hydroxy acid and this then reacts with a second molecule of the phenol with the loss of water to form the phthalein.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

HYDROCARBO BASES AND A STUDY OF ORGANIC DERIVATIVES OF MERCURY AND OF LEAD.

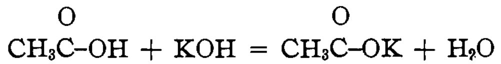
BY LAUDER W. JONES AND LOUIS WERNER.

Received May 14, 1918.

Introduction.

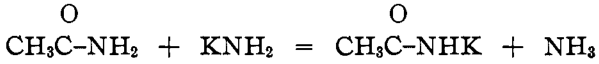
During the early development of the theory of Arrhenius, one of the most convincing arguments in support of his theory was the precise manner in which it explained the phenomenon of neutralization. The union of positive hydrogen ions with negative hydroxyl ions was fundamental to all processes of neutralization involving the interaction of aquo bases with aquo acids. Later, quantitative exactness was given to the explanation, when the ionization constant of water was determined in many independent ways, and the results were found to agree very closely, although the methods employed differed quite widely in character.

The interesting investigations of Franklin,[1] Kraus and others have familiarized us with a different class of bases and acids which have been called ammono bases and ammono acids. "The acids of this system are the acid amides and imides, including the amides and imides of non-metallic elements; the bases of the system are the metallic amides and imides, the salts are metal derivatives of acid amides and imides." As Franklin says, he "has developed a system of acids, bases and salts in which nitrogen occupies a position similar to that occupied by oxygen in the system of Lavoisier." The following equations illustrate the relations between aquo and ammono derivatives:



$$CH_3\overset{O}{C}\text{-}OH + KOH = CH_3\overset{O}{C}\text{-}OK + H_2O$$

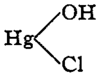
Aquo acid. Aquo base. Aquo salt.



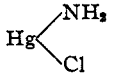
$$CH_3\overset{O}{C}\text{-}NH_2 + KNH_2 = CH_3\overset{O}{C}\text{-}NHK + NH_3$$

Ammono acid. Ammono base. Ammono salt.

Basic salts of the ammono type exist:



Aquo basic salt.



Ammono basic salt.

Developments of this kind have inclined chemists[2] to favor a more com-

---

[1] *Am. Chem. J.*, **45**, 291 (1912).

[2] Stieglitz, "Qual. Chem. Anal.," 1, 177, note (1911).

prehensive connotation for the terms base and acid. The property of neutralizing acids, that is, of suppressing hydrogen ions, is not restricted to aquo bases and ammono bases. In fact, any compound, MX, composed of cation M^+ and an anion X^- may function as a base in this particular sense. Its neutralizing effect is determined, in general, by the nature of the compound HX formed by the union of hydrogen ions with the negative radical X′, and, in particular, by the ionization constant of this compound. It has come to be recognized that aquo bases, salts of the acid water, are not unique since salts of all other slightly dissociated acids possess the ability, in varying degrees, to diminish the hydrogen-ion concentration of acid solutions, and may be said to neutralize acids.

Hydrogen Bases and Hydrocarbo Bases.

But this property is not limited strictly to those substances which have been demonstrated to be ionogens. It is peculiar to many other compounds which, as yet, the usual experimental methods have not shown to be electrolytes. Thus, hydrides of metals, such as sodium hydride, NaH, calcium hydride, CaH_2, and others, as well as metal organic compounds,[1] such as zinc alkyls, aluminium alkyls, react with acids and suppress hydrogen ions, *e. g.*,

$$NaH + HX = NaX + H_2.$$

$$Zn(CH_3)_2 + 2HX = ZnX_2 + 2CH_4.$$

If we may regard this property of such compounds as sufficient reason for classifying them as bases, hydrides of this character may be designated *hydrogen bases*, and the metal organic compounds may be called *hydrocarbo bases*. When compared with aquo bases and ammono bases, the striking resemblance in chemical behavior of these substances towards hydrogen ions would seem to demand some factor common to all as the cause of the analogy.

The electron conception of valence, as it has been applied recently in explaining certain chemical phenomena, claims that the forces which hold atoms together in molecules are electrical in nature and consist essentially of fields of forces established between the negative electrons of, and the positive surfaces, or cores, of the various atoms composing the molecules.

The negative electrons which are particularly responsible for the immediate union of atoms, Stark[2] calls valence electrons. In the union of two atoms to form a molecule, it is assumed that in molecules these valence electrons change their positions relative to the surfaces of the uncombined atoms, and that, in some cases, they may become more intimately associated with one atom than with the other. Thus, a com-

---

[1] Stieglitz, *Loc. cit.*

[2] Stark, "Die Elektrizität im Chemischen Atom," Leipzig (1915).

pound composed of two univalent atoms, A and B, may have either one of two electronic formulas,

$$\underset{\text{(I).}}{A_{+}-B} \quad \text{or} \quad \underset{\text{(II).}}{A-_{+}B.}$$

In Formula I, it is assumed that the atom A in combining with B has been affected in such a manner that one of its valence electrons approaches B, and in chemical reactions, involving the separation of A and B, may remain combined with B. In Formula II it is the atom A which has attracted a negative electron from B, and may separate from the molecule AB in possession of this electron. Both formulas, therefore, represent polar compounds; they are called *electromers.*[1]

In terms of this theory, the most obvious explanation of the similar reactivity of these various classes of substances would be to consider all groups combined with metal atoms in these compounds negative[2] in the electronic sense. There is little question concerning the negative character of the hydroxyl radical furnished by aquo bases.

$$\underset{\text{Aquo base.}}{\text{Ca}\begin{array}{l}+-\text{OH}\\+-\text{OH}\end{array}} \qquad \underset{\text{Hydrogen base.}}{\text{Ca}\begin{array}{l}+-\text{H}\\+-\text{H}\end{array}} \qquad \underset{\text{Ammono base.}}{\text{Ba}\begin{array}{l}+-\text{NH}_2\\+-\text{NH}_2\end{array}} \qquad \underset{\text{Hydrocarbo base.}}{\text{Zn}\begin{array}{l}+-\text{CH}_3\\+-\text{CH}_3\end{array}}$$

Their reactions with acids would assume a form similar to the action of aquo bases with acids, except for the fact that hydrides and metal organic compounds of this type are not known to be ionogens,

$$\text{Na}_{+}-\text{H} + \text{H}_{+}-\text{Cl} = \text{Na}_{+}-\text{Cl} + \text{H}_{+}-\text{H}$$

$$\text{Zn}\begin{array}{l}+-\text{CH}_3\\+-\text{CH}_3\end{array} + 2\text{H}_{+}-\text{Cl} = \text{Zn}\begin{array}{l}+-\text{Cl}\\+-\text{Cl}\end{array} + 2\text{H}_{+}-\text{CH}_3$$

In certain other respects, metal organic compounds resemble aquo bases and ammono bases.

