Cover Essay

The Rise and Fall of Tetraethyllead. 1. Discovery and Slow Development in European Universities, 1853−1920

When tetraethyllead was first prepared as a pure compound in 1859, it was merely one of many new main-group organometallic compounds prepared during the rush to develop this new area during the 15 years following Edward Frankland's preparation of the methyl- and ethylzinc compounds in 1849.[1] At that time there was no hint that it would become very important commercially, with an annual production of over one-half billion pounds to meet the demands of the automobile age. The story of the rise and fall of tetraethyllead is an interesting one, and despite the fact that it is now in the "chemical doghouse" (along with some other well-known compounds and materials), it deserves the cover of our journal as we tell its story.

It was Carl Jacob Löwig (1803−1890, Figure 1) who reported the preparation of the first alkyllead compounds in 1853.[2] Löwig is less well-known than the great chemists of the time, such as Berzelius, Bunsen, Wöhler, Liebig, Frankland, Cahours, and Friedel, but during his long career he made some important contributions. He is perhaps best known for coming in close second in two major discoveries: that of elemental bromine and that of the first main-group organometallic compound.[3] Before he went to Heidelberg to study chemistry in the laboratory of Leopold Gmelin in 1825, Löwig, working at home, obtained a red liquid by passing chlorine into the concentrate of the water from a salt spring near his home town of Kreuznach in Germany followed by ether extraction and evaporation of the ether extracts. This red liquid, which he brought along to Heidelberg, interested Gmelin greatly and he asked Löwig to study it in detail. While Löwig was doing so, Antoine-Jerome Balard's account of his preparation of bromine from a concentrate of seawater and its identification as a new element appeared in the *Annales de chimie et de physique* in 1826. Undeterred, Löwig, the "scooped" codiscoverer, continued his investigations of bromine and its compounds, discovering bromine hydrate, bromal hydrate, and bromoform, and writing a monograph, *Bromine and Its Chemical Relations*, in 1829. In 1833 he became professor of chemistry at the newly founded University of Zürich, where he began his research on organometallic compounds. During his 20 years in Zürich, Löwig also was very active in the analysis of Swiss mineral waters and wrote the monumental *Chemie der organischen Verbindungen*. In 1853, he was appointed as Robert Bunsen's successor to the chair of chemistry at the University of Breslau in Silesia (now in Poland). In Breslau he continued his work on organometallic compounds[1] and was active in starting the Silesian chemical industry. He was still lecturing at the University in his mid-80s.

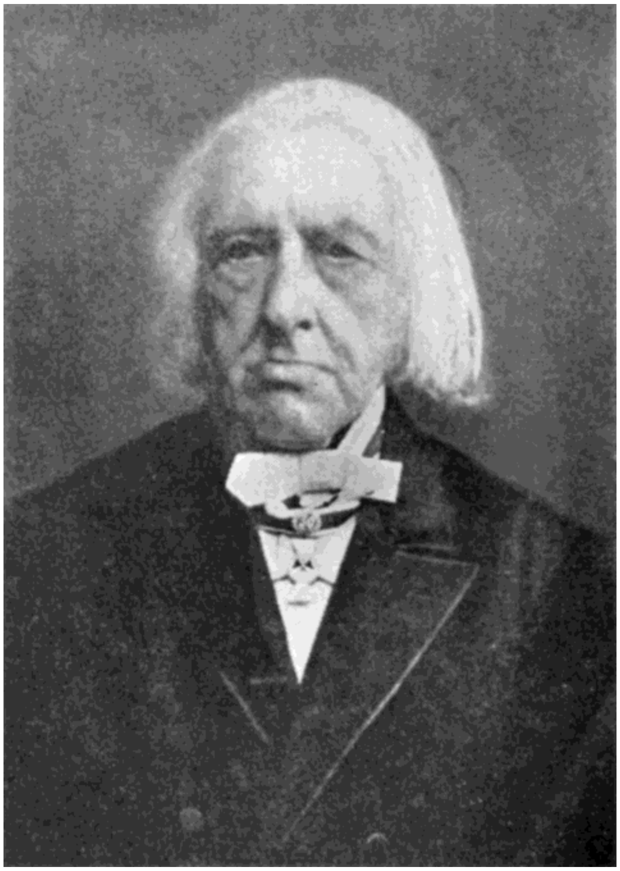

Figure 1. Carl Jakob Löwig. Reproduced courtesy of the Library and Information Centre, Royal Society of Chemistry.

In his preparation of the first ethyllead compounds,[2] Löwig used the same general procedure he had used earlier (and described in detail) for the preparation of ethyltin compounds.[4] Ethyl iodide was added to a 6:1 by weight Pb/Na alloy. After the initially vigorous reaction was over, the reaction mixture was extracted with diethyl ether with exclusion of air. Removal of ether left what Löwig described as an inseparable mixture of "radicals". (In the early days of organometallic chemistry, metal alkyls, in the light of the then prevailing "radical theory" championed by Berzelius and Bunsen, were considered to be "radicals", what we call "groups" today.[1]) This product was a colorless, mobile

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[1] For an account of these early days of organometallic chemistry see: Seyferth, D. *Organometallics* **2001**, *20*, 2940−2955.

[2] Löwig, C. *J. Prakt. Chem.* **1853**, *60*, 304; *Ann.* **1853**, *88*, 318.

[3] See ref 1 for an account of the priority dispute between Löwig and Edward Frankland (which Frankland won) for the discovery of the first organometallic compound.

[4] Löwig, C. *Ann.* **1852**, *84*, 308.

10.1021/om030245v CCC: $27.50

liquid that was insoluble in water and soluble in ether and ethyl acetate. It had no strong odor, did not fume in air, but burned when ignited in air, giving off dense fumes of lead oxide. Explosive reactions occurred on addition of iodine and especially of bromine. Löwig wrote the formula $Pb_2(C_4H_5)_3$ (or Pb_2Ae_3) for what he believed to be the main component of his product mixture (the atomic weight of C was believed to be 6—not 12—in1853) and called it *Methplumbäthyl*. In this nomenclature (which did not gain acceptance) he regarded his metal-containing "radicals" as derived from a hydrocarbon "radical", substituting the carbon content by an equivalent amount of the metal and the hydrogen content by an equivalent amount of the organic group, ethyl in this case. In 1853 "methyl" was C_2H_3, thus "$Pb_2(C_4H_5)_3$" (where C_4H_5 is today's C_2H_5 group). The product mixture was not analyzed; therefore, we can make no guess as to its exact composition.

When an ether solution of the product mixture was allowed to evaporate partially in air, an insoluble white, amorphous solid precipitated in unspecified yield. This solid formed crystalline salts when treated with acids.

Treatment of the product mixture with silver nitrate in ethyl acetate solution resulted in reduction to metallic silver. Filtration, followed by addition of aqueous KOH and, subsequently, more water and ether, gave an ether solution of *Methplumbäthyloxid*, $[(C_2H_5)_3Pb]_2O$, as we would write it today. Evaporation of the ether left a heavy oil that crystallized on standing. The vapors produced when this compound was heated caused violent sneezing, a property common to all the organolead compounds reported by Löwig. Solutions of Löwig's oxide had an unpleasant, sharply corrosive taste and produced a highly unpleasant feeling in the throat (!). (To taste one's products was common practice in the mid-1800s. In the case of many organometallic compounds this could lead to rather unpleasant surprises.) Löwig's strongly basic oxide rapidly absorbed carbon dioxide from the air to form the carbonate, $(Pb_2Ae_3)O{\cdot}CO_2$ ($\equiv[(C_2H_5)_3Pb]_2CO_3$), a crystalline, poorly soluble solid which had a strongly burning taste. The analysis that Löwig reported (Pb, 63.87, 63.74; C, 23.93, 23.40; H, 4.74, 5.00) is in good agreement with that required for bis(triethyllead) carbonate (Pb, 63.87; C, 24.06; H, 4.62). A reaction of the oxide with dilute H_2SO_4 in ethyl acetate produced bis(triethyllead) sulfate. The latter, when treated with aqueous HCl (or, alternatively, with KBr) gave $(C_2H_5)_3PbCl$ and $(C_2H_5)_3PbBr$, respectively, as analytically pure, crystalline solids. Thus, Löwig had opened up the field of organolead chemistry, but on reading his paper it is not at all clear of what organolead compounds his "mixture of radicals" was composed. The two likely candidates are tetraethyllead, $(C_2H_5)_4Pb$, and hexaethyllead, $(C_2H_5)_3Pb{-}Pb(C_2H_5)_3$. The latter is readily oxidized by air, while the former is not. Thus, the initial product of the oxidation of Löwig's product mixture would have been the ether-soluble $[(C_2H_5)_3Pb]_2O$ and the precipitate would have been the insoluble carbonate. Left in solution would be the unoxidized tetraethyllead, which apparently was not isolated and probably went down the drain. Unfortunately, Löwig's paper gives no information about product yields. However, as we shall see, the method of synthesis, the reaction of an ethyl halide with a sodium/lead alloy, with some modifications, was used some 70 years later in the large-scale, commercial preparation of tetraethyllead.

