bromide and potassium iodide solutions. The water solubility of mercuric bromide has been re-determined.

The equilibrium constants for the formation of the complex ions of mercuric halides have been evaluated. These calculations indicate that $HgBr_3^-$, HgI_3^- and $HgI_4^=$ are formed. Earlier work indicated the formation of $HgCl_3^-$ with small amounts of $(HgCl_2)_x$ and $(HgCl_2)_xCl^-$.

The anomalous solubility of mercuric chloride in low concentrations of chloride solutions is accounted for on the basis of polymerization of mercuric chloride. Other evidence is cited to indicate the existence of polymerized mer-

curic chloride molecules.

A number of different independent arguments are presented to indicate that the chief ion formed in the chloride solutions is the $HgCl_3^-$ ion.

The equilibrium constants and ΔF_{298}° of several of these ions have been evaluated. They have been shown to be in agreement among themselves and with other known data.

The free energy of formation of the various halide ions from mercuric halide and the halide ions is $HgCl_3^-$, $\Delta F_{298}^\circ = -1700$ cal.; $HgBr_3^-$, $\Delta F_{298}^\circ = -365$ cal.; HgI_3^-, $\Delta F_{298}^\circ = +430$ cal.; $HgI_4^=$, $\Delta F_{298}^\circ = -2100$ cal.

COLUMBUS, OHIO   RECEIVED JULY 7, 1939

The Redistribution Reaction. I. The Random Intermolecular Exchange of Organic Radicals

BY GEORGE CALINGAERT AND HAROLD A. BEATTY

This is the first of a series of papers describing a hitherto unrecognized type of intermolecular exchange of organic radicals. The systematic study of this reaction has yielded simple laws governing its course, and supplies a ready interpretation of the small amount of related data scattered through the literature. The results obtained offer interesting suggestions regarding the behavior of the covalent bond as well as possibilities for new methods of probing into this field. The reaction also constitutes a new tool for the synthesis of several types of organic compounds. This first paper defines the nature of the reaction, using illustrations from the field of organo-metallic compounds, and constitutes a general introduction to subsequent papers which will cover specific phases of the subject.

Introduction.—A wide variety of reactions is known in which atoms or radicals linked by covalent bonds are transferred from one molecule to another through exchange with an atom or radical of another kind. For example, in the Jacobsen reaction, bromobenzene under the influence of aluminum chloride yields a mixture containing benzene and p-dibromobenzene, as well as other products. Likewise, under the influence of the same catalyst, toluene is converted into a mixture containing, in addition to toluene itself, benzene and several polymethylated benzenes.

Reactions of this type are also known in the field of organo-metallic compounds. Dialkylzinc compounds have long been prepared by heating alkylzinc halides, which are converted into a mixture of the dialkyl compound and the zinc halide, the former being removed as formed, by distillation. A few cases also have been reported where the radicals exchanged were similar instead of dissimilar: for example, the interchange of methyl and ethyl radicals in organo-silicon compounds,[1] of phenyl and tolyl radicals in triarylbismuth compounds[2] and of halogen atoms in ethylene chlorobromide.[3]

Except in the last case, little or no indication has been given of the existence of an equilibrium, and in most cases a considerable amount of side reaction takes place. Also, the conditions used, namely, elevated temperatures or the presence of a powerful catalyst or both, suggest that the reactions are closely related to the irreversible decompositions of the compounds involved.

In the studies which will be reported in the present series of papers, it has been found that by a judicious choice of operating conditions and catalyst, it is possible to bring about an extensive

(1) Dolgov and Volnov, *Zhur. Obshchei Khim.*, Khim. Ser., **1**, 91 (1931).