(*a*) *They form basic salts:*

---

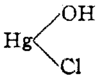
[1] Fry, *Z. physik. Chem.*, **76**, 387 (1911).

[2] Berzelius, "Lehrbuch der chemie," Vol. I, p. 61 (1836). "There are those who believe that hydrogen might combine with potassium to yield a compound in which hydrogen played the rôle of an electronegative element."

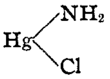
Brodie (*Phil. Trans.*, **1850**, 759) used positive and negative signs to designate the contrast or the relation existing between atoms entering into combination. This relation Brodie also calls chemical difference. He gave the following expression

$$\overset{+\,-}{\text{Cu}_2\text{H}} + \overset{+\,-}{\text{HCl}} = \overset{+\,-}{\text{Cu}_2\text{Cl}} + \overset{+\,-}{\text{H}_2\text{H}}$$

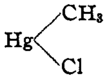
to represent the action of hydrochloric acid upon copper hydride described by Wurtz. (Abegg, *Anorganische Chem.*, **2**, [1], 589; *Z. anorg. Chem.*, **39**, 340 (1904)). The action of water upon sodium hydride was explained as follows: "Hydrogen of the hydride combines with H^+ of the water to give H_2, which, in this case, may be constituted as a compound $H_{+}-H$ of polar different, but materially like atoms."



Aquo basic salt.



Ammono basic salt.



Hydrocarbo basic salt.

(*b*) They enter into reactions involving double decomposition, and exchange negative alkyls, R—, for negative chlorine, negative hydroxyl and other negative groups:

$$\mathrm{Zn(R)_2} + \mathrm{2HOH} = \mathrm{Zn(OH)_2} + \mathrm{2RH}$$

$$\mathrm{Zn(R)_2} + \mathrm{2NH_3} = \mathrm{Zn(NH_2)_2} + \mathrm{2RH}$$

$$\mathrm{Zn(R)_2} + \mathrm{Cl_2C(CH_3)_2} = \mathrm{ZnCl_2} + \mathrm{R_2C(CH_3)_2}$$

$$\mathrm{3Zn(R)_2} + \mathrm{2PCl_3} = \mathrm{3ZnCl_2} + \mathrm{2R_3P}$$

(*c*) One metal may be displaced by another:

$$\mathrm{3Hg(R)_2} + \mathrm{2Al} = \mathrm{3Hg} + \mathrm{2Al(R)_3}$$

In marked contrast to these hydrocarbo bases stand these organic derivatives whose alkyl groups are not exchangeable for negative hydroxyl or other negative groups, but for *positive hydrogen*. In such compounds, the electronic conception of valence recognizes substances with the polar differences among the constituent atoms so adjusted that the alkyl groups tend to function positively in chemical changes. Thus:

$$\mathrm{Cl}{-}{+}\mathrm{R} + \mathrm{H}{+}{-}\mathrm{OH} = \mathrm{Cl}{-}{+}\mathrm{H} + \mathrm{HO}{-}{+}\mathrm{R}$$

$$\mathrm{O}\begin{matrix}{-}{+}\mathrm{R}\\ {-}{+}\mathrm{R}\end{matrix} + \mathrm{H}{+}{-}\mathrm{OH} = \mathrm{O}\begin{matrix}{-}{+}\mathrm{R}\\ {-}{+}\mathrm{H}\end{matrix} + \mathrm{HO}{-}{+}\mathrm{R}$$

$$\begin{matrix}{-}{+}\mathrm{R}\\ \mathrm{N}{-}{+}\mathrm{R}\\ {+}{-}\mathrm{R}\end{matrix} + 3\mathrm{H}{+}{-}\mathrm{OH} = \begin{matrix}{-}{+}\mathrm{H}\\ \mathrm{N}{-}{+}\mathrm{H}\\ {-}{+}\mathrm{H}\end{matrix} + 3\mathrm{HO}{-}{+}\mathrm{R}$$

In one important respect, hydrogen bases and hydrocarbo bases, such as $\mathrm{Zn(R)_2}$, differ from aquo bases and ammono bases; they are powerful reducing agents. This property is explained by the pronounced tendency of negative hydrogen to become positively charged, and of negative alkyl groups (or a carbon atom in such groups) to lose negative electrons and to assume positive charges. On the other hand, negative hydroxyl and negative amino ($\mathrm{NH_2}$) do not readily suffer a similar change to corresponding negative groups.

$$\mathrm{H}^- \xrightarrow{-e} \mathrm{H} \xrightarrow{-e} \mathrm{H}^+ .$$

$$\mathrm{CH_3^-} \xrightarrow{-e} \mathrm{CH_3} \xrightarrow{-e} \mathrm{CH_3^+}$$

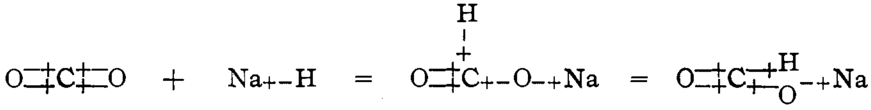
Free radicals.[1]

The reducing properties of metal hydrides is too well known to require more than a single illustration. Carbon dioxide reacts with sodium hydride to yield a formate.[2] This reaction may be explained in terms of positive and negative valences as follows:

---

[1] Fry, *Z. physik. Chem.*, **90**, 458 (1915).

[2] Moissan, *Compt. rend.*, **136**, 723 (1903); Fry, THIS JOURNAL, **36**, 268 (1914).

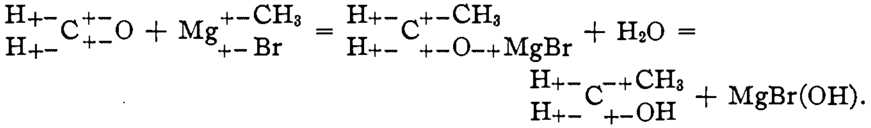


$$\mathrm{O}\substack{-+\\-+}\mathrm{C}\substack{+-\\+-}\mathrm{O} + \mathrm{Na}_{+-}\mathrm{H} = \mathrm{O}\substack{-+\\-+}\overset{\substack{\mathrm{H}\\|\\+}}{\mathrm{C}}{}_{+-}\mathrm{O}_{-+}\mathrm{Na} = \mathrm{O}\substack{-+\\-+}\mathrm{C}\substack{-+\mathrm{H}\\+-\mathrm{O}}{}_{-+}\mathrm{Na}$$

(I). (II).

