCl	EtBr	$PbCl_2$	$PbBr_2$
Et_3PbCl[a] 32.5	15.1	8.6						2.4	4.3		9.4	
Et_3PbBr[b] 40.0	17.1		11.2					2.8		5.8		10.6
Et_2PbCl_2[c] 28.1		9.4						1.4	8.5		18.4	
Et_2PbBr_2[d] 51.1	9.5		1.6							21.1		39.9
Et_2PbBr_2[e] (room temp.) 122.8	1.0		42.4		1.7					45.9		77.5
Et_3PbOH[f] 40.8	15.8			7.4		14.4		0.3				
$Et_2Pb(OH)_2$[g] 32.9						29.6		3.6				
$(Et_3Pb)_2CO_3$[h] 1.58	13.5			2.7		3.9	10.7	0.9				
Et_2PbCO_3[i] 25.8	(0.1)			0.5		4.6	19.8	0.5				

The solubility data employed in following the decomposition reactions are given in Table I. These solubility figures were also used to advantage in purifying the salts to be decomposed, and they have been found useful in separating compounds of these types. For the organic compounds, the data were determined by adding a weighed sample of the purified compound (usually about 20 mg.) to 5 ml. of solvent. If all the salt dissolved, the solution was cooled to the saturation point, and the procedure was repeated with larger quantities of solute until saturation was reached at room temperature. If only part of the sample dissolved, the solution was shaken for thirty minutes and filtered, and the lead was determined by the dithizone method[11] after decomposition with nitric acid. For the inorganic compounds, one gram of the purified solid was shaken with 300 ml. of solvent. After filtration, the solution was evaporated *in vacuo* and the residue was taken up with nitric acid. If the amount of lead was small, it was determined by the dithizone method; otherwise, the ammonium molybdate method was used.

Materials.—The ethyllead compounds were prepared by methods previously described[1,3,7c] and purified by recrystallization from appropriate solvents.

Steam Distillation Procedure.—As an example of the experimental procedure, the steam distillation of triethyllead bromide will be described in some detail.

The apparatus consists of a 500-ml. three-neck decomposition flask fitted at one side neck with a calibrated trap for the collection of tetraethyllead and a reflux condenser connected through a Dry Ice-trap to a gas buret. The other side neck is fitted with a nitrogen inlet. The entire apparatus is operated inside a black paper hood to exclude direct daylight.

After the apparatus was flushed with nitrogen, 300 ml. of freshly boiled distilled water was heated to boiling in the flask. When the system reached equilibrium a sample of triethyllead bromide, freshly recrystallized from hexane, was weighed into a filter thimble or weighing bottle and dropped into the flask through the middle neck. Decomposition began immediately with the distillation of droplets of tetraethyllead and the evolution of gas at roughly equivalent rates. The condenser water was maintained at 45° in order to permit the passage of ethyl bromide. The reaction was stopped after 2.2 hours (72.0% complete).

The distillate of tetraethyllead analyzed 63.48% lead and had a density of 1.645 at 23.5° as compared with 64.06% and 1.647 for pure tetraethyllead. The ethyl bromide content was calculated by difference from the lead analysis and total weight.

The material in the Dry Ice-trap was fairly pure ethyl bromide, as indicated by the measured values of the density and refractive index: $d^{23.5}_4$ 1.445 (*cf.* 1.450) and $n^{20}D$ 1.4233 (*cf.* 1.4239). The density was measured by comparing the weights of approximately equal volumes of mercury and the unknown liquid in a capillary tube of about 0.4 mm. diameter. For the volatile liquid, the tube was sealed at the ends. This method was accurate to 0.002 unit on a sample of 0.02 ml. of pure ethyl bromide.

The residue in the decomposition flask consisted of aqueous solution and a solid residue. The aqueous solution was analyzed after combination with a water wash, and the solid residue was extracted with ether. The small quantity of residue which still remained was dissolved in nitric acid for lead analysis.

The hydrocarbon portion of the gas, which was diluted with nitrogen, was found on analysis to have a H/C ratio of 2.38. The analysis, together with the molecular weight (computed from the weight of the gas in a 100 ml. pipet) indicated that the hydrocarbon gas was a mixture of large amounts of methane and ethylene and smaller amounts of ethane and acetylene. The errors in these determinations were high because the gas consisted principally of nitrogen. In view of the nearness of the H/C ratio to the theoretical value of 2.5 for butane, this value was assumed for the purpose of calculating ethyl balances in all the runs.

The results are presented in Table II.

Of the other ethyllead compounds investigated, the chlorides and the carbonates were decomposed in exactly the same manner as the triethyllead bromide. In the cases of the remaining compounds, the mixtures were heated

---

[11] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York, N. Y., 1944, pp. 282–292.