(2) Challenger and Allpress, *J. Chem. Soc.*, **119**, 913 (1921); Challenger and Ridgway, *ibid.*, **121**, 104 (1922).
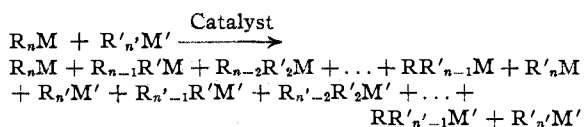
(3) Dougherty, THIS JOURNAL, **51**, 576 (1929).

interchange of similar radicals, and of certain similar atoms, between molecules of the same chemical class. In contrast to most of the cases reported above, the present reaction takes place smoothly, without noticeable evolution of energy, and the resultant product is free from the secondary or decomposition products usually found in reactions involving the liberation of functional groups or atoms without substitution. While this reaction has been found to take place quite generally, and with several different classes of compounds, including alkyl halides, esters of organic acids, and organo-metallic compounds, the present general exposition will be based on the last-named compounds, which have proved to be particularly suitable for quantitative study.

The Exchange of Radicals in Organo-Metallic Halides.—As will be shown later, the present reaction is closely related to the interchange between radicals and halogen atoms in organo-metallic halides, and for that reason this type of reaction will be considered first. It is well known that several metallic halides react with organo-metallic compounds in accordance with the general equation

$$R_nM + M'X_n' \longrightarrow R_{n-m}MX_m + R_mM'X_{n'-m}$$

the extent to which the reaction takes place depending upon the nature of the metals (or metal), the R group and the halogen involved.[4] In some cases which have been studied more extensively, notably that of the system $R_2Mg +$ MgX_2, the existence of a state of equilibrium has been established definitely.[4b]

In a previous report from this Laboratory,[5] it was shown that in the case of ethyllead halides, such a transformation did take place in both directions, between any of the possible stable components of the system, as indicated schematically below

$$R_4Pb \rightleftharpoons R_3PbX \rightleftharpoons R_2PbX_2 \rightleftharpoons [RPbX_3]$$
$$\qquad\qquad\qquad\downarrow\qquad\qquad\quad\downarrow$$
$$\qquad\quad R_2 + PbX_2 \quad RX + PbX_4$$

The study of equilibrium in such a system as this is rendered difficult, if not impossible, by the instability of some of the compounds involved, as indicated above by the vertical arrows;

(4) For a discussion of this subject, see (a) Challenger, Pritchard and Jinks, *J. Chem. Soc.*, **125**, 864 (1924); (b) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, Vol. I, Chapter 4.

(5) Communication to the Mid-West Regional Meeting of the American Chemical Society, Columbus, Ohio, November, 1937; to be published.

nevertheless the formation of all these compounds in the system has been established with certainty.

It may be inferred from the above that the interchange of organic radicals and halogen atoms in organo-metallic compounds is quite general, and this suggests the use of this reaction to effect the interchange of organic radicals themselves between different molecules.

The first step in the broadening of our knowledge of the reactions in this field consisted in testing the possibility of the occurrence of this interchange between a fully alkylated metal atom and its corresponding monohalide, a case in which the reaction conceivably might not take place, as it does not lead to the formation of any new compound. This interchange was tested with triethyllead chloride and tetraethyllead, the latter compound containing the radioactive isotope of lead, Radium D, as an indicator. It was found that, even at room temperature and without a catalyst or solvent, radioactivity was detected after a short time in the triethyllead chloride, and after one day the lead obtained from both the tetraethyllead and triethyllead chloride showed the same intensity of radioactivity, and continued to do so. This demonstrates the rapid interchange of the chlorine atoms and ethyl radicals in accordance with the equation

$$Et_4Pb^* + Et_3PbCl \rightleftharpoons Et_3Pb^*Cl + Et_4Pb$$

The same reaction was then studied in the case where the alkyl groups present in the tetraalkyllead compounds are different from those present in the chloride: the pair, tetramethyllead plus triethyllead chloride, was used. Here again the reaction took place readily, but a complex mixture was obtained. Careful fractional distillation of the tetraalkyllead portion of the product showed the presence of all the five possible compounds containing either or both methyl and ethyl groups, that is, tetramethyllead, trimethylethyllead, dimethyldiethyllead, methyltriethyllead, and tetraethyllead. The alkyllead halide portion of the product was analyzed separately, and it was likewise shown conclusively that all the four possible trialkyllead chlorides were present. These results are represented by the equation