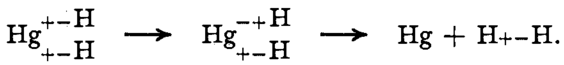
After the addition of sodium hydride to give an intermediate compound I, negative hydrogen may lose two negative electrons, which the carbon atom may acquire. In this sense, the mechanism consists in the reduction of the carbon atom at the expense of negative electrons furnished by negative hydrogen atom of the hydride.

All synthetic reactions which make use of aldehydes, ketones, or esters of acids in conjunction with zinc alkyls, or Grignard's reagent, probably involve not only addition, but are accompanied by reduction, effected by the negative alkyl groups of the metal organic compound. Thus, esters of organic acids yield ketones, or tertiary alcohols; aldehydes and ketones give alcohols, etc.



$$\begin{array}{l}\mathrm{H}_{+-}\\\mathrm{H}_{+-}\end{array}\mathrm{C}\substack{+-\\+-}\mathrm{O} + \mathrm{Mg}\begin{array}{l}{}_{+-}\mathrm{CH_3}\\{}_{+-}\mathrm{Br}\end{array} = \begin{array}{l}\mathrm{H}_{+-}\\\mathrm{H}_{+-}\end{array}\mathrm{C}\begin{array}{l}{}_{+-}\mathrm{CH_3}\\{}_{+-}\mathrm{O}_{-+}\mathrm{MgBr}\end{array} + \mathrm{H_2O} = \begin{array}{l}\mathrm{H}_{+-}\\\mathrm{H}_{+-}\end{array}\mathrm{C}\begin{array}{l}{}_{-+}\mathrm{CH_3}\\{}_{+-}\mathrm{OH}\end{array} + \mathrm{MgBr(OH)}.$$

Methyl Derivatives.—It seems probable that the failure on the part of chemists to prepare hydrides of certain metals (see p. 1259, footnote, Abegg) such as mercury, lead, silver gold, etc., is associated in some very intimate way with the tendency of negative hydrogen to lose negative electrons, while, at the same time, the cations of these metals readily acquire negative electrons and pass into the state of free metal. If, therefore, a mercury hydride represented by the formula $\mathrm{H}_{-+}\mathrm{Hg}_{+-}\mathrm{H}$ could be prepared, it would be expected that an exchange of two negative electrons between hydrogen and mercury would result in the formation of an electromer, $\mathrm{H}_{+-}\mathrm{Hg}_{+-}\mathrm{H}$, which, in turn, would dissociate to give free mercury and a molecule of hydrogen, $\mathrm{H}_{+-}\mathrm{H}$.



$$\mathrm{Hg}\begin{array}{l}{}_{+-}\mathrm{H}\\{}_{+-}\mathrm{H}\end{array} \longrightarrow \mathrm{Hg}\begin{array}{l}{}_{-+}\mathrm{H}\\{}_{+-}\mathrm{H}\end{array} \longrightarrow \mathrm{Hg} + \mathrm{H}_{+-}\mathrm{H}.$$

Although mercury hydride has never been isolated, many dialkyl[1] and diaryl derivatives of mercury are known, and are comparatively stable substances. But it has been shown that mercury diethyl dissociates at about 200° to give metallic mercury and butane. In this case also, the dissociation, considered electronically, implies that one of the

---

[1] Abegg, *Z. anorg. Chem.*, 39, 340 (1904). "If alkyl is substituted for hydrogen, then the nitrogen valences act towards carbon, and its negative valences are doublets, much stronger than those of hydrogen, as the existence of many organic derivatives of metals, whose analogous hydrogen derivatives are missing, would indicate."

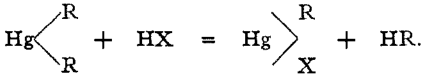
alkyl groups functions negatively, while the other group functions positively.

$$\mathrm{Hg}\begin{matrix}{}^{-+}\mathrm{C_2H_5}\\ {}_{+-}\mathrm{C_2H_5}\end{matrix} \longrightarrow \mathrm{Hg} + \mathrm{C_2H_5{-+}C_2H_5}.$$

If such a difference in the polar characteristics of the two groups exists, the chemical reactions of these dialkyl derivatives should furnish some experimental evidence in support of the claim; there should be some variation in the ease of replacement of the two radicals. Furthermore, if both radicals could be eliminated by hydrolysis, the products should be *metallic mercury, an alcohol and a hydrocarbon.*

$$\mathrm{Hg}\begin{matrix}{}^{-+}\mathrm{R}\\ {}_{+-}\mathrm{R}\end{matrix} + \begin{matrix}\mathrm{H{+-}OH}\\ \mathrm{H{+-}OH}\end{matrix} = \mathrm{Hg} + \begin{matrix}\mathrm{HO{-+}R}\\ \mathrm{H{+-}R}\end{matrix} + \mathrm{H_2O}.$$

It has been shown that differences of the character mentioned above actually manifest themselves in certain chemical reactions of these substances. Thus, when mercury dialkyls are treated carefully with such acids as acetic acid, hydrochloric acid, sulfuric acid, one of the alkyl groups is eliminated quite readily as a *hydrocarbon.*



$$\mathrm{Hg}\langle\begin{matrix}\mathrm{R}\\ \mathrm{R}\end{matrix} + \mathrm{HX} = \mathrm{Hg}\rangle\begin{matrix}\mathrm{R}\\ \mathrm{X}\end{matrix} + \mathrm{HR}.$$

Even oxidation with permanganate removes only one radical, and produces compounds of the type R-Hg-OH.

The substances, RHgX, are salts, ionogens, and experiments have shown that they dissociate to give complex positive ions, RHg^+, and negative ions, X^-. McCoy, as well as Kraus, presented evidence which seems to indicate that complex ions of this kind separate as free radicals at a mercury cathode and form unstable amalgams.

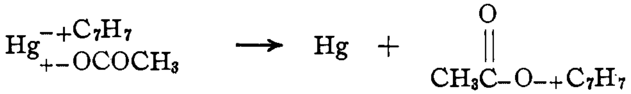
Halogen salts of this type react with moist silver oxide to give compounds RHg-OH which are pronounced bases, far more active than mercuric hydroxide. This behavior suggests that the alkyl groups in these salts exert an effect similar to that produced by the introduction of alkyl radicals in place of hydrogen in ammonium compounds. The chemical behavior of amines, considered electronically, requires that alkyl groups associated with nitrogen function positively (see above). By analogy, therefore, alkyl groups in these mercury salts may be assumed to function positively, $\mathrm{R{+-}Hg{+-}X}$.