Klippel repeated Löwig's preparation of *Methplumbäthyl* a few years later, finding that use of an alloy of 3 parts of lead to 1 of sodium resulted in a more rapid reaction that gave a higher yield of "Pb_2Ae_3".[5] Exposure to light resulted in decomposition of the product with deposition of lead and formation of "new volatile radicals". Klippel noted that when the ether solution of the organolead product of the C_2H_5I + Pb/Na reaction was allowed to partially evaporate, the yield of $[(C_2H_5)_3Pb]_2CO_3$ (now identified as such) was very low—which he blamed on the volatility of the initial product, the oxide and the carbonate. More likely, the low yield of the carbonate was "real" and the major product was tetraethyllead, which again was not isolated.

All of this chemistry was called into question by A. Ghira of the University of Padova in 1894.[6] On repeating Löwig's C_2H_5I + Pb/Na procedure, he reported that he observed no vigorous, exothermic reaction; in fact no ethyllead product was formed at all. Since Löwig had reported a violent reaction, Ghira added a bit of water to the ethyl iodide and tried the reaction again. This time a very small amount ("*una piccola quantità*") of a product Ghira claimed was tetraethyllead was obtained. Since a small amount of water gave a positive result, Ghira tried a reaction with a large amount of added water ("*acqua in maggior quantità*"—exact amount not specified). Not surprisingly, a violent, exothermic reaction ensued, giving an organolead product in unspecified yield. This product appeared to be tetraethyllead. Ghira said that it was identical with a sample prepared by the reaction of diethylzinc with $PbCl_2$ (vide infra) and, also, its lead analysis was correct for $(C_2H_5)_4Pb$. Ghira concluded that Löwig's and Klippel's products actually were impure tetraethyllead. Ghira's claim that water is required for a successful reaction of ethyl iodide with sodium/lead alloy may sound strange, but, in fact, once tetraethyllead became an important commercial product, many patents claimed that water and alcohols, in small to gross amounts, are promoters for the reaction of ethyl halides with sodium/lead alloy.[7] However, the prevailing opinion of later workers was that Ghira's results and conclusions are questionable. Nevertheless, his claim that tetraethyllead was the major product was correct.

The synthetic papers of the 1850s and 1860s are difficult to assess. They usually contain no detailed experimental section as we know it today. Often amounts of reactants and solvents used are not given, and many times the papers are vague about reaction times. Product yields often are not reported. The papers of Löwig, Klippel, and Ghira are lacking in such useful information. However, once a product was isolated, its characterization, including elemental analysis, was thorough and described in great detail.

The question of the identities of the products of the C_2H_5I + Pb/Na reaction was revisited by Julius Tafel of the University of Würzburg in 1911.[8] The formation of triethyllead compounds on reaction of the organolead

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[5] Klippel, C. *J. Prakt. Chem.* **1860**, *81*, 287.
[6] Ghira, A. *Gazz. Chim. Ital.* **1894**, *24*, I, 42.
[7] Shapiro, H.; Frey, F. W. *The Organic Compounds of Lead*; Wiley-Interscience: New York, 1968; pp 35–40.
[8] Tafel, J. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 323.

Figure 2. George Bowdler Buckton. Reproduced courtesy of the Library and Information Centre, Royal Society of Chemistry.

reaction product with silver nitrate followed by KOH (Löwig) or with I_2 (Klippel) might be taken to indicate that the product was the very reactive hexaethyldilead. However, Tafel discovered that tetraethyllead also reacts with these reagents with cleavage of one ethyl group to give triethyllead products: $[(C_2H_5)_3Pb]_2O$ via $(C_2H_5)_3PbNO_3$ and $(C_2H_5)_3PbI$. Thus, since, according to Klippel, only a small amount of $[(C_2H_5)_3Pb]_2O$ was formed in the air oxidation of the original organolead product, the main component of the latter was tetraethyllead (confirming Ghira's contention).

Tetraethyllead was isolated and characterized as a pure compound first by George Bowdler Buckton.[9] Buckton (1818−1905, Figure 2) was one of the early English organometallic chemists. Despite being crippled in an accident when he was a boy, he pursued an active career in chemical research until 1865, when he married and retired to his country home. There he had a laboratory but devoted himself-to his other interests of entomology, astronomy (making his own telescopes and building his own observatory), photography, and other branches of science, as well as oil and water color painting. Earlier, he had studied at the Royal College of Chemistry in London, where he carried out research on the platinum bases and later served as research assistant of A. W. Hofmann. Among his contributions were the synthesis of dimethylmercury (1857), of ethyl derivatives of mercury, tin, and lead (1859), of methyl- and ethylantimony compounds, including (possibly) pentamethylantimony (1861), and (with W. Odling) the first syntheses of trimethyl- and triethylaluminum by reaction of aluminum metal with the respective dialkylmercurial (1865).

Buckton's synthesis of tetraethyllead was effected by the reaction of diethylzinc with an excess of lead dichloride:[10] "Chloride of lead turns black immediately [formation of metallic lead] it comes in contact with zincethyl. It sinks in the liquid and forms a crust which is so hard that it will be found more convenient to operate in a bottle than in a retort. In the former vessel the chloride may be incorporated with zincethyl without fear of fracture." (In view of the high reactivity of diethylzinc toward atmospheric oxygen and moisture, the reaction was carried out in a protective coal gas atmosphere.) Subsequently, the reaction mixture was heated at 100 °C for several minutes in a water bath and then cooled. The liquid phase was pipetted off and hydrolyzed with dilute aqueous HCl. Buckton had some trouble distilling his product:

> "Considerable difficulty was experienced in freeing this radical (Buckton, following Frankland, thought that his alkyllead product was a "radical") entirely from ether. When distilled, the thermometer rises rapidly to nearly 204°, at about which point the vapour suddenly decomposes with a slight explosion and deposit of metallic lead. This difficulty was overcome by conducting the distillation under reduced atmospheric pressure, in a simple condenser a sketch of which is annexed (Figure 3).
>
> The apparatus was found very conveniently to permit of frequent change of the receiver, without disturbing the tightness of the various joints. When the barometer stood at 30.5 inches, the radical passed over without the least decomposition at a temperature of 152 °C, under a pressure of about 7.5 inches of mercury, thus depressing the boiling point in a remarkable degree."

Buckton made no mention of the formation of metallic lead in the reaction and did not write an equation describing the formation of his product, which he believed to be the "radical" *plumbic diethyl*, $Pb(C_4H_5)_2$. His analytical data (C, 29.62, 29.74; H, 6.14, 6.32) were in fair agreement with the values calculated for $(C_2H_5)_4Pb$ (C, 30.08; H, 5.05). The product was described as "a colorless and limpid fluid" that was soluble in ether but not in water. It burned brightly, with an orange flame tinged at the edges with pale green, giving off fumes of lead oxide. Violent reactions occurred when iodine and bromine were added to it. Treatment with gaseous HCl gave "hydride of ethyl" (C_2H_6) and *chloride of diplumbic triethyl*, $Pb_2(C_5H_4)_3Cl$ ($\equiv(C_2H_5)_3PbCl$) (eq 1) as "long

$$2Pb(C_4H_5)_2 + HCl \rightarrow Pb_2(C_4H_5)_3Cl + C_4H_5H \quad (1)$$

colourless needles which have a strong penetrating odour." The chloride was converted to $[(C_2H_5)_3Pb]_2SO_4$ by treatment with dilute aqueous H_2SO_4 and to $[(C_2H_5)_3Pb]_2O$ by reaction with KOH. These triethyllead derivatives are volatile, and Buckton reported that their vapors irritate the eyes and mucous membranes of the throat.

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[9] Spiller, J. *J. Chem. Soc.* **1907**, 663 (obituary).

[10] Buckton, G. B. (a) *Proc. R. Soc. London* **1859**, *9*, 309, 685. (b) *Philos. Trans. R. Soc. London* **1859**, *149*, 417. (c) *Ann.* **1859**, *109*, 218. (d) *Ann.* **1859**, *112*, 220.