$$Et_4Pb +\left\{\begin{array}{l} Me_4Pb + Me_3EtPb + Me_2Et_2Pb + \\ \qquad\qquad\qquad MeEt_3Pb + Et_4Pb \\ + Me_3PbCl + Me_2EtPbCl + \\ \qquad\qquad\qquad MeEt_2PbCl + Et_3PbCl \end{array}\right.$$

$$\left.Me_4Pb + \atop Et_3PbCl \right\}\longrightarrow$$

Equilibrium Interchange of Radicals in Metal Alkyls.—In the next step of this investigation,

the amount of alkyllead salt was decreased to catalytic quantities, and two different tetra-alkyllead compounds were used. Again, extensive interchange of the alkyl groups took place at low temperature, and the product contained all the possible tetraalkyl compounds. Yet in the absence of the catalyst, there was no detectable reaction, even after prolonged heating. This indicated that the presence of the alkyllead salt caused the alkyl groups in tetraalkyllead compounds to become mobile to the extent of migrating from one molecule to another, as represented by the equation

$$R_4Pb + R'_4Pb \longrightarrow R_4Pb + R_3R'Pb + R_2R'_2Pb + RR'_3Pb + R'_4Pb$$
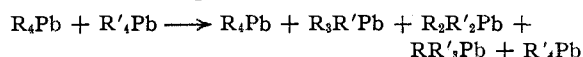
An investigation was then made to determine how general the reaction was for different R radicals and whether it would take place as well with other metals, and by means of other catalysts. It was found, indeed, to be quite general. Numerous tests were made, using two or more different radicals, including methyl, ethyl, n-propyl, iso-propyl, s-butyl, t-butyl, phenyl, and p-tolyl, bound to one or more metals, including lead, tin, silicon, and mercury. In all cases, interchange took place freely, and ample evidence was found of the formation of all the possible compounds between the R groups and M atoms present. Whenever compounds of two different metals reacted under similar conditions, as a rule they also reacted with one another, again yielding all the possible compounds of both metals. Thus, the equation which expresses the products obtained from two different R groups bound to two different M atoms of different valences, and which illustrates the type of result obtained from all these transformations in general, is

$$R_nM + R'_{n'}M' \xrightarrow{\text{Catalyst}}$$
$$R_nM + R_{n-1}R'M + R_{n-2}R'_2M + \ldots + RR'_{n-1}M + R'_nM$$
$$+ R_{n'}M' + R_{n'-1}R'M' + R_{n'-2}R'_2M' + \ldots +$$
$$RR'_{n'-1}M' + R'_{n'}M'$$

Numerous catalysts also were found, most of which consisted, either directly or through secondary reaction, of halides or organic halides of elements susceptible of forming organo-metallic compounds. The activities of the various catalysts differed, and compounds of different metals reacted at different rates, depending on the temperature and on the kind and amount of catalyst. Usually, the reaction time was limited to five

hours or less, and the reaction velocity was increased by elevating the temperature to 60–80° or, for some of the heavier R groups or less active catalysts, to 100–180°. To obtain these temperatures, and at the same time to provide stirring and to exclude air, it was convenient to add an inert solvent such as hexane or decalin, and to reflux the mixture. There was no evidence that these solvents participated in any way in the reaction. Experimental information and data on these topics will be presented in detail in a subsequent paper; illustrations of some of the systems tested, including different compounds and catalysts, are given in Tables I and II.

TABLE I

EXAMPLES OF METALS AND RADICALS WHICH DISPLAY INTERCHANGE

Reaction conditions, in general: a total of 0.3 mole organo-metallic compound, 1 g. AlCl₃, and 50 ml. hexane, heated to the boiling point, 60–80°, for 5–7 hours.