But still more convincing evidence in support of this deduction has been secured recently in this laboratory by a study of the hydrolysis of various mercury alkyls and aryls in the presence of acetic acid. In general, our result may be said to confirm the assumption that under these conditions the two radicals in such compounds may function differently. Methyl derivatives and phenyl derivatives show variations which are still under investigation. Thus, mercury dibenzyl,[1] mercury diethyl,

---

[1] Wolf, *Ber.*, 46, 64 (1913).

mercury diisoamyl, when heated with glacial acetic acid at temperatures near 200°, gave *almost quantitative yields of metallic mercury.* Only one of the radicals was eliminated as hydrocarbon, while the second radical separated as an alcohol (or ester of acetic acid). Mercury dibenzyl gave metallic mercury, toluene and benzyl acetate, with considerable dibenzyl, probably formed by direct dissociation. When the weights of toluene and of benzyl acetate found by experiments were expressed in terms of the weight of benzyl radical required to form them, it was observed that these two values were approximately equal. Furthermore, mercury benzyl acetate, when heated with acetic acid, gave *no toluene* and *no dibenzyl;* metallic mercury and benzyl acetate were the exclusive products.



$$\mathrm{Hg}^{-+C_7H_7}_{+-OCOCH_3} \longrightarrow \mathrm{Hg} + \mathrm{CH_3}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{-O-+C_7H_7}$$

These results seem to substantiate the claim that one radical may function positively, while the other functions negatively.

But, according to Schorlemmer,[1] when mercury dialkyls are decomposed by concentrated mineral acids, the products are a mercury salt and a hydrocarbon. Some experiments carried out by us seem to confirm this conclusion. Mercury dibenzyl, with concentrated hydrochloric acid, gave mercuric chloride and toluene, with some tarry matter, but no benzyl chloride or benzyl alcohol. The conclusions to be drawn from these results appear to contradict those reached when acetic acid was employed; they require that the formula of mercury dialkyls should contain two negative radicals,

$$\mathrm{Hg}^{+-R}_{+-R} + 2\mathrm{H{+}{-}Cl} = \mathrm{Hg}^{+-Cl}_{+-Cl} + 2\mathrm{R{-}{+}H}.$$

If, however, the polarity of atoms or groups in molecules depends solely upon the relative positions of valence electrons, it is conceivable that, in nicely balanced arrangements of atoms, the relative positions of these electrons may be changing. The mobility of electrons has ceased to be purely speculative; it is a fact demonstrated by precise experimental methods. In other words, electromers may exhibit the phenomenon of tautomerism. It is no longer a matter of surprise that structure tautomers show two or more distinct types of chemical reactions, which presuppose the existence of different isomeric substances in equilibrium. In the present instance, the two sets of reactions shown by mercury dialkyls suggest the existence of tautomeric electromers[2] in equilibrium,

---

[1] Schorlemmer, *Ann.*, **132**, 234(1864).

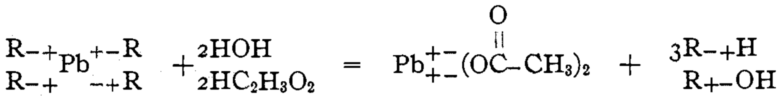
[2] Jones, *Am. Chem. J.*, **48**, 26 (1912); Fry, *Z. phys. Chem.*, **176**, 391 (1911); THIS JOURNAL, **36**, 265 (1914); Lewis, *Ibid.*, **38**, 762 (1916).

$$\mathrm{Hg}\begin{smallmatrix}+-\mathrm{R}\\ +-\mathrm{R}\end{smallmatrix} \rightleftarrows \mathrm{Hg}\begin{smallmatrix}-+\mathrm{R}\\ +-\mathrm{R}\end{smallmatrix}$$

(I). (II).

The transformation of one electromer into the other is brought about by a change in the relative positions of two negative electrons, "atoms of electricity," which, in Formula I are represented as more intimately associated with the radical R, while in Formula II they have a closer relationship to the mercury atom. Similarly, in the case of structure tautomers, one or more atoms are assumed to select new positions with respect to other atoms in the molecules of isomers in dynamic equilibrium.

Lead Derivatives.—When the properties of derivatives of quadrivalent lead are considered, it becomes evident that an analogy may be drawn between them and mercury derivatives. Two of the 4 valences of lead manifest themselves only under favorable conditions and readily cease to act; that is, quadrivalent lead compounds easily revert to derivatives of bivalent lead. This property suggested that lead alkyls with 4 alkyl groups, when subjected to treatment with acetic acid, would part with 3 alkyl groups in the form of hydrocarbon, while the fourth alkyl radical would separate as an alcohol. At the same time, a derivative of bivalent lead, in this case lead acetate, would be formed,



$$\begin{matrix}\mathrm{R}-+ & & +-\mathrm{R}\\ & \mathrm{Pb} & \\ \mathrm{R}-+ & & -+\mathrm{R}\end{matrix} + \begin{matrix}2\mathrm{HOH}\\ 2\mathrm{HC_2H_3O_2}\end{matrix} = \mathrm{Pb}^{+-}_{+-}(\mathrm{O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH_3})_2 + \begin{matrix}3\mathrm{R}-+\mathrm{H}\\ \mathrm{R}+-\mathrm{OH}\end{matrix}$$

Experiments with lead alkyls have confirmed these conclusions. Thus, lead tetraethyl when heated with acetic acid gave ethane, ethyl alcohol (as ethyl acetate) and lead acetate. The amount of ethane formed corresponded almost exactly to the volume which would result if 3 of the ethyl radicals had separated as hydrocarbon.

Maximum Positive or Negative Valence of Other Elements.

Certain other elements, in combination with particular atoms or groups, seem reluctant to manifest their maximum negative or positive valence. This is notably the case with nitrogen and with carbon. Thus, in ammonium compounds, one group is always negative and the remaining 4 are positive.

$$(\mathrm{A}^+)_4 \equiv \mathrm{N} + - \mathrm{B}.$$

The algebraic sum of negative and positive valences of combined nitrogen never exceeds 3 negative in any known case.

Similarly, many carbon compounds react as if some peculiar condition in the carbon atom prevented it from combining with a maximum positive valence of 4, or, in terms of the electron theory, of parting with 4 negative electrons. This may be illustrated by a few simple tetrasubstitution products of methane; many more complicated cases might be chosen.

CI_4	$C(NO_2)_4$.
CBr_4	$CBr_2(NO_2)_2$.
CCl_4	$CI(NO_2)_3$.

Gustavson[1] found that tetraiodomethane, heated with water at 100°, gave almost a quantitative yield of iodoform. Nef[2] showed that treatment with one equivalent of alcoholic potash, sodium ethylate, or with alcohol alone at 100°, converted it quantitatively into iodoform. Furthermore, Nef proved that carbon tetrachloride when heated with alcoholic potash (4 equivalents) at 100°, gave orthoformic ethyl ester entirely free from carbonic ethyl ester. Bolas and Groves[3] heated tetrabromomethane with alcohol at 100° and obtained bromoform, aldehyde and hydrogen bromide. Tetranitromethane, with a solution of potassium hydroxide, gives the potassium salt of trinitromethane and potassium nitrate. Iodotrinitromethane, with potassium hydroxide, gave the potassium salt of trinitromethane and KI with KIO_3.