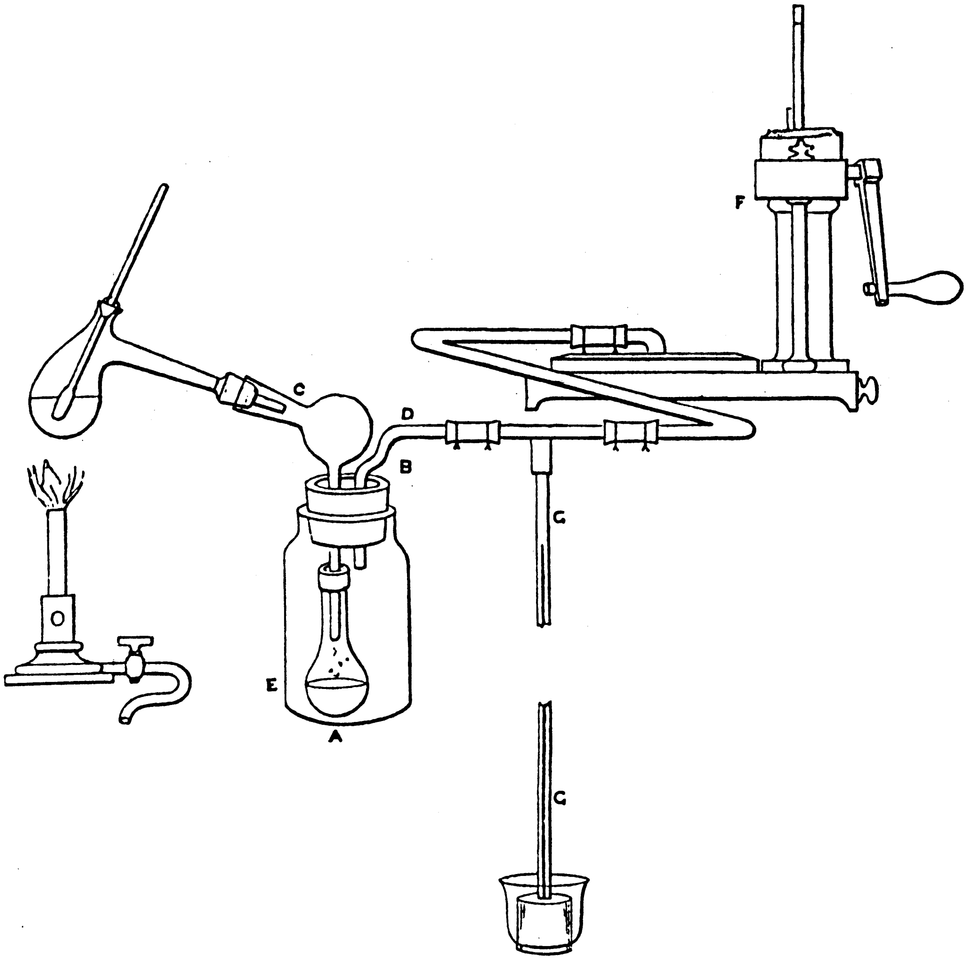

Figure 3. Buckton's apparatus for distilling tetraethyllead: (A) a wide-mouthed bottle; (B) a well-ground stopper formed from a piece of stout glass tube, 2 in. in diameter (the stopper is ground rather than tapered to prevent adhesion); (C) a small quilled condenser; (D) tube connected by caoutchouc with mercurial gauge; (G) mercurial gauge; (F) air pump. The tubes C and D are cemented into the stopper B by plaster of Paris and a layer of resinous cement to close the pores. E is a small receiver capable of being changed when needed (from ref 10b by permission of the Royal Society).

In France, Auguste Cahours (Figure 4), the first French organometallic chemist,[11] also studied alkyllead compounds.[12] He also described the preparation of *plombo-di-éthyle* and the derived chloride and oxide without going into detail, since these had been reported earlier by Buckton. For the synthesis reaction he wrote eq 2. (The French chemists in those days wrote their

$$2PbCl + Zn^2(C^4H^5)^2 \rightarrow Pb + Pb(C^4H^5)^2 + 2ZnCl \quad (2)$$

formulas with the number of atoms or groups in a compound as superscripts.) This equation recognized the formation of lead metal and the fact that a valence disproportionation had occurred, which, of course, is what actually takes place in the conversion of $PbCl_2$ to Pb(0) and, ultimately, $(C_2H_5)_4Pb$.

An improved synthesis of tetraethyllead was reported in 1879 by Edward Frankland[1] and Awbrey Lawrance.[13] The $PbCl_2 + (C_2H_5)_2Zn$ reaction was carried out essentially as described by Buckton, but now the workup was different. Instead of distilling the $(C_2H_5)_4Pb$ at reduced pressure (which led to some loss in yield), the crude tetraethyllead was purified by steam distillation: "The product of the reaction was slowly mixed with a large volume of water in a capacious flask or retort, which was then placed in an oil bath and its contents distilled in a current of steam so long as any heavy oily drops passed over. The distillate consisted of water and a heavy layer of plumbic tetraethide." The latter was sufficiently pure for further use. A control experiment established that steam had no effect on tetraethyllead. By 1879 the present atomic weight scale was in place and Frankland suggested that the $PbCl_2 + (C_2H_5)_2Zn$ reaction proceeded as shown in eqs 3 and 4.

$$PbCl_2 + 2ZnEt_2 \rightarrow PbEt_2 + 2ZnEtCl \quad (3)$$

$$2PbEt_2 \rightarrow Pb + PbEt_4 \quad (4)$$

Tetraethyllead was reported first in 1859. Two years later it was joined by tetramethyllead, which also

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(11) Auguste Cahours (1813−1891). Studies at the École Polytechnique, 1833−1835; in Chevreul's laboratory at the Muséum d'Histoire Naturelle, Ph.D. 1845. Later professor of chemistry at the École de Polytechnique and École Central in Paris. Discovered amyl alcohol 1837, toluene 1834, anisole 1841, methyl salicylate 1843, allyl alcohol 1856, phellandrene 1841. Studies of abnormal vapor densities, variation of density of acetic acid vapor between 124 and 336 °C and of substituted acetic acids. Preparation of acid chlorides using PCl_5. Preparation of organometallic derivatives of tin, lead, arsenic, aluminum, beryllium, zinc, and mercury (1853−1880). Short biography: Payen, J. In *Dictionary of Scientific Biography*; Gillispie, C. C., Ed.; Charles Scribner: New York, 1971; Vol. III, pp 10−11.

(12) Cahours, A. (a) *Ann. Chim. Phys.* **1861**, *62*(3), 257. (b) *Ann.* **1862**, *112*, 65.

Figure 4. Auguste André Thomas Cahours. Reproduced courtesy of the Library and Information Centre, Royal Society of Chemistry.

became important commercially in later years. The preparation of tetramethyllead by two methods was reported by Cahours in 1861.[12] The reaction of methyl iodide with a 5:1 Pb/Na alloy was followed by extraction of the resulting mixture with ether. The ether extracts were evaporated in a current of hydrogen or carbon dioxide, leaving the crude product. The reaction of dimethylzinc with $PbCl_2$ was recommended as a simpler procedure that gives a purer product in higher yield. (Unfortunately, these papers of Cahours are devoid of experimental details. Thus, no mention is made of metallic lead being formed in the latter reaction.) The product was described as a colorless, mobile liquid with an odor reminiscent at the same time of camphor and mold ("*l'odeur forte et toute spéciale rappelle à la fois le camphre et le moisi*"). It boiled at ~160 °C and could be distilled at atmospheric pressure under an inert atmosphere without decomposition. Decomposition began a little above the boiling point. Cahours' C, H analysis indicated that he had isolated a pure product: Anal. Found: C, 17.75; H, 4.56. Calcd for $(CH_3)_4Pb$: C, 17.97; H, 4.53. He called it *plombo-dimethyle*, $Pb(C_2H_3)_2$. Its reactions with concentrated HCl, HBr, and I_2 gave $(CH_3)_3PbCl$, $(CH_3)_3PbBr$, and $(CH_3)_3PbI$, respectively.