Metals	Radicals	Halides[a]
Me₄Pb + Et₄Pb	Me₄Pb + Et₄Pb	Me₃PbCl + Et₃PbCl[b]
Me₄Sn + Et₄Sn	Me₃BtPb + MeEt₃Pb[c]	Me₃EtPbCl[b]
Me₂Hg + Et₂Hg[c]	Me₂Et₂Pb	Me₄Pb + Et₃PbBr
Et₄Si + Pr₄Si[d]	Me₃-i-PrPb	Me₄Pb + Et₃PbCl
Me₄Sn + Et₄Pb	Et₄Pb + Pr₄Pb	Et₄Pb + Me₃PbBr
Et₂Hg + Me₄Pb	Et₃-n-Pr₂Pb	
	Me₂-i-Bu₂Pb	
	Me₄Pb + Ph₄Pb	
	Ph₄Pb + (p-tolyl)₄Pb[e]	
	Me₃-t-BuPb[f]	

[a] No AlCl₃ used. [b] Acetone used as solvent. [c] No solvent used. [d] Temperature 180°. [e] Temperature 100°. [f] Temperature 130°; some decomposition occurred, probably as a result of the instability of the poly-t-butyllead compounds.

TABLE II

EXAMPLES OF CATALYSTS

Reaction tested, except as noted, with 0.3 mole mixed Me₄Pb + Et₄Pb, 50 ml. hexane or decalin, 1–2 g. catalyst, heated to 80° for five to six hours.

ZnCl₂[a,b,c]	Me₂AlCl	Me₃PbI[d,e]
ZnF₂[a]	Bu₃Al₂I₃[f]	PCl₃[a]
HgCl₂[a]	ZrCl₄[a]	AsCl₃[a,b]
BF₃ gas	SnCl₄[a,b,g]	BiCl₃[a]
AlCl₃	Et₃SnBr[d]	FeCl₃[a]
AlBr₃[d]	Et₃PbCl[e]	PtCl₄[h]

[a] Temperature 160–175°. [b] Some decomposition occurred. [c] Time 24 hours. [d] Reaction not complete in time allowed. [e] Catalyst 13 g. [f] Catalyst 5 g. [g] Reacted vigorously, forming lead chloride. [h] Temperature 100°.

Characteristics of the Reaction.—In most organic reactions involving the intermolecular transfer or metathetical substitution of radicals, functional groups, or atoms, yields of 80 to 90% of a single product are usually considered excellent, and it is generally accepted that a substan-

tial fraction of the compounds entering the reaction is diverted through competitive side reactions, including decompositions, polymerization, etc. In contrast, the type of reaction described in the present paper shows as one of its distinctive characteristics the essential absence of decomposition or other side reactions. In general, this was evidenced by the fact that there was no observable evolution of gas, or precipitation of metal, or heat of reaction, and that the recovery of the reactants was complete except for normal handling losses. The few exceptions, such as those noted in Tables I and II, could be ascribed to the use of high temperatures and the thermal instability at these temperatures of some of the compounds formed, or to the occurrence of irreversible reactions between the compounds and the catalyst when the latter was present in substantial amount. Quantitative evidence for the absence of side reactions in a typical normal case is given in the third paper of this series.[6]

Moreover, it was found that—after a period of time which depends on the temperature, the catalyst, and the compounds used—the system reached a constant composition which was not changed by further prolonged contact with the catalyst. This final composition is an equilibrium, since it can be reached from any direction, that is, starting with any initial mixture (or mixed-radical compound) which contains altogether the same proportions of each different kind of atom and radical involved. For example, an equimolecular mixture of tetramethyllead and tetraethyllead, or of trimethylethyllead and methyltriethyllead, or the single compound, dimethyldiethyllead, each gives the same final product. Also, these equilibria are entirely unaffected by the usual factors such as solvent, catalyst, or even temperature, and the equilibrium composition is a function only of the mole fraction of the various R and M components present in the system.