The particular atoms or radicals associated with the carbon atom in these compounds are the ones which chemists consider to be "negative groups" *par excellence*, and, therefore, would seem to be especially suited to force the carbon atom to manifest a maximum positive valence of 4. But the behavior of these derivatives towards hydrolyzing agents reveals the fact that, in each case, one of the groups is more readily separated than the remaining 3 and, furthermore, that *positive hydrogen* takes the place of this particular group in the methane derivative, which implies that the group replaced is positive also. If complete hydrolysis of the resulting trisubstitution products is experimentally possible, formic acid or some derivative of formic acid is produced, that is, the 3 remaining groups are to be regarded as *negative* electronically, since they are replaced by *negative* hydroxyl. The hydrolyses (two stages) may be represented in a single equation as follows:

$$(\mathrm{A}^-)_3\overset{+}{\underset{+}{+}}\mathrm{C}{-}{+}\mathrm{A} + 4\mathrm{H}{+}{-}\mathrm{OH} = 3\mathrm{A}{-}{+}\mathrm{H} + (\mathrm{HO}^-)_3\overset{+}{\underset{+}{+}}\mathrm{C}{-}{+}\mathrm{H} + \mathrm{A}{+}{-}\mathrm{OH}$$

Bivalent Carbon.

It is probable that the dissociation of carbon compounds into bivalent carbon (methylene) derivatives, so exhaustively applied by Nef in the interpretation of reactions among organic compounds, is merely a manifestation of this tendency on the part of the carbon atom to assume by preference a condition in which neither the sum of the positive valences

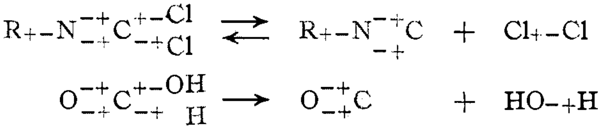
---

[1] *Ann.*, **172**, 173 (1874).

[2] *Ibid.*, **308**, 173 (1898).

[3] *J. Chem. Soc.*, **23**, 164 (1870); **24**, 783 (1871); *Ann.*, **156**, 60 (1870); 160, 160 (1871).

nor of the negative valences reaches a maximum value of 4.[1] Since, therefore, there will always be, potentially at least, two groups or atoms of opposite polarity attached to any carbon atom in an organic compound, of these two atoms or groups are capable of forming an independent molecule, they may separate, and thus produce a bivalent carbon residue. Thus,



$$\mathrm{R}_{+}{-}\mathrm{N}^{-+}_{-+}\mathrm{C}^{+-\mathrm{Cl}}_{-+\mathrm{Cl}} \rightleftarrows \mathrm{R}_{+}{-}\mathrm{N}^{-+}_{-+}\mathrm{C} + \mathrm{Cl}_{+}{-}\mathrm{Cl}$$

$$\mathrm{O}^{-+}_{-+}\mathrm{C}^{+-\mathrm{OH}}_{-+\;\mathrm{H}} \longrightarrow \mathrm{O}^{-+}_{-+}\mathrm{C} + \mathrm{HO}{-}_{+}\mathrm{H}$$

EXPERIMENTAL PART.

I. Aromatic Derivatives of Mercury.

A. Benzyl Derivatives. 1. Preparation of Mercury Dibenzyl and of Benzyl Mercuric Chloride.—Mercury dibenzyl was prepared according to the method of P. Wolff.[2] The compound described by Pope and Gibson was benzyl mercuric chloride and not mercury dibenzyl. The yield of mercury dibenzyl by Wolff's method was small, since the chief product of the reaction was benzyl mercuric chloride. His method was modified as follows:

A Grignard reagent was made with 3.8 g. of magnesium and 20 g. of benzyl chloride. To this solution 21.4 g. of mercuric chloride was added, and the mixture was heated gently for several hours. The resulting product was treated with water, and the ether layer was separated from the water and impure benzyl mercuric chloride. When the ether was distilled, a residue remained which consisted chiefly of mercury dibenzyl. After it had been recrystallized from alcohol, it weighed only 10 g.

It was found that a decided improvement in the yield resulted, if one equivalent of benzyl mercuric chloride, instead of one equivalent of mercuric chloride, was added to the Grignard reagent. Thus, 40 g. of mercury dibenzyl was formed from 3.8 g. magnesium, 20 g. of benzyl chloride and 35 g. of benzyl mercuric chloride.

2. Mercury Dibenzyl and Acetic Acid.—Fifteen g. of mercury dibenzyl and 30 cc. of glacial acetic acid were heated in a sealed tube for 7 hours at 160 to 170°. When the tube was opened, no pressure was observed, and the liquid was colorless. The metallic mercury, separated mechanically from the acetic acid solution, weighed 7.776 g. If all of the mercury present in 15 g. of mercury dibenzyl had been liberated in the me-

---

[1] Nef, THIS JOURNAL, 30, 645 (1908). Nef assumed that the 4 valences of the carbon atom are not equivalent but "are equivalent in pairs only, as shown by the following expression, $\pm \mathrm{C} . \mp$" But he affirms that "the plus and minus signs do not necessarily mean positively and negatively charged valences, but are simply used to discriminate between two different kinds of affinity units."

[2] *Ber.*, 46, 64 (1913); *J. Chem. Soc.*, 101, 735 (1912).

tallic state, the weight of mercury should have been 7.862 g. Therefore, 98.9% of this amount was found in the metallic state.

The acetic acid solution was subjected to fractional distillation. The Fraction F which boiled below 120° contained practically all of the toluene and acetic acid. The residue (R) in the distilling flask possessed the characteristic jasmine odor of benzyl acetate.

Without attempting to separate the toluene from acetic acid, the entire Fraction F was treated with fuming nitric acid and sulfuric acid. After several hours this mixture was poured into 75 cc. of water. The dinitrotoluene which deposited was dried and recrystallized from 80 cc. of 50% alcohol; it weighed 1.8 g.

Since the yield of dinitrotoluene is not quantitative, the following method was employed to make a correction: Preliminary experiments had shown that the amount of toluene formed from 15 g. of mercury dibenzyl lay somewhere between 1.5 g. and 2 g. Therefore, a mixture of 30 cc. of acetic acid with 1.74 g. of pure toluene was nitrated, with the conditions the same as those described above. The average yield of purified dinitrotoluene was 1.6 g. Consequently, the weight of dinitrotoluene actually obtained must be multiplied by the factor 1.087 to find the weight of toluene present originally in the acetic acid solution.