In Russia, Alexander M. Butlerov (Figure 5),[14] the first chemist of that country to carry out research in the new field of organometallic chemistry, had discovered some regularities in the boiling points of some of the peralkylmetal compounds that had been prepared thus far: that addition of a CH_2 group added ~20−30 °C to the boiling point of a compound (for instance, $(CH_3)_3As$, bp 120 °C, vs $(CH_3CH_2)_3As$, bp 180 °C−3 CH_2 groups added, hence 60 °C/3 = 20 °C increment per CH_2). Tetramethyllead (bp 160 °C according to Cahours) and tetraethyllead (bp ~200 °C according to Buckton) gave a CH_2 boiling point increment of 10 °C. Butlerov, feeling that something was wrong, repeated Cahours' synthesis of tetramethyllead by the reaction of dimethylzinc with $PbCl_2$.[15] Butlerov's liquid product had a boiling point of 110 °C (which has stood the test of time), giving a CH_2 bp increment of 22.5 °C, which pleased him no end. Butlerov also differed with Cahours about the odor of tetramethyllead, saying that it had a weak odor reminiscent of raspberries and mold. Also, Butlerov found the thermal stability of $(CH_3)_4Pb$ to be greater than had been described by Cahours. However, an attempt to determine the vapor density of tetramethyllead by the Dumas method resulted in a violent

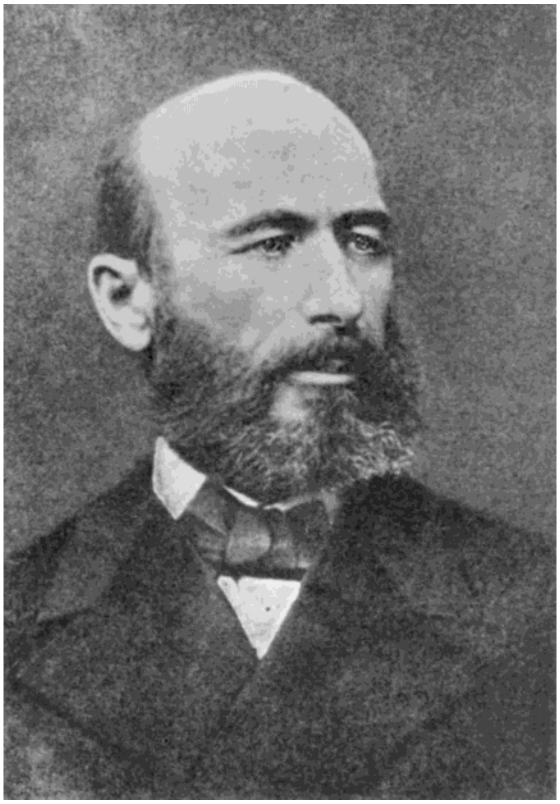

Figure 5. Alexander Mikhailovich Butlerov. Reproduced courtesy of the Library and Information Centre, Royal Society of Chemistry.

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(13) Frankland, E.; Lawrance, A. *J. Chem. Soc.* **1879**, *35*, 244.

(14) Alexander Mikhailovich Butlerov (1828−1886). One of the leading organic chemists in the mid-19th century. Studied chemistry at Kazan University with Zinin and Klaus. Masters degree, 1851. Dr. of Chemistry and Physics, 1854. Professor of chemistry at Kazan University. A year abroad visiting laboratories in Europe, 1857−1858; synthesis of methylene iodide while in Wurtz's laboratory in Paris. In 1868 professor at the University of Saint Petersburg. Pioneer and champion of the structural theory of organic chemistry. Synthesis of formaldehyde polymer, "dioxymethylene", from CH_2I_2 and synthesis of hexoses from formaldehyde. Preparation and study of *tert*-butyl alcohol and other tertiary alcohols by reaction of zinc alkyls with acid chlorides. Preparation of isomeric butanes and butenes, isobutylene oligomers. Use of zinc alkyls in organic synthesis. Preparation of trimethylacetic acid, determination of structure of pinacolone. First clear statement of theory of tautomerism. Biography: Leicester, H. M. *J. Chem. Educ.* **1940**, *17*, 203. An appreciation: Arbuzov, B. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 2035.

(15) Butlerov, A. *Z. Chem. Pharm.* **1862**, *6*, 497.

explosion that destroyed the apparatus and formed metallic lead. On the other hand, the method of Gay-Lussac was successful, giving a vapor density of 9.52 at 130 °C vs a theoretical vapor density of 9.25 if a formula of $(CH_3)_4Pb$ was assumed, leaving no doubt, as Butlerov said, about the tetraatomicity of lead. Thus, Cahours may have been the first to prepare tetramethyllead, but Butlerov did a better job of it.

In 1900 Victor Grignard reported his discovery of the reagents that bear his name, and 4 years later they were first used in the preparation of organolead compounds by Pfeiffer and Truskier.[16] Tetraphenyllead was prepared by the reaction of C_6H_5MgBr with $PbCl_2$ in diethyl ether (eq 5), but their description of the preparation of

$$4C_6H_5MgBr + 2PbCl_2 \rightarrow Pb + Pb(C_6H_5)_4 + 4MgClBr \quad (5)$$

tetraethyllead by reaction of C_2H_5MgBr in diethyl ether with $PbCl_2$ is problematic. It was reported that the product, obtained after hydrolysis of the reaction mixture and evaporation of the dried ether layer, was a colorless oil which “according to its properties, was mainly tetraethyllead”. However, the authors did not distill the oil since, as they said, its distillation could not be effected because of its ready decomposition. One may ask, if they believed their product was mainly $(C_2H_5)_4Pb$, why did they not try to distill it at reduced pressure as Buckton had done or steam-distill it, as Lawrance and Frankland had done? However, no details were reported. To assess the effectiveness of the Grignard procedure, Pfeiffer and Truskier treated the undistilled product with gaseous HCl; triethyllead chloride was obtained and the “very good yield” of this product was taken to be indicative of a very good yield of $(C_2H_5)_4Pb$. However, since both tetraethyllead and hexaethyldilead react with HCl to give triethyllead chloride, this conclusion was a dubious one.

The synthesis of tetraalkyllead compounds by the Grignard procedure was studied very thoroughly by two young German chemists at the Technische Hochschule of Berlin, Gerhard Grüttner[17] and his graduate student, Erich Krause,[18] in 1916.[19] They found that the Grignard synthesis of tetramethyllead by reaction of methylmagnesium chloride with $PbCl_2$ in ether worked well, giving $(CH_3)_4Pb$ as the only ether-soluble product in good yield according to eq 5 (CH_3 instead of C_6H_5). Extension of this procedure to the preparation of $(C_2H_5)_4Pb$ and $(n\text{-}C_3H_7)_4Pb$ was accompanied by problems. Exposure of the ether layer obtained after hydrolysis of the reaction mixture in the case of the tetraethyllead preparation to the air resulted in precipitation of a white solid, an ethyllead carbonate. Attempted distillation of the liquid residue that remained after removal of the ether under a stream of CO_2 at 20 mmHg resulted in formation of lead metal at ~80 °C. At slightly higher temperature a light green-yellow liquid distilled, with continuous gas evolution and formation of more metallic lead. Repeated distillations were required before no further deposition of lead occurred. The air-stable distillate then was pure tetraethyllead, bp 83 °C at 13−14 mmHg. This procedure gave 85 g of $(C_2H_5)_4Pb$ and 10 g of lead metal in a reaction of 300 g of C_2H_5MgCl with 300 g of $PbCl_2$. The same observations were made in the case of the $n\text{-}C_3H_7MgCl + PbCl_2$ reaction. Here the gas evolution during the distillation was more vigorous. However, it was possible to obtain pure $(n\text{-}C_3H_7)_4Pb$, albeit in poor yield. Higher tetraalkyllead compounds, e.g., tetraisobutyllead, could not be obtained by this procedure. Grüttner and Krause ascribed these difficulties to the formation of intermediate “unsaturated” organolead compounds, R_3Pb (or $R_3Pb-PbR_3$) or R_2Pb. The amount of these formed in the $RMgX + PbCl_2$ reaction increases and their thermal stability decreases with increasing size of the alkyl group. Thus, attempted distillation of the isobutyllead reaction product at 2 mmHg resulted in explosive decomposition.

Krause considered the reaction of the ethyl Grignard reagent with $PbCl_2$ to proceed stepwise as shown in eqs 6−8.[20]

$$2C_2H_5MgBr + PbCl_2 \rightarrow (C_2H_5)_2Pb + MgCl_2 + MgBr_2 \quad (6)$$

$$3(C_2H_5)_2Pb \rightarrow 2(C_2H_5)_3Pb + Pb \quad (7)$$

$$4(C_2H_5)_3Pb \rightarrow 3(C_2H_5)_4Pb + Pb \quad (8)$$

The sum total then is eq 9.

$$4C_2H_5MgBr + 2PbCl_2 \rightarrow (C_2H_5)_4Pb + Pb + 2MgCl_2 + 2MgBr_2 \quad (9)$$

All presently available evidence indicates that $R_3Pb^\bullet$ radicals do not exist as stable species: i.e., that $R_3Pb-PbR_3$ compounds do not dissociate in solution or in the solid.[21] Thus, $(C_2H_5)_3Pb$ should be replaced by 0.5 $(C_2H_5)_3Pb-Pb(C_2H_5)_3$ in eqs 6 and 7.