TABLE II (*Continued*)

$Pb(OH)_2$	$PbCO_3$	CO_2	Reactions	%	% dec.
			$3\ Et_3PbCl = 2\ Et_4Pb + PbCl_2 + EtCl$	65.6	73.5
			$2\ Et_3PbCl = Et_4Pb + PbCl_2 + 2\ Et$	34.4	(7.6 hr.)
			$3\ Et_3PbBr = 2\ Et_4Pb + PbBr_2 + EtBr$	79.2	72.0
			$2\ Et_3PbBr = Et_4Pb + PbBr_2 + 2\ Et$	20.8	(2.2 hr.)
			$2\ Et_2PbCl_2 = Et_3PbCl + PbCl_2 + EtCl$	67.0	100.0
			$Et_2PbCl_2 = PbCl_2 + 2\ Et$	33.0	(0.4 hr.)
			$Et_2PbBr_2 = PbBr_2 + 2\ Et$	36.9	100.0
			$2\ Et_2PbBr_2 = Et_3PbBr + PbBr_2 + EtBr$	6.1	(7.6 hr.)
			$3\ Et_2PbBr_2 = 2\ PbBr_2 + Et_4Pb + 2\ EtBr$	57.0	
			$Et_2PbBr_2 = PbBr_2 + 2\ Et$	27.0	98.6
			$2\ Et_2PbBr_2 = Et_3PbBr + PbBr_2 + EtBr$	70.0	(100 hr.)
			$3\ Et_2PbBr_2 = 2\ PbBr_2 + Et_4Pb + 2\ EtBr$	3.0	
1.9			$2\ Et_3PbOH = Et_4Pb + Pb(OH)_2 + 2\ Et$	12.6	81.9
			$2\ Et_3PbOH = Et_2Pb(OH)_2 + Et_4Pb$	87.4	(5.0 hr.)
2.8			$Et_2Pb(OH)_2 = Pb(OH)_2 + 2\ Et$	100.0	10.0
					(7.0 hr.)
	0.5	6.1	$(Et_3Pb)_2CO_3 = Et_4Pb + Et_2PbCO_3$	69.3	100.0
			$(Et_3Pb)_2CO_3 + H_2O = Et_3PbOH + CO_2$	9.0	(6.8 hr.)
			$(Et_3Pb)_2CO_3 + H_2O = Et_4Pb + Et_2Pb(OH)_2 + CO_2$	21.7	
	0.4	5.0	$Et_2PbCO_3 + H_2O = Et_2Pb(OH)_2 + CO_2$	77.1	23.2
			$2\ Et_2PbCO_3 + H_2O = Et_3PbOH + PbCO_3 + CO_2 + EtOH$	22.9	(13 hr.)

[a] Et_3PbCl recrystallized from benzene. [b] Et_3PbBr recrystallized from hexane. [c] Et_2PbCl_2 recrystallized from acetone at low temperature. Decomposition complete in two minutes after a thirty-second induction period; run stopped after twenty-six minutes. In another experiment the reaction mixture was heated three hours to demonstrate the decomposition of the Et_3PbCl formed as a product of the initial disproportionation of the Et_2PbCl_2. [d] Et_2PbBr_2 recrystallized from acetone. Heated to b. p. over period of three hours because evolution of gas was too rapid for control under the usual conditions. [e] Decomposition practically complete in fifty hours. [f] Aqueous solution heated to boiling over a period of 1 hr. After reaction, solution contained no alcohol by iodoform or chromate test. [g] Aqueous solution heated to boiling two hours. [h] Apparatus modified by substitution of liquid air-trap for Dry Ice-trap and by insertion of a Drierite tube and two Ascarite tubes between the reflux condenser and the trap. $(Et_3Pb)_2CO_3$ prepared by carbonation of hydroxide and freed of bicarbonate by vacuum desiccation. [i] Et_2PbCO_3 prepared by carbonation of dihydroxide, extracted with ether, and dried *in vacuo*.

from room temperature to the boiling point over periods of several hours. The results of these experiments will also be found in Table II.

Decomposition of Diethyllead Dibromide in Nitrogen at Room Temperature.—The apparatus used for this reaction is shown in Fig. 1. It was designed to permit the decomposition to proceed in a closed system containing dry nitrogen. It consisted of a Töpler pump, a one-liter graduated cylinder containing the sample of the salt suspended on a calibrated Jolly balance, a condensing trap cooled in a Dry Ice-bath, and a mercury bubble-flow indicator. A side tube was connected to a gas reservoir for collecting and measuring products volatile at −70°.

The pump consisted of a mercury piston and two valves formed by steel balls resting on ground glass seats. The graduated cylinder was painted black; whenever an observation was to be made on the Jolly balance, a small window was washed clear with paint remover. The balance consisted of a helical spring wound from 0.078-cm. steel music wire. The sample was contained in a filter paper cup suspended from the spring, the position of which was read by means of a cathetometer. There was practically no hysteresis in the spring, and permanent set during the run was negligible.

With the sample in place, the system was flushed with nitrogen previously dried by passage through Dehydrite, and closed. Cathetometer readings were taken over a period of one hundred hours. Decomposition was practically complete in fifty hours. No gas was evolved. The data are presented in Table II.