The residue (R), which contained benzyl acetate and dibenzyl, was dissolved in a little alcohol, any acetic acid present was carefully neutralized, and 50 cc. of 0.5 *N* alcoholic potash was added to the neutral solution. After this mixture had been refluxed for several hours, it required 10.1 cc. of *N* sulfuric acid to neutralize the excess of potassium hydroxide. Therefore, 30 cc. 0.5 *N* alcoholic potash were used to decompose the benzyl acetate. This gave 2.267 g. as the weight of benzyl acetate. It was possible to separate benzyl acetate from the residue (R) by fractional distillation, but the results were not so accurate.

After the determination of benzyl acetate was completed, the alcoholic solution which remained was distilled to remove alcohol and water. Dibenzyl was extracted from the other solids by means of alcohol. It was recrystallized from alcohol and weighed 3.05 g.

Summarizing the experimental results, 15 g. of mercury dibenzyl gave the following values:

Mercury = 7.776 g. (calculated 7.862 g.)
Toluene = 1.756 g.
Benzyl acetate = 2.267 g.
Dibenzyl = 3.05 g.

If these weights of toluene and of benzyl acetate are estimated as the benzyl radical, the values obtained are

C_7H_7 from toluene = 1.735 g.
C_7H_7 from benzyl acetate = 1.367 g.

With allowance for the errors which were inherent in the methods employed to estimate toluene as well as the ester, these values may be considered approximately equal. The sum of the metallic mercury, dibenzyl, and the two values for the radical benzyl amounts to 13.928 g., which shows that all but about one gram of the 15 g. of mercury dibenzyl used has been accounted for in the products isolated.

3. Benzyl Mercuric Acetate and Acetic Acid.—Benzyl mercuric acetate was prepared by the action of mercuric acetate upon mercury dibenzyl, according to the method of Wolff.[1] The yield was practically quantitative.

Ten g. of benzyl mercuric acetate and 20 cc. of glacial acetic acid were heated in a sealed tube at 170° for 7 hours. There was no evidence of pressure upon opening the tube, and the mixture was colorless. Benzyl acetate and metallic mercury were the only products formed; *no dibenzyl or toluene could be found.* Benzyl acetate was separated from acetic acid by fractional distillation. Thus, 10 g. of benzyl mercuric acetate gave

	Calc.	Found.
Mercury	5.721 g.	5.427
Benzyl acetate	4.279 g.	3.540

B. Other Aromatic Derivatives of Mercury.

Mercury diphenyl and phenyl mercuric acetate were heated with acetic acid at a temperature ranging from 220 to 230°. The sole organic products of the reactions were benzene, diphenyl and tar. No phenol or phenol esters were found.

In view of the success met with in making mercury dibenzyl from benzyl magnesium chloride and benzyl mercuric chloride, it seemed feasible to prepare mercury phenylbenzyl, $C_6H_5 — Hg — CH_2C_6H_5$, a mixed compound. No such derivatives of mercury have been made. It was observed, however, that phenyl magnesium bromide did not react with benzyl mercuric chloride, and that phenyl mercuric chloride, when allowed to interact with benzyl magnesium chloride, gave only dibenzyl.

II. Aliphatic Derivatives of Mercury.

General Methods.

Estimation of Gases.—Since the hydrolysis of alkyl mercury and lead compounds would yield gaseous, as well as solid and liquid products, it became necessary to modify the method which was used in the study of the aromatic derivatives. Two tubes were employed with each dialkyl compound. One tube contained only a small amount of the substance for the estimation of gaseous products; while a second tube, which contained a larger quantity of the mercury derivative, served for the determination of the ester. The reason for this will be apparent.

The tube in which the gaseous products were to be estimated contained

---

[1] *Ber.*, 46, 64 (1913).

a small weighed amount of the compound mixed with two volumes of glacial acetic acid. Before the tube was sealed, all air in it was displaced by carbon dioxide. After the tube had been heated for several hours, it was clamped in a vertical position, capillary upward, and a piece of rubber tubing was forced over the capillary. A large Y-tube was slipped into the other end of the rubber tube, so that each arm of the Y-tube could be connected with a Schiff azotometer, filled with a 30% solution of potassium hydroxide.

Before the capillary of the sealed tube was broken, one of the azotometers was connected, and carbon dioxide was passed through the Y-tube and its connections. The second azotometer was adjusted, and the capillary was broken. When the gas ceased to flow, one azotometer was removed, and carbon dioxide was passed through the Y-tube until all the gas in the connections had been forced over into the other azotometer.

At this stage the apparatus was quickly dismantled, and the drawn-out end of the sealed tube was cut off to form an opening large enough to admit a two-holed rubber stopper which was provided with a tube long enough to reach to the bottom of the bomb tube, and also with a short tube. After all air in these connections had been displaced, the stopper was adjusted to the bomb tube, and a stream of carbon dioxide was passed through the long tube until all gas remaining in the bomb tube had been driven through the shorter tube into the azotometer. This method was employed in the study of all alkyl derivatives of mercury and of lead.

Estimation of Esters.—The sealed tubes used to estimate the esters usually contained from 10 g. to 15 g. of the compound. During the heating, it was found necessary to open these tubes from time to time in order to release the pressure. This was a very objectionable feature, especially in the case of the more volatile esters, since it involved considerable loss of ester, which accounts, in part, for the fact that the experimental values obtained for methyl and ethyl esters are far below the calculated values. The small amount of material with which it was necessary to work made it impossible to secure a quantitative separation of these esters from acetic acid by fractional distillation. On this account the esters were determined by treatment with a standard solution of alcoholic potash.

A. Mercury Di-isoamyl.

This substance was prepared according to a method described by Marquardt.[1] Sodium amalgam (0.25%) was treated with isoamyl iodide in the presence of a small amount of ethyl acetate. The yield was small and not uniform in amount.

1. **Mercury Di-isoamyl and Acetic Acid.**—A sealed tube containing 1.169 g. of mercury di-isoamyl and 3 cc. of glacial acetic acid was heated

---

[1] *Ber.*, **21**, 2038 (1888).

between 190 to 200° for 16 hours. The gas formed in the tube was collected as described in the general method, except that the operation was carried out in a cupboard heated to 45° to keep isopentane in the gaseous condition. The volume of gas collected over 30% potassium hydroxide solution was 111.2 cc. at 741 mm. and 45° (85.2 cc. dry gas at 0° and 760 mm.).

A sample of this gas, 81 cc. (61.8 cc. at 0° and 760 mm.), was dried and analyzed by combustion.

CO_2, 0.5510; H_2O, 0.2624; C, 0.1503; H, 0.0294.

These values for carbon and hydrogen lie so close to the values for pentane that there can be no question that the gas burned was pentane. If the gas had been pure pentane, free from air, 61.8 cc. would have weighed 0.2009. The sum of the weights of carbon and hydrogen actually obtained was 0.1794 g. Consequently the sample contained 89.32% pentane.