In view of this, it seemed logical to make the simplest possible hypothesis as to the nature of the process: to wit, that the interchange occurs *at random*. This was found to be the case: the final composition of any system agrees with that calculated from the laws of probability alone. The distinctive characteristics of this reaction and of the resulting equilibrium—the freedom from side reactions, and the absence of

(6) Calingaert and Soroos, THIS JOURNAL, **61**, 2758 (1939).

chemical or energy factors affecting this random equilibrium—seem to justify identifying them by new names, and it is proposed to call the reaction the "Redistribution Reaction," and its product a "Random Equilibrium Mixture."
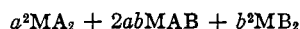
Random Distribution: The Application of the Laws of Probability.—To illustrate the application of the laws of probability to this random distribution of the interchanged radicals or atoms, consider the simple case of a single metal, M, and two organic radicals, A and B, the mole fractions of which are a and b, respectively, where $a + b = 1$. Imagine that all the radicals have been removed from the M atoms, and are to be returned thereto at random. Then the probability that the first valence of M will be satisfied by A is a, and by B, is b; so that the concentrations will be

$$a\text{MA} \quad \text{and} \quad b\text{MB}$$
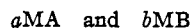
For the second valence, the same holds, and applies independently to MA and MB, giving, respectively

$$a^2\text{MA}_2 + ab\text{MAB} \quad \text{and} \quad ab\text{MAB} + b^2\text{MB}_2$$

or

$$a^2\text{MA}_2 + 2ab\text{MAB} + b^2\text{MB}_2$$
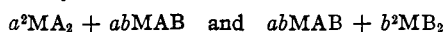
Applying the same method of deduction to the more general case of one kind of central atom (or group) M, of valence n, and s different kinds of substituent radicals (or atoms), $R_1, R_2, \ldots, R_s$, whose mole fractions are $r_1, r_2, \ldots, r_s$, respectively, gives as a result that the concentration of any one of the possible compounds, $M(R_1)_a(R_2)_b \ldots (R_s)_j$ (where $a + b + \ldots + j = n$) is equal to

$$\frac{n! \, (r_1)^a (r_2)^b \ldots (r_s)^j}{a! \, b! \ldots j!}$$

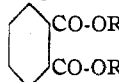and the total number of different $R_n M$ compounds is equal to

$$\frac{(n + s - 1)!}{n! \, (s - 1)!}$$

When more than one kind of central atom or group, M, is present, these two general formulas apply independently to each kind of M taken in conjunction with the R groups attached to it.

The above formulas reduce to rather simple forms in the case of systems containing few constituents. Thus, when there is only one central group M of valence n and two different kinds of radicals ($s = 2$), the number of different compounds is equal to $(n + 1)$, and the concentration of each is given by the corresponding term of the binomial expansion of $(r_1 + r_2)^n$. Denoting

TABLE III

NUMBER, CONCENTRATIONS, AND EXAMPLES OF R_nM COMPOUNDS

Valence of M = n	No. of compds. R_nM	Concentration of R_nM, $R_{n-1}R'M$, ..., R'_nM					Examples of types of compds.
1	2	r	$(1 - r)$				$CH_3CO\text{-}OR$; Et-X; R-Na; R-HgCl
2	3	r^2	$2r(1 - r)$	$(1 - r)^2$			$R_2\text{-}Hg$; $R_2\text{-}PbCl_2$; $X_2\text{-}C_2H_4$;
3	4	r^3	$3r^2(1 - r)$	$3r(1 - r)^2$	$(1 - r)^3$		$R_3\text{-}Bi$; $R_3\text{-}PbBr$
4	5	r^4	$4r^3(1 - r)$	$6r^2(1 - r)^2$	$4r(1 - r)^3$	$(1 - r)^4$	$R_4\text{-}Sn$

r_1 by r, and r_2 by $(1 - r)$, the corresponding values for valences of M from 1 to 4 are given in Table III, which includes examples of corresponding types of compounds.