At the end of the run a sample was removed for analysis and the remainder was extracted with 660 ml. of benzene, an adequate amount to extract all triethyllead bromide. The amount of diethyllead dibromide extracted was negligible in view of the low solubility of this compound in benzene. A portion of the benzene solution was evaporated to dryness at 0° *in vacuo* and the residue was weighed. Part of the resulting residue was recrystallized and identified as triethyllead bromide from its melting point. An aliquot of the solution was analyzed for lead as a check on this conclusion.

The condensate in the cold trap consisted of ethyl bromide and a mixture of hydrocarbons ranging in boiling point up to about 150°.

Discussion

In the light of the new information presented, the reactions of the alkyllead compounds become more comprehensible. It is important to note that the triethyllead halides decompose less rapidly than the corresponding dihalides (both at room temperature and when steam distilled), whereas for the hydroxides and carbonates, the reverse is true.

The relatively low stabilities of even the most stable alkyllead compounds investigated explain some of the anomalies in the literature of these

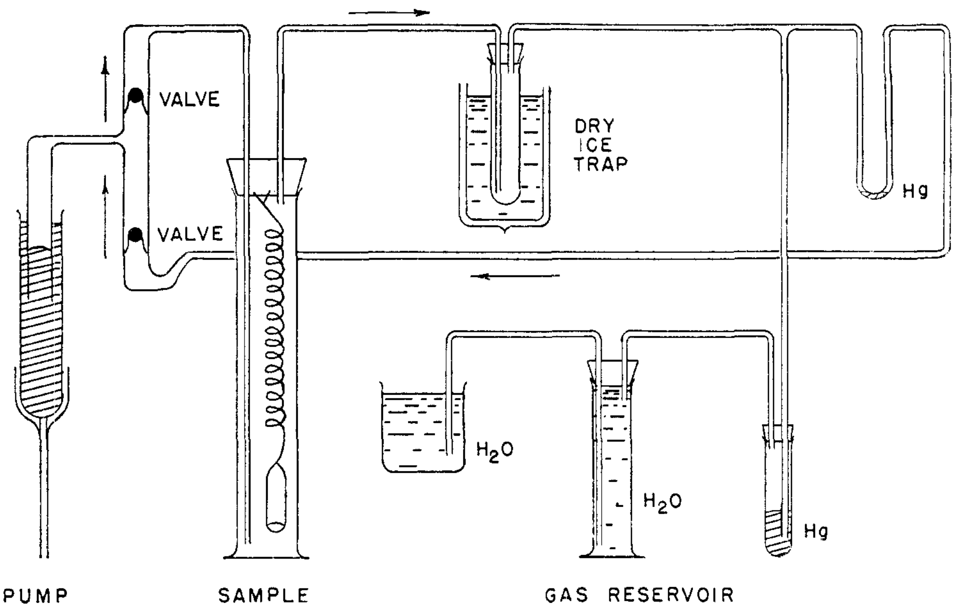

Fig. 1.—Apparatus for room temperature decomposition of diethyllead dibromide.

compounds. For example, in his exhaustive work on the preparation of R_4Pb compounds containing more than one type of alkyl group, Erich Krause[3] reported that R_3PbBr compounds in which more than one kind of alkyl group is present could be used in the further synthesis of pure compounds only when freshly prepared. This observation, which has been confirmed in this Laboratory, is explained by the present results, since the R_3PbBr compounds are sufficiently unstable to be converted reversibly into R_2PbBr_2 compounds, with, in each instance, a possibility of change in the kind of alkyl group attached to the lead atom.

From the present data on ethyllead compounds, we cannot, with certainty, lay down the general rule that all alkyllead chlorides, bromides, hydroxides and carbonates behave in accordance with the equations given in this paper. However, the observations of Krause,[3] Evans,[4] Gilman[5] and Austin,[6] referred to above, provide additional evidence that the disproportionation mechanism is valid for all alkyllead chlorides and bromides; the mechanisms presented for ethyllead hydroxides and carbonates are less certainly amenable to logical extension throughout the alkyl series.

Acknowledgment.—The authors are indebted to Dr. O. Edward Kurt and Mr. Charles M. Gambrill for helpful advice and for assistance in the solubility measurements.

Summary

The mechanisms of the decomposition of the ethyllead chlorides, bromides, carbonates and hydroxides on steam distillation were investigated. Triethyllead bromide was also studied under conditions of spontaneous decomposition at room temperature. Both disproportionation and direct decomposition to lead halides and hydrocarbons were observed.

The triethyllead halides decompose less rapidly under conditions of steam distillation than the corresponding dihalides, the chlorides being relatively more stable than the bromides, while the triethyllead hydroxide and carbonate decompose more rapidly than the corresponding diethyllead compounds.

DETROIT, MICHIGAN RECEIVED APRIL 27, 1948