If only one amyl radical separated as pentane, 1.169 g. of mercury di-isoamyl should have given the following value:

Isopentane: Calc. at 0° and 760 mm., 75.8 cc. Found: 76.1 cc.

2. A sealed tube containing 8.6 g. of mercury di-isoamyl and 17 cc. of glacial acetic acid was heated at 200° for 16 hours. Isoamyl acetate was separated from acetic acid by fractional distillation. The mercury was collected mechanically and weighed. The results were as follows:

	Calc.	Found.
Hg	5.032 g.	4.730
Amyl acetate	3.265 g.	1.690

B. Mercury Diethyl.

Mercury diethyl was prepared according to the method of Frankland and Duppa.[1] Ethyl iodide was treated with 0.25% sodium amalgam in the presence of a small amount of ethyl acetate. The product obtained was dissolved in ether, and mercury diethyl was separated by fractional distillation. The yield was small. Mercury diethyl boiled at 158°.

1. **Mercury Diethyl and Acetic Acid.**—When 0.9863 g. of mercury diethyl was heated with glacial acetic acid in a sealed tube at 180° to 190° for several hours, 114.9 cc. of gas at 30° and 745 mm. was collected over a 30% potassium hydroxide solution. This volume corrected would be 98.02 cc.

An analyses of 65.6 cc. of this gas was made. Bromine water absorbed 1.4 cc., probably ethylene. No loss in volume occurred on passing the gas over palladium. The volume of air contained in the palladium tube was 10.75 cc., which was, therefore, admixed with the sample of gas under analysis after the gas had passed through this tube. Ethane

---

[1] *Ann.*, 130, 105 (1864).

was estimated by exploding a mixture of 6.4 cc. of this residual gas with oxygen.

Contraction in volume after explosion	12.8 cc.
Loss in volume over KOH	10.2 cc.

These values show that the gas burned was ethane, with no hydrocarbon of higher molecular weight. From these data the following values may be calculated for the original sample of gas (65.6 cc.) taken for analysis:

Ethylene	2.14%
Hydrogen	0.00
Ethane	93.25

Assuming that only one ethyl radical separated as ethane, the values are as follows:

Ethane: Calc. 85.5 cc. Found: 91.4 cc.

2. A second sample of mercury diethyl, 14.8 g., was heated with 29 cc., of glacial acetic acid for 16 hours at 220°. The metallic mercury separated from the acid solution weighed 10.595 g. The acid solution was subjected to fractional distillation, and all that boiled below 101° was used for the estimation of ethyl acetate.

This fraction was neutralized, and about 50 cc. of alcohol with 50.2 cc. of 0.5 *N* potassium hydroxide solution (alcohol) were added. After this mixture had been refluxed for several hours, the excess of potassium hydroxide was determined by titration with normal sulfuric acid, requiring 4.12 cc. Therefore, 41.96 cc. 0.5 *N* alcoholic potash were required to decompose the ester. Ethyl acetate was salted out of the acetic acid solution by means of calcium chloride, but only a part of it was secured in this way. Summing up the results, the following values are observed:

	Calc.	Found.
Hg	11.476 g.	10.595 g.
Ethyl acetate	5.029 g.	1.848 g.

C. Mercury Dimethyl.

The method suggested by Frankland and Duppa was used in the preparation of this substance. It is advantageous to substitute methyl acetate for ethyl acetate as a catalyzer, since it is difficult to eliminate ethyl acetate from the finished product. Mercury dimethyl boiled at 95°.

1. **Mercury Dimethyl and Acetic Acid.**—When 1.597 g. of mercury dimethyl was heated to 250° with 2.5 cc. of glacial acetic acid, 213.3 cc. at 743 mm. and 30° (181.5 cc. corrected) of gas were obtained. 99 cc. of this gas was analyzed. No loss in volume occurred when the sample was treated with bromine water. When passed through the palladium tube, there was no decrease in volume. The air contained in the palladium tube amounted to 10.75 cc., which diluted the sample to this extent.

A mixture of 9.5 cc. of this residual gas with oxygen to a total volume of 96.9 cc. was exploded in a gas pipet.

Contraction in volume after explosion	15.00 cc.
Loss over KOH	7.54 cc.

This shows that the hydrocarbon present was methane unmixed with higher members of the series. From the data given, the composition of the original sample of gas was as follows:

Ethylene	None
Hydrogen	None
Methane	87.99%

If only one methyl radical separated as methane the values should be as follows:

Methane: Calc. at 0° and 760 mm., 155.3 cc. Found: 159.7 cc.

2. Three experiments were carried out with mercury dimethyl with the object of finding methyl acetate as one of the products formed during the action of acetic acid upon it, but none could be detected. A large amount of brown amorphous material was observed, and the quantity of metallic mercury formed showed that the compound was completely decomposed. Thus, in one experiment, 12.79 g. of mercury dimethyl gave 10.9 g. of mercury, while the calculated amount should be 11.04 g.

Apparently, the decomposition of this compound took place in a manner which differed materially from that observed in the case of other mercury derivatives described above. Since the first radical eliminated from these mercury alkyls always separates as hydrocarbon (see Introduction), and the amount of methane secured corresponded quite closely to the calculated value, it seems probable that the separation of the second methyl group in some way complicated the reaction. The study of this reaction will be continued.

III. Aliphatic Derivatives of Lead.

A. Lead Tetraethyl.

1. **The Preparation of Lead Tetraethyl.**—A great deal of confusion occurs in the literature concerning the preparation of pure lead tetraethyl. Bucton[1] described a product which he prepared by the action of zinc diethyl upon lead chloride. This product was not pure, but boiled between 198° and 202° with some decomposition. Recently, Pfeiffer[2] prepared this compound, but did not isolate it in the pure condition. He converted it into triethyl lead chloride. With a few slight modifications, no special difficulty was met with by us in preparing lead tetraethyl by Pfeiffer's method.

A Grignard reagent was made with 50 g. of ethyl iodide and 7.5 g. of magnesium. To this solution, 50 g. of thoroughly dried lead chloride were added in small portions while the mixture was shaken vigorously. After this mixture had been heated on a water bath for 6 hours water was added,

---

[1] *Ann.*, **112**, 226 (1859).

[2] *Ber.*, **37**, 1127 (1904).

and the ether layer which separated was dried over calcium chloride. The ether was removed and the residue was distilled *in vacuo*. The distillate was not pure lead tetraethyl, since, shortly after distillation, the liquid became turbid and, after it had stood a week, deposited an amorphous brown solid, sometimes accompanied by clear, white crystals. This precipitation continued for several weeks, and then ceased. When the liquid was redistilled, a pure product was obtained.