A much better laboratory preparation of tetraethyllead that could be extended to the preparation of higher tetraalkyllead compounds was developed by Grüttner and Krause. The Grignard synthesis was carried out as before with hydrolytic workup. When the ether layer, which at this point contained both $(C_2H_5)_4Pb$ and $(C_2H_5)_6Pb_2$, was cooled to −65 to −70 °C and bromine was added until its color was no longer discharged, a

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[16] Pfeiffer, P.; Truskier, P. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 1125.

[17] Gerhard Grüttner (1889−1918), Ph.D. in organometallic chemistry with S. Hilpert at University of Berlin, 1914. *Privatdozent* at the Technische Hochschule Berlin until his early death, caused by pneumonia, at age 29. Very productive research in organometallic chemistry: P, As, Sb analogues of piperidine and pyrrolidine, metal displacement reactions, organotin, silicon and lead chemistry. Obituary: Hofmann, K. A. *Ber. Dtsch. Chem. Ges.* **1918**, *51*, 1205.

[18] Erich Krause (1895−1931). Chemistry studies at Technische Hochschule Berlin, 1913−1917, with G. Grüttner (Ph.D. 1917, research on organolead compounds). *Privatdozent*, 1923. Professor (*Extraordinarius*), 1927, at Technische Hochschule Berlin. Productive, but sadly short, research career in organometallic chemistry: organozinc, cadmium, thallium, aluminum compounds; symmetrical and unsymmetrical tin and lead alkyls; alkylmetal fluorides; brominolysis of metal alkyls; the first organosilver compound, C_6H_5Ag; hexaaryldilead and -ditin compounds; triphenylborane and its alkali metal adducts. During the years of his final illness, with the help of Aristid von Grosse, he wrote the bulk of the masterful monograph, *Die Chemie der metallorganischen Verbindungen*. Obituary: Hofmann, K. A.; Renwanz, G. *Ber. Dtsch. Chem. Ges.* **1932**, *65*, A29. See also ref 20, pp V−VII.

[19] Grüttner, G.; Krause, E. *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 1415.

[20] Krause, E.; von Grosse, A. *Die Chemie der metall-organischen Verbindungen*, Gebrüder Bornträger: Berlin, 1937; organolead chapter, pp 372−429.

[21] Reference 7, pp 164−166. However, such dissociation might occur under appropriate thermal or photolytic conditions.

solution of triethyllead bromide resulted (eqs 10 and 11).

$$(C_2H_5)_3Pb\text{-}Pb(C_2H_5)_3 + Br_2 \rightarrow 2(C_2H_5)_3PbBr \quad (10)$$

$$(C_2H_5)_4Pb + Br_2 \rightarrow (C_2H_5)_3PbBr + C_2H_5Br \quad (11)$$

This solution then was treated with the appropriate quantity of C_2H_5MgBr to give tetraethyllead which now was free of other lead compounds and could be distilled without decomposition. No lead was lost when this procedure was used. Grüttner and Krause applied this procedure to the preparation of many other symmetrical and unsymmetrical tetraalkyllead compounds and studied their chemistry in detail. They published eight more papers together,[22] and after Grüttner's death Krause continued research on organolead chemistry until 1930.

As Krause noted in his book,[23] alkyllead compounds were expected to be toxic, but less so than the dialkylmercurials. However, the toxic effects of the alkyllead compounds appeared to be cumulative. Krause said that in the laboratory a good hood should be sufficient to protect the chemist from these effects. In any case, the peculiar sweet odor of the tetraalkylleads would serve as a warning of their presence. However, the tetraalkyllead compounds must be more treacherous, for Krause is quoted as follows:[24]

> "The compounds (i.e., tetraalkylleads) seem to possess, even in very reduced doses, the malicious and creeping poisonous effects which are possessed by inorganic lead compounds... (However), they do not produce the typical symptoms of lead poisoning, ... but a slow weakening and enfeebling of the whole body, which ultimately results in death. Frequently, the effects of poisoning appear only after a long "latent" period. ... I have used every possible means of precaution ..., nevertheless, I think that I have severely damaged my health."

We will hear more about the toxic effects of tetraalkyllead compounds in Part 2.

The laboratory syntheses of tetraethyl- and tetramethyllead were now well in hand. At this point tetraethyllead was just another organometallic compound, one of many known by now, notable only for the difficulties encountered by the early workers in its synthesis and characterization. But this would soon change. Tetraethyllead was headed for the Big Time.

Interlude. Fritz Paneth Generates Free Methyl and Ethyl Radicals by Pyrolysis of Tetramethyl- and Tetraethyllead

Main-group organometallic chemistry began in 1849 with Edward Frankland's attempts to prepare the ethyl "radical" by the action of metallic zinc on ethyl iodide. The gaseous product that he isolated actually was *n*-butane, the ethyl radical coupling product. (He later also isolated the disproportionation products, ethane and ethylene.) His belief that it was the ethyl radical quickly was shown by others to be incorrect, although he did not believe that right away. Then, by carrying out the RI + Zn reaction under different conditions, he prepared and isolated dimethyl- and diethylzinc. These were the first main-group organometallic compounds, which led Frankland into a new and fruitful research area, and eventually, he gave up the search for organic "radicals". As time went by, the electron was discovered and, subsequently, recognition of the electronic structure of the atoms of the periodic table by Niels Bohr gave rise to the idea of the electron pair covalent bond. The triphenylmethyl radical had been prepared and isolated by Moses Gomberg in 1900. His claim that his product was a real free radical was greeted with skepticism. It took some 12 years before many chemists were willing to believe that triphenylmethyl indeed was a free radical. Shortly thereafter, the theoretical approaches to covalent bonding of Kossel, G. N. Lewis, and Langmuir made free radicals as "odd electron" species believable. However, simple alkyl free radicals remained elusive.

The discovery that pyrolysis of tetramethyllead in the gas phase gives methyl radicals and that their existence could be shown by their gas-phase chemistry was made by Fritz Paneth and Wilhelm Hofeditz at the University of Berlin in 1929.[25] Paneth's earlier studies on the preparation of volatile metal hydrides led him into the new area of the chemistry of alkyl free radicals, but before describing this work, a discussion of the interesting life and career of Fritz Paneth is in order.[26]

Friedrich Adolf Paneth (1887−1958, Figure 6) was born in Vienna and spent his childhood in that city. He studied chemistry at the University of Vienna and in Munich (with A. von Baeyer) and was awarded his Ph.D. by the University of Vienna in 1910. His thesis research, directed by Zdenko Skraup, was in the area of synthetic organic chemistry, a field to which he never returned. From 1912 to 1917 he had an appointment at the Institute for Radium Research in Vienna. In 1918 he was in Prague as assistant to Hönigschmid. Appointment as Professor (*Extraordinarius*) at the University of Hamburg followed. Paneth left Hamburg in 1922 to take up a professorship at the University of Berlin. During his tenure in Berlin he spent the 1926−1927 academic year at Cornell University as the George Fisher Baker Lecturer. In 1929 he was called to the University of Königsberg in East Prussia as Professor and Director of the Chemical Institute. As Emeléus tells us,[26a] Paneth was on a lecture tour in England in 1933 when Hitler came to power in Germany and that made him choose to stay in England. What was happening in Germany was not to his liking and also, although he was raised as a Protestant, his parents were of Jewish descent. In England he first spent 5 years at the Imperial College of Science and Technology as a guest and then one 1 year as Reader in Atomic Chemistry in the University of London. In 1939 he was appointed Professor of Chemistry and Director of the Laboratories at the University of Durham. During World War II

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[22] (a) Grüttner, G.; Krause, E. *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 1125. (b) **1916**, *49*, 1546. (c) **1916**, *49*, 2666. (d) **1917**, *50*, 202. (e) **1917**, *50*, 278. (f) **1917**, *50*, 574. (g) **1917**, *50*, 1557. (h) Grüttner, G.; Krause, E. *Liebigs Ann. Chem.* **1918**, *415*, 338.

[23] Reference 20, p 388.

[24] Hounshell, D. A.; Smith, J. K., Jr. *Science and Corporate Strategy. DuPont R&D, 1902−1980*; Cambridge University Press: Cambridge, U.K., 1988; p 152.

[25] (a) Paneth, F.; Hofeditz, W. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 1335. (b) *Nature* **1929**, *124*, 161.