From a knowledge of the composition of the original mixture, or from the over-all analysis of the product, the values of the r's are determined, and the expected concentrations in the final mixture can be calculated. As an illustration, the calculated concentrations of all five constituents in the system R_4M containing two kinds of groups, R and R', is shown in Fig. 1, for the whole range from $r = 0$ to $r = 1$.
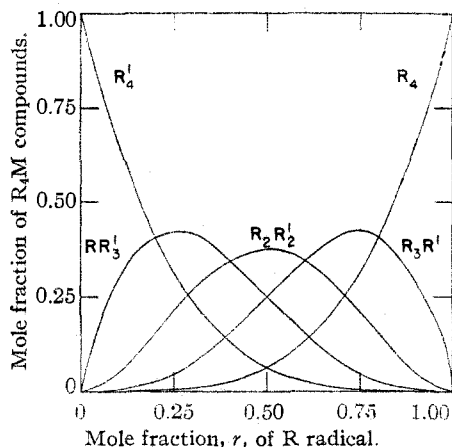
Fig. 1.—Composition of random equilibrium mixtures of the type $(R_nR'_{4-n})M$.

Experimental Confirmation of Random Equilibrium Mixtures.—The experimental data covering many of the systems which underwent the redistribution reaction were tested in this manner, with convincing results. In general, the analytical procedure consisted in washing or extracting the final reaction mixture to remove the catalyst, together with organo-metallic halides if present; the volatile metal alkyls (or other volatile compounds) were then separated by fractional distillation[7]; the less volatile metal aryls were

(7) The procedure followed and results obtained are described in the second paper of this series, by Calingaert, Beatty and Neal, THIS JOURNAL, **61**, 2755 (1939).

analyzed by freezing-point determinations, and the halides, if any, were identified by methods (which will be described elsewhere) based on solubility and alkylation.

Since these studies in general were regarded as being exploratory in a new field, and it was desired to extend their scope as far as was expedient within the time available, it was advantageous in some cases to carry out the analyses only partially, or semi-quantitatively, to an extent sufficient to show that the redistribution reaction had occurred and that the composition of the product was at least roughly in accord with that estimated for a random equilibrium mixture.

The typical results obtained in most cases are illustrated, for six representative mixtures, by Figs. 2–5. These give the experimental distillation data plotted on a volume percentage basis, in comparison with the ideal distillation curves which were calculated for random equilibrium mixtures of the over-all compositions indicated by the experimental data. It is clear that these typical results show a very satisfactory agreement with the predicted values. The identity in composition shown in Fig. 2 for the prod-
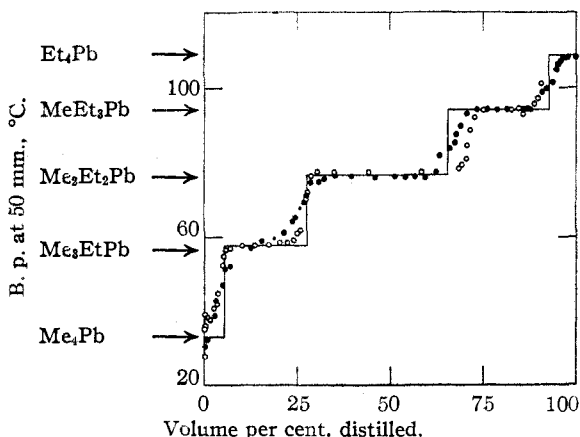