2. **Lead Tetraethyl and Acetic Acid.**—It was found necessary to heat lead tetraethyl with glacial acetic acid to a temperature of 250 to 260° for 16 hours in order to decompose it completely. Thus, 0.47 g. with 1 cc. of glacial acetic acid yielded 121.9 cc. of gas at 740 mm. and 30° over 30% potassium hydroxide. The corrected volume would be 103.6 cc. A sample of this gas, 72.7 cc., was analyzed. Bromine water absorbed 6.1 cc., probably ethylene. There was no loss in volume when the gas was passed over palladium. The palladium tube held 10.75 cc. of air, which was admixed with the sample at this point in the analysis. A mixture of 6.6 cc. of this residual gas with oxygen to a total volume of 98.2 cc. was exploded.

Contraction in volume	14.1 cc.
Loss in volume over NaOH	11.3 cc.

The hydrocarbon was ethane unmixed with higher members of the series. From these data the composition of the original sample may be calculated:

Ethylene	8.39%
Hydrogen	None
Ethane	91.08%

If 3 of the ethyl radicals in lead tetraethyl had separated as ethane, the values would have been as follows:

Ethane: Calc. 97.76 cc. Found: 94.06 cc.

When 9.951 g. of lead tetraethyl were heated with 20 cc. of glacial acetic acid at 250 to 260°, ethyl acetate, lead acetate and ethane were formed. The acid solution was subjected to fractional distillation. The fraction which boiled at 101° was neutralized and heated with 40 cc. of 0.5 N alcoholic potash. It required 15 cc. of normal sulfuric acid to neutralize the excess of potassium hydroxide. Consequently, the amount of ethyl acetate present was 0.443 g. If one ethyl radical separated in the form of ethyl acetate, the calculated amount of ester would be 2.709 g.

B. Lead Tetramethyl.

1. **The Preparation of Lead Tetramethyl.**—A Grignard reagent prepared from 9 g. of magnesium turnings and 52.5 g. of methyl iodide in 250 cc. of absolute ether was treated with 52.5 g. of carefully dried lead chloride. After this mixture had been heated for 5 hours, water was

added. The ether layer was separated and dried over calcium chloride. By fractional distillation lead tetraethyl, boiling at 110°, was obtained.

2. **Lead Tetramethyl and Acetic Acid.**—In one experiment, 0.5997 g. of lead tetramethyl was treated with 3 cc. of glacial acetic acid between 250° and 260° for 16 hours. In all 186.2 cc. of gas was collected over 30% potassium hydroxide at 28° and 751 mm. The corrected volume would be 161.85 cc.

An analysis of 70.2 cc. of gas was made. No absorption occurred with bromine water. When passed over palladium, no diminution in volume was observed. The volume of air in the palladium tube was 10.75 cc. which was added to the sample after it had been passed through the tube. A mixture of oxygen with 7.1 cc. of this residual gas was exploded. The total volume before explosion was 95.8 cc.

Contraction in volume	11.2 cc.
Loss in volume over KOH	5.50

The hydrocarbon was methane unmixed with higher hydrocarbons of the series.

The original sample of the gas had the following composition:

Ethylene	None
Hydrogen	None
Methane	89.33%

Assuming that 3 methyl groups separated as methane, the values are as follows:

Methane: Calc. 151.0 cc. Found: 144.4 cc.

3. A mixture of 9.3288 g. of lead tetramethyl and 20 cc. of glacial acetic acid was heated for 16 hours between 250° and 260°. Since the methyl acetate could not be separated quantitatively by fractional distillation, the distillate which boiled below 101° was neutralized and treated with 50 cc. of 0.5 *N* alcoholic potash. It required 18.9 cc. of normal sulfuric acid to neutralize the excess of potassium hydroxide. This gave 0.4526 as the amount of methyl ester, while the calculated amount was 2.585 g.

II. Aromatic Derivatives of Lead.

When lead tetraphenyl was treated with glacial acetic acid, the products found were benzene, lead acetate, and some tar. No phenol could be detected. Experiments were carried out to prepare lead tetrabenzyl by the action of lead chloride upon benzyl magnesium chloride. A dark gray mixture of finely divided lead, together with dibenzyl and insoluble magnesium salts was the result. The ether layer contained only dibenzyl, and dibenzyl was all that could be extracted by means of alcohol or benzene from the residue insoluble in ether.

Summary.

It is suggested that certain metal hydrides may be called hydrogen bases, and metal organic compounds of the type of zinc alkyls may be

termed hydrocarbo bases. The behavior of mercury dialkyls and diaryls towards hydrolyzing agents, especially glacial acetic acid, lead to the conclusion that these compounds behave as electromers and that the two radicals seem to be one positive and the other negative, $R_{+-}Hg_{+-}R$. The products obtained by the action of acetic acid, *viz.*, metallic mercury, a hydrocarbon, RH, and an alcohol ROH, seem to substantiate this claim. Similarly tetralkyl lead compounds react as if 3 of the radicals were negative and the fourth radical positive, $(R^-)_3 \overset{+}{\underset{+}{+}} Pb{-}{+}R{-}$.

CINCINNATI, OHIO.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

AN ATTEMPT TO FILTER THE ENZYMES OF MILK.[1]

BY JEAN PICCARD AND MARY RISING.

Received May 25, 1918.

Milk, cow's as well as human, contains certain enzymes of unknown origin and chemical constitution.[2] Since nature provides these compounds in natural foods for the young it is safe to assume that they have their important uses, although unknown to us.

If this conclusion is warranted, the value of a sterilized milk with active enzymes is apparent. For artificial feeding of infants boiled, "pasteurized" or "certified" milk is used. Boiled milk contains no enzymes, these being destroyed at a temperature of 72–80°. Milk, pasteurized for 30 minutes at 60°, gives a positive test for enzymes; but the milk is not filtered and suspended dirt remains in it, and there is no certainty that all the dangerous germs and their spores are killed at the relatively low temperature. Certified milk is obtained by methods in which special precautions are observed, but such milk contains, nevertheless, bacteria which multiply rapidly. Milk sterilized by filtration would be free from germs and suspended impurities and any change of the enzyme would be avoided.

With this ultimate aim the experiments described in this paper were undertaken for the purpose of discovering a method of filtering milk enzymes. Repeated attempts by us to accomplish this have met with failure, and no filter has been found with pores large enough to allow the passage through them of the colloidal enzyme body, without at the same time allowing the passage of bacteria. The results obtained and observations made should, however, prove of value to these interested in this problem.

Certified milk about 12 hours old was used in our experiments. We

---

[1] The work reported on in this paper will form part of the dissertation of Miss Rising for the degree of Doctor of Philosophy at the University of Chicago.

[2] J. König, "Chemie der menschlichen Nahrungs und Genussmittel.," 3, pp. 238–9.