[26] (a) Emeléus, H. J. *Biogr. Mem. Fellows R. Soc.* **1960**, *6*, 227. (b) Spittler, E. G. In *Dictionary of Scientific Biography*; Gillispie, C. C., Ed.; Charles Scribner: New York, 1974; Vol. X, p 288. (c) Wänke, H. *Angew. Chem.* **1959**, *71*, 441. (d) Hahn, O. *Z. Elektrochem.* **1957**, *61*, 1121.

Figure 6. Friedrich Adolf (Fritz) Paneth. Reproduced courtesy of the Library and Information Centre, Royal Society of Chemistry.

Paneth was head of the chemistry division of the Joint British-Canadian Atomic Energy team in Montreal. Paneth stayed in Durham until his retirement in 1953, when he returned to Germany to become a Director of the Max Planck Institute of Chemistry in Mainz, a post he held until his death.

Paneth's research interest were very broad. Emeléus quotes a colleague:[26a] "He knew no boundaries in science. Though primarily a chemist, his work touched astronomy, physics, geology and, indeed, whatever happened to be related in any way to the subject of his immediate concern." He made significant contributions in his studies of classical radioactivity, including the development of radioactive tracer techniques, in the early years of his career. Through his work with the products of the radioactive decay of uranium and thorium, he was led to a study of the preparation of volatile metal hydrides: minute quantities of another gas accompanied the hydrogen formed when a magnesium foil on which Th*B*, a bismuth isotope, had been deposited, was dissolved in acid. This radioactive gas was decomposed when it was passed through a red-hot tube, and Paneth concluded that it was a bismuth hydride. More will be said about Paneth's work on gaseous hydrides a bit later.

Another area which occupied Paneth for the rest of his life in one way or another was his study of methods for the isolation and measurement of very small quantities of a gas—helium and other gases of low abundance found in the atmosphere. A useful application of these procedures was found in the determination of the age of meteorites by measuring their helium content, since his analytical method was capable of measuring 10^{-10} mL of gaseous helium. He also measured the helium content of the atmosphere as a function of height above the surface up to a height of 100 km. Also studied were the concentrations of other noble gases in the atmosphere, and a method for the determination of ozone in trace quantities was developed.

Paneth's interests extended to the history of science, cosmology, and the origin of the universe. However, it is Paneth's work with tetraalkyllead compounds that is of interest in our discussion of the history of tetraethyllead. This research grew out of the studies on gaseous metal hydrides. Having identified a radioactive, gaseous bismuth hydride, Paneth began a study of the preparation of volatile hydrides of the heavy main-group elements Bi, Po, Sn, and Pb by other procedures using nonradioactive materials. Ultimately, his greatest success was the preparation of the then unknown stannane, SnH_4, in gram quantities by the electrolysis of solutions of $SnSO_4$ using lead electrodes,[27] but it is his experiments directed at the preparation of plumbane, PbH_4, which are of interest here. One of the procedures used involved reaction of lead particles (obtained by pouring molten lead into water) with hydrogen in a silent electric discharge in a flow-through apparatus. Reactions in which highly purified lead and hydrogen were used were unsuccessful, but in the presence of an organic catalyst such as methane the reaction proceeded well and a lead mirror, indicative of the formation of unstable PbH_4, was formed in the quartz tube leading from the discharge zone.[28] In a larger, more complicated apparatus, U-tubes cooled with liquid air served to trap any PbH_4 that had been formed. However, although PbH_4 was thus trapped, methane was not an unreactive catalyst; higher hydrocarbons were formed from it in the electric discharge, and these also were collected in the U-tube, making separation of PbH_4 impossible. After thermal decomposition of the trap contents, a lead mirror was formed, proving that PbH_4 had been formed. That under these conditions, in the presence of methane, methyllead compounds also might have been formed must have crossed Paneth's mind, for in a footnote he mentioned that hot-tube pyrolysis of tetramethyllead gave a lead mirror. In further studies, mentioned only in passing by Paneth, evidence apparently was obtained that the action of a silent electric discharge on a hydrogen/methane gas stream did indeed result in formation of free CH_3, but the final product was a mixture of hydrocarbons. To have a cleaner route to this interesting species, Paneth and Hofeditz turned to the pyrolysis of tetramethyllead.[25] The apparatus constructed for this purpose is shown in Figure 7. Hydrogen, generated by reaction of zinc with sulfuric acid in a Kipp generator and dried and purified, was passed into the previously evacuated apparatus through a stopcock (1). Tetramethyllead (purified by shaking for several days with freshly prepared, dry silver oxide to remove traces of methyl iodide from its preparation in which CH_3MgI was used), in vessel A, was cooled with liquid air and the system was evacuated. Subsequently, the liquid air Dewar flask was replaced by a −70 to −75 °C acetone

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[27] (a) Paneth, F. *Z. Elektrochem.* **1923**, *29*, 97. (b) Paneth, F.; Rabinowitsch, E. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 1877. (c) Paneth, F.; Haken, W.; Rabinowitsch, E. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 1891.

[28] (a) Preliminary report including also experiments in which sparking between lead electrodes in a hydrogen stream was used: Paneth, F. *Z. Elektrochem.* **1920**, *26*, 452. (b) Paneth, F.; Matthies, M.; Schmidt, E. *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 775.

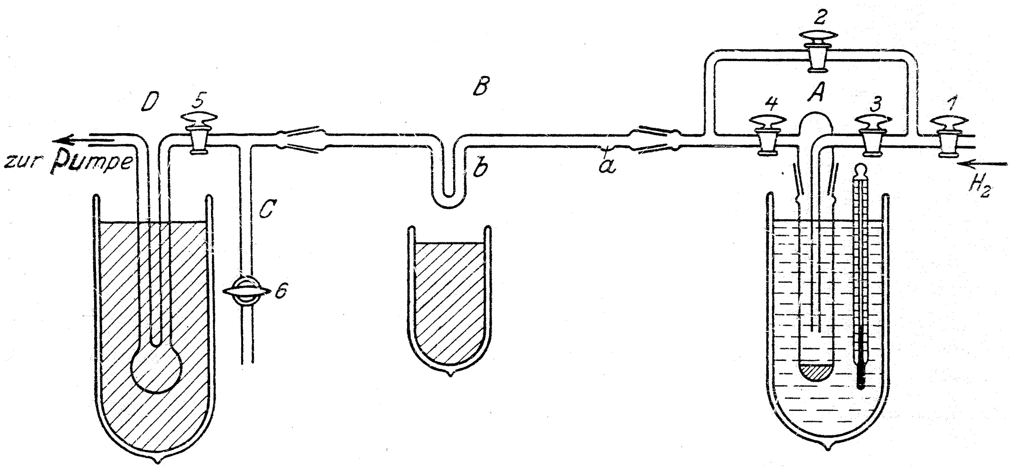

Figure 7. Overview of Paneth's flow-through apparatus for the generation and trapping of methyl radicals (from ref 25a by permission of Wiley/VCH).

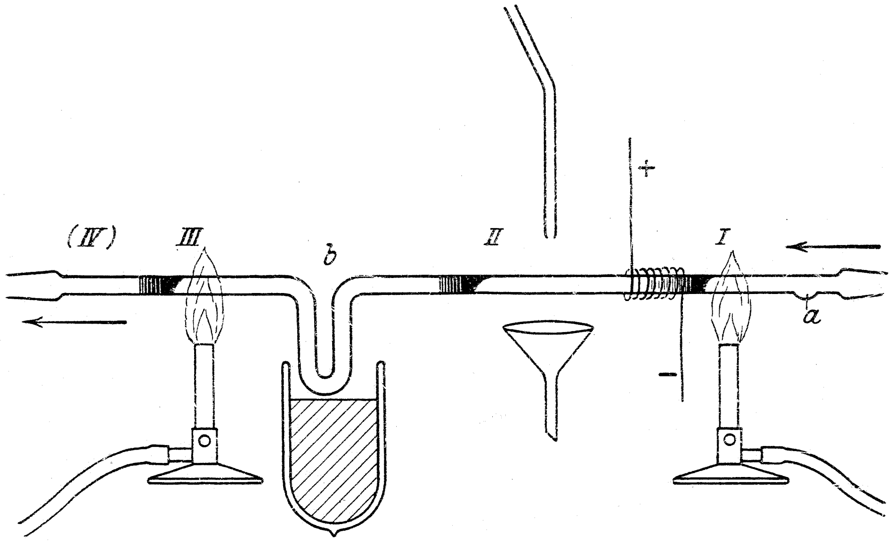

Figure 8. Pyrolysis experiment as carried out in Paneth's apparatus (from ref 25a by permission of Wiley/VCH).

bath. The inlet tube in vessel A was ca. 2 cm above the surface of the frozen $(CH_3)_4Pb$ (mp −27.5 °C; bp 110 °C); under these conditions the vapor pressure of tetramethyllead is sufficiently high so that the required small quantities can be carried out by the hydrogen stream. The system was connected to a quartz tube (B; 60 cm in length, 5 mm in diameter) with a U-tube (b). Tube B, via a stopcock (5) through a mercury trap (D), led to the vacuum pumps. The pyrolysis experiment was carried out at 1.5−2 mmHg as shown in Figure 8. A mechanical pump and a mercury diffusion pump ensured a rapid gas stream of 12−16 m/s during the experiment, since it was imperative to remove the CH_3 radicals quickly from the hot zone.