Fig. 2.—Distillation of the reaction product from: ○, Me_3EtPb + $MeEt_3Pb$; ●, Me_4Pb + Et_4Pb. Solid line calculated for random equilibrium mixture having [Me] = 0.50.
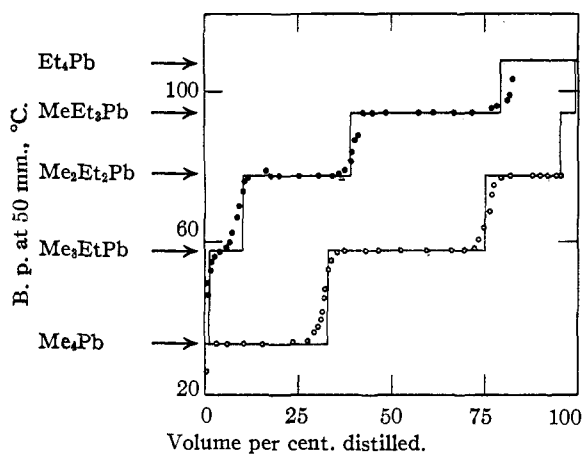
Fig. 3.—Distillation of the reaction product from Me₄Pb + Et₄Pb. Solid line calculated for random equilibrium mixture having O [Me] = 0.776; ● [Me] = 0.345.

ucts from two entirely different mixtures of the same over-all composition, and the marked difference between this product and those from two similar mixtures of somewhat different over-all composition (shown in Fig. 3) is noteworthy. The distillation shown in Fig. 4, although not
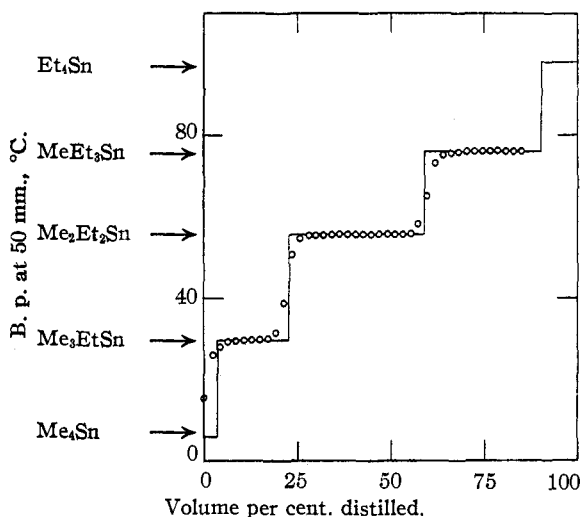

Fig. 4.—Distillation of the reaction product from Me₄Sn + Et₄Sn. Solid line calculated for random equilibrium mixture having [Me] = 0.46.

completed, is ample evidence for the agreement with theory in this case. In the particular experiment with two metals illustrated by Fig. 5, the separation and analysis of the various fractions was not rigorous, and as a result the over-all composition was not known with certainty. Hence, the ideal distillation curve is not given, but the results are considered adequate to indicate the presence of all ten possible compounds.

As the care and accuracy of the analyses increase the agreement with theory becomes more exact, and is within the experimental error of less than 1%.[7]
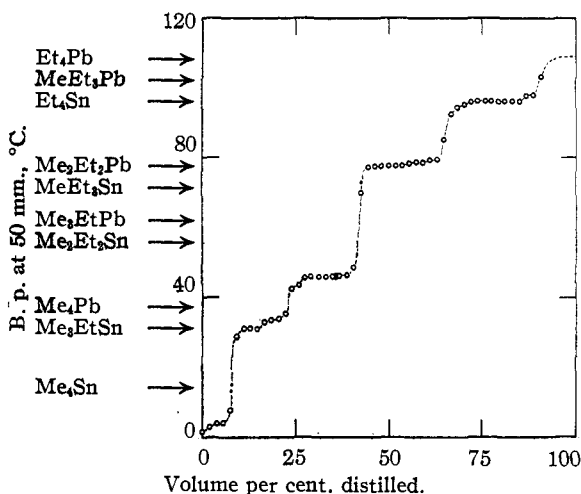

Fig. 5.—Distillation of the reaction product from Me₄Sn + Et₄Pb (experimental curve only).

Discussion.—It is worthy of emphasis that, although organo-metallic compounds have been used for illustration here, the redistribution reaction is not limited to this field. The content of the present paper is designed to serve only as a general presentation of the subject, and subsequent contributions will cover, individually, specific points of interest in both organo-metallic compounds and other fields. Although we are not prepared to consider the scope of this reaction and its implications at this time, a few salient points may be mentioned here.

While the mechanism of the reaction clearly involves atoms and radicals, it is evident, from common knowledge of the conditions under which free atoms or radicals exist, that these are not present as such. Free radicals, of the kinds to be expected here, if liberated in a liquid phase would result in the formation of a variety of secondary products which are totally absent in the present reaction. Dissociation into ionized radicals also appears improbable, especially for the halogen-free alkyls; in accord with this, solvents are not required and, if added, do not appear to influence the reaction proper.

Accordingly, a mechanism involving the formation of molecular complexes or coördination compounds with the catalyst is indicated. The catalysts used are such as can be converted, in the reaction mixture, into the form of organic or

organo-metallic compounds which contain the radicals to be interchanged. Then the possibility is evident for the interchange to occur when the reactants and the catalyst are united together in a complex.
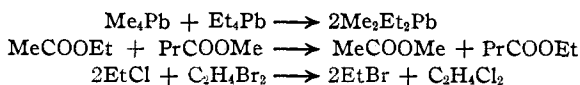
While the molecular activation required to form such complexes might be anticipated as the result of the action of powerful catalysts such as aluminum chloride, it would hardly have been expected with catalysts such as trialkyllead halides. Moreover, in some of the metal aryls at higher temperatures there is a spontaneous interchange of radicals without the presence of any catalyst, suggesting that the catalyst merely accelerates a process, the possible occurrence of which is inherent in the reactants themselves. This argues for a considerably greater flexibility of the covalent bonds in the metal alkyls and aryls than would commonly be assigned to compounds of their structure and chemical stability, and it is not evident how this can be ascribed to the existence of mesomeric or electromeric forms or to a state of resonance.

Information as to the relative mobilities or reactivities of the radicals, and as to the preferential association between different central atoms and radicals, can be obtained in one and the same system, when more than two different radicals or more than one central atom are present. Even when only one central group and two kinds of radicals are employed, the formation of random equilibrium mixtures implies that the energy of formation of the different compounds in each system is a linear function of the molecular weight, and (surprisingly) is not affected by the symmetry (or asymmetry) of the molecules. For example, the energy of formation of one mole each of tetramethyllead and tetraethyllead is equal to that of one mole each of trimethylethyllead and methyltriethyllead.

For studies of reaction kinetics in the liquid phase, catalyzed reactions such as described here, which reach an equilibrium in a measurable time and are free from side reactions and specific solvent effects, are particularly suitable. Also, the occurrence of two or more simultaneous reactions in such systems as R_4M or R_3M permits

an internal check on the relative rates of the different reactions, regardless of the absolute rates, and this in turn provides a distinctive method of approach to the determination of the reaction mechanism.

In addition to opening up avenues of theoretical investigation, the redistribution reaction is adaptable as a new method of organic synthesis. As one illustration, metathesis can now be induced directly between similar compounds which are usually inert to one another, such as esters; more broadly, mixed compounds, such as mixed esters of polybasic acids, mixed polyhalides, and mixed organic compounds of polyvalent metals, can be prepared by direct metathetical reactions which may afford a considerable saving of time and material over the classical step-wise methods. A few examples of this type are

$$Me_4Pb + Et_4Pb \longrightarrow 2Me_2Et_2Pb$$
$$MeCOOEt + PrCOOMe \longrightarrow MeCOOMe + PrCOOEt$$
$$2EtCl + C_2H_4Br_2 \longrightarrow 2EtBr + C_2H_4Cl_2$$

Here the arrows indicate a suitable combination of reaction, separation, and re-cycle processes.

Summary

A hitherto unrecognized type of reaction is described, in which all the radicals or atoms of one kind, present in a mixture in which they are linked to one or more central groups or atoms of