Initially a thin lead mirror was formed by heating at point II with a Bunsen burner over 1−2 min while the $(CH_3)_4Pb$ and H_2 carrier gas were passed through tube B. Subsequently, the heated portion of the tube was cooled with a hydrogen stream (by appropriate regulation of stopcocks 2−4). Afterward, a lead mirror was formed in a similar manner at point I. As this was done, one observed that the lead mirror downstream at II diminished and finally disappeared. This effect diminished with increasing distance between points I and II; it was still observed when this distance was 30 cm. Cooling tube B just before point II with a stream of cold water (as shown) had no effect. A control experiment showed that disappearance of the lead mirror at II was not affected by a pure hydrogen stream. Paneth emphasized that absolutely pure reagents were required if these phenomena were to be observed. In particular, traces of oxygen and H_2S in the hydrogen interfere. These experiments proceeded as described when purified, oxygen-free nitrogen was used in place of hydrogen as carrier gas.

To obtain some information about the nature of the gaseous product formed when the lead mirror at point II disappeared, tube B was heated at point III during such an experiment. This resulted in formation of a new lead mirror immediately after III, which suggested that the gaseous product was a stable lead compound, most likely tetramethyllead. If a lead mirror was present at point IV during this experiment, the gaseous products formed at III caused it to disappear.

The gaseous product of tetramethyllead thermolysis, which Paneth called an "aggressive agent" (*aggressives Agens*), was found capable of causing mirrors of other metals to disappear: Sb, Bi, and Zn. In the case of zinc, the volatile product formed when the zinc mirror was caused to disappear, which condensed as a white solid, was identified as dimethylzinc.

Paneth's conclusion was that the thermolysis of tetramethyllead resulted in formation of metallic lead and free, gaseous methyl radicals which, according to the experiments mentioned above, were stable *in the gas phase* for a limited time. (When they were condensed with liquid air in the U-tube (b) and warmed to room temperature afterward, no "aggressive" behavior was observed.) Paneth and Hofeditz carried out experiments that showed $(CH_3)_4Pb$ decomposition to be a unimolecular process and that gave a rough value for the half-life of the gaseous methyl radical of 0.0058 s. Returning to the earlier experiments in which the preparation of PbH_4 was attempted by reaction of lead particles with hydrogen in the presence of methane in a silent electric discharge, Paneth now was certain, in view of the present results, that the isolation of PbH_4 had been made impossible by the formation of $(CH_3)_4Pb$ (via methyl radicals from the methane), which has a volatility probably similar to that of PbH_4.

Paneth's explanation of his results in terms of the formation of free methyl radicals in the gas-phase thermal decomposition of tetramethyllead was questioned by G. Schultze and E. Müller of the Technische Hochschule Danzig.[29] These workers had investigated the reaction of lead mirrors (via $(CH_3)_4Pb$ thermolysis) and "active hydrogen". In their experiments the lead mirror became hot under an activated hydrogen stream and disappeared within minutes. When the reaction tube was heated with a flame some distance from where the lead mirror had been, a new lead mirror was formed. Attempts to condense the volatile PbH_4 that was the assumed product were unsuccessful; only metallic lead was formed. Concerning Paneth's experiments, Schultze and Müller suggested that it was active hydrogen, not the methyl radical, which was the "aggressive agent" that removed the lead mirrors (as was the case in their experiments). The active hydrogen, they suggested, could be formed by decomposition to the initially formed methyl radicals (presumably to give CH_2 and H, although they did not say so). Paneth did not take kindly to this suggestion.[30] He summarized Schultze and Müller's conclusion as saying "Active hydrogen causes lead mirrors to disappear; the agent formed in the thermal decomposition of tetramethyllead causes lead mirrors to disappear. Consequently, this agent is not methyl, rather it is active hydrogen." Paneth, in a footnote, said he did not want to call this conclusion nonsense, but he did want to mention, as illustration of the type of false, illogical conclusion that Schultze and Müller favored, an example from a book by K. O. Erdmann, *Die Kunst Recht zu Behalten* (*The Art of Being Right*): "All geese have two legs; this girl has two legs; therefore, this girl is a goose." After this put-down, Schultze and Müller were not heard from on this subject again.

Francis O. Rice (1890–1989), then at Johns Hopkins University (later at Catholic University in Washington, DC), also a pioneer in aliphatic free radical chemistry, was more appreciative of Paneth's methyl radical work. Rice had explained the high-temperature thermal decomposition of aliphatic hydrocarbons in terms of primary C–C bond homolytic cleavage to give free alkyl radicals; therefore, a new route to free alkyl radicals that occurred under milder conditions was of interest. The initial experiments of Rice and co-workers completely confirmed Paneth's results, and an improved system for generating gaseous free methyl radicals with a simpler apparatus (Figure 9) was developed.[31] The key change was that instead of hydrogen or nitrogen, which required an elaborate pumping system, water vapor was used as the carrier gas, its advantage being that it could be frozen out with liquid air before reaching the pump. Thus, only a simple oil pump was needed. Control experiments had shown that water vapor reacted neither with tetramethyllead nor with methyl radicals. Furthermore, if a 1% solution of tetramethyllead in heptane or acetone was placed in trap B, no other carrier gas was required and vessel A was not needed. The source of the metal mirror downside from the furnace was a piece of metal that was heated to 500–600 °C in the furnace section. Rice and co-workers measured the half-life of methyl radicals thus generated to be 0.001–0.002 s. The free, gaseous radicals formed in Rice's pyrolysis of aliphatic hydrocarbons, as expected, also removed metal mirrors, and to identify them, their reactions with elemental mercury were used. Dialkylmercurials were formed. By reaction with mercuric chloride or bromide, they could be converted to the well-known, usually solid alkylmercuric halide.

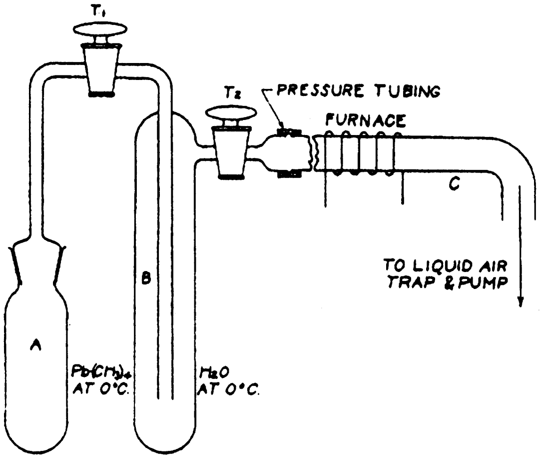

Figure 9. F. O. Rice's apparatus for the generation and trapping of methyl radicals (from ref 31).

In 1930 tetraethyllead already had become an important commercial product, greatly appreciated by the motoring public (and by the companies that manufactured it and used it as an antiknock additive in gasoline). Therefore, it might seem no surprise that Paneth next turned his attention to tetraethyllead, our cover molecule. However, in his papers on tetraethyllead theromolysis (or in any of his other papers), Paneth makes no mention of this new industrial application of tetraethyllead—despite the fact that this application was based on the thermal decomposition of tetraethyllead in the gasoline combustion engine. Admittedly, in the antiknock application no one really cared what happened to the ethyl radicals—it was the lead part of the

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[29] Schultze, G.; Müller, E. *Z. Phys. Chem. B* **1929**, *6*, 267.
[30] Paneth, F. *Z. Phys. Chem. B* **1930**, *7*, 155.
[31] Rice, F. O.; Johnston, W. R.; Evering, B. L. *J. Am. Chem. Soc.* **1932**, *54*, 3529.

Table 1. Compounds Formed by the Reaction of Free Methyl and Ethyl Radicals with Arsenic, Antimony, and Bismuth

		arsenic		antimony		bismuth	
temp of the mirror	compds formed	methyl	ethyl	methyl	ethyl	methyl	ethyl
cold	trialkyls	$As(CH_3)_3$	$As(C_2H_5)_3$	$Sb(CH_3)_3$	$Sb(C_2H_5)_3$	$Bi(CH_3)_3$	$Bi(C_2H_5)_3$
	dialkyls	$[As(CH_3)_2]_2$	$[As(C_2H_5)_2]_2$	$[Sb(CH_3)_2]_2$			
	monoalkyls	cyclo-$[As(CH_3)]_5$	cyclo-$[As(C_2H_5)]_5$				
hot	trialkyls	$As(CH_3)_3$	$As(C_2H_5)_3$	$Sb(CH_3)_3$	$Sb(C_2H_5)_3$	$Bi(CH_3)_3$	$Bi(C_2H_5)_3$
	dialkyls	$[As(CH_3)_2]_2$	$[As(C_2H_5)_2]_2$	$[Sb(CH_3)_2]_2$	$[Sb(C_2H_5)_2]_2$	$[Bi(CH_3)_2]_2$	
	monoalkyls	cyclo-$[As(CH_3)]_5$	cyclo-$[As(C_2H_5)]_5$				

tetraethyllead that provides the effective antiknock agent, PbO—but still, one might have expected Paneth to be aware of this important new aspect of organolead chemistry and to have mentioned it.

In their studies with tetraethyllead, Paneth and Lautsch used an apparatus almost identical with that shown in Figures 7 and 8.[32] Because of the lower vapor pressure of tetraethyllead, the latter was kept at −25 °C. Heating of tube B was accomplished using a spiral electrical resistance wire. In some reactions a 1:3 helium/neon mixture was used as carrier gas rather than hydrogen. The observations made in these experiments were much the same as those with tetramethyllead. Lead mirrors as far away as 40 cm from the decomposition zone were "erased" by the ethyl radicals, forming a clear, volatile liquid product. The latter in turn underwent thermal decomposition to give a lead mirror. The gaseous ethyl radicals also attacked mirrors of arsenic, antimony, zinc, and cadmium. Further work identified the ethyl radical/zinc reaction product as diethylzinc, while reaction of C_2H_5 with an antimony mirror gave $(C_2H_5)_3Sb$. An English group published a brief note to report that they could "confirm entirely the experiments of Paneth and Lautsch".[33]

Further studies[34] showed that at least one-third of the ethyl radicals combined to form *n*-butane. That this probably is a wall reaction was shown by the fact that an increase in the diameter of the reaction tube from 0.4 to 0.5 cm to 1.45 cm resulted in an increase in the observed half-life of the gaseous ethyl radical from ~0.005 to 0.015 s. Gas kinetic studies and theoretical calculations led to the following ideas concerning the fate of the ethyl radicals after their generation: every radical that impinges on the reactive metal mirror (e.g., Pb or Zn) sticks to the metal on the first collision. After a sufficient number of radicals, through surface diffusion, have accumulated at a metal atom, a definite ethyl−metal compound ($(C_2H_5)_4Pb$ or $(C_2H_5)_2Zn$) is formed, which is carried off by the rapid gas stream. Only a small fraction of the radicals, after collision with the tube surface (glass or quartz), sticks to the surface. Secondary reactions of these surface-confined radicals then give inactive organic products, mostly *n*-butane.

In work started in Königsberg and continued at Imperial College, Paneth studied the applications of his methyl and ethyl radical chemistry in the synthesis of organometallic compounds.[35] We have already seen that ethyl radicals react with lead and zinc mirrors to form tetraethyllead and diethylzinc, respectively, and also that methyl radicals "erase" antimony, bismuth, and zinc mirrors and that the ethyl radical causes mirrors of arsenic, antimony, and cadmium to disappear. Now the products of such reactions actually were isolated and characterized. The results obtained using group 15 element mirrors are given in Table 1. It may be noted that heating the mirror causes the number of products to increase in some cases. Using an antimony mirror gave bright red needles of the very oxygen-sensitive $(CH_3)_2SbSb(CH_3)_2$, "antimony cacodyl", whose attempted preparation by earlier workers had been unsuccessful, for the first time.

Also prepared in this study were dimethyl- and diethylberyllium. In these reactions the silica wall of the reaction tube had to be protected from the beryllium mirror (obtained by the thermolysis of a sample of diethylberyllium donated by Henry Gilman) by gold foil.

In these preparative experiments the radical concentration needed to be higher. This was achieved by maintaining the lead alkyl radical sources at a higher temperature: tetramethyllead at −40 °C and tetraethyllead at 0 °C. It was noted that the temperature at which tetraethyllead is decomposed should not exceed 600 °C. At 800 °C there is appreciable decomposition of C_2H_5 to CH_3; at 950 °C this decomposition is total, as shown in experiments with antimony and beryllium mirrors, only the methyl derivatives being obtained.

Attempts to cleanly generate higher alkyl radicals by R_4Pb thermolysis were unsuccessful, in the main as a result of alkyl fragmentation.[36] When tetra-*n*-propyllead was used as the radical source, reaction at 400 °C with an antimony mirror apparently gave $(CH_3)_4Sb_2$; with a zinc mirror, dimethylzinc was isolated, but higher zinc alkyls may have been present as well. The probable propyl radical decomposition course is $CH_3CH_2CH_2^\bullet \rightarrow CH_3^\bullet + CH_2{=}CH_2$. Attempts to prepare free isobutyl radicals by thermolysis of tetraisobutyllead, $[(CH_3)_2CHCH_2]_4Pb$, at ~300 °C were equally unsuccessful. Antimony mirrors reacted with the gaseous products to give chiefly $(CH_3)_4Sb_2$. The benzyl radical was produced not from an organolead compound but by thermolysis of tetrabenzyltin at dull red heat at 2 mmHg. Reaction of the benzyl radicals with metallic mercury gave dibenzylmercury in low yield.

The gas-phase and the liquid-phase pyrolyses of tetraethyllead were studied in later years by other workers using more modern methods. Kinetic and product studies were carried out.[37] There are several rate studies of tetraethyllead decomposition in the gas phase. The rate expression for this first-order process

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[32] (a) Paneth, F.; Lautsch, W. *Naturwissenschaften* **1930**, *18*, 307. (b) *Nature* **1930**, *125*, 564. (c) *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2702.

[33] Pearson, T. G.; Robinson, P. L.; Stoddart, E. M. *Nature* **1932**, *129*, 832.

[34] (a) Paneth, F.; Herzfeld, K. *Z. Electrochem.* **1931**, *37*, 577. (b) Paneth, F.; Lautsch, W. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2708.

[35] (a) Paneth, F. *Trans. Faraday Soc.* **1934**, *30*, 179. (b) Paneth, F.; Loleit, H. *J. Chem. Soc.* **1935**, 366.

[36] Paneth, F.; Lautsch, W. *J. Chem. Soc.* **1935**, 380.

[37] Reference 7, pp 63−75.

as determined by Pratt and Purnell[38] is

$$k = (4 \times 10^{12})e^{-37\,000/RT}\ \mathrm{s}^{-1}$$

Pratt and Purnell studied the products of the decomposition by GLC. The initial products were directly derived from the ethyl radical: the disproportionation products, ethane and ethylene, and the coupling product, *n*-butane, as well as hydrogen. At later stages a multiplicity of products was observed: 17 GLC peaks alone in the C_1 to C_6 range. Thus, the thermal decomposition of gaseous tetraethyllead is much more complex than Paneth had found using his simple approach.

Concluding Remarks

Thus far, tetraethyllead has been living in the academic world in Europe, the subject of the studies of professors and their students, whose findings were published in the journals of their day. Several preparative routes to $(C_2H_5)_4Pb$ and its smaller brother, $(CH_3)_4Pb$, have been reported, but new ones will be found. Especially noteworthy was the discovery by Paneth and his students that the gas-phase thermolysis of tetramethyl- and tetraethyllead gives the free methyl and ethyl radicals, respectively, and that these have significant lifetimes in the gas phase and the potential for useful synthetic applications.

It was also found that tetraethyllead is rather toxic, and this property ultimately will result in its fall from the pinnacle of commercial success.

In Part 2, tetraethyllead will be translated from the academic laboratories in Europe to the industrial world in the United States when Thomas Midgley and his colleagues discover that it is a very effective antiknock agent just at the time when the Automobile Age had begun to take off.

Acknowledgment. I am most grateful to Professor Herbert Schumann of the Technische Universität Berlin for information concerning Gerhard Grüttner and Erich Krause. My thanks to Professor Arnold L. Rheingold for the cover molecule. The photographs of Löwig, Buckton, Cahours, Butlerov, and Paneth were purchased from the Library and Information Center of the Royal Society of Chemistry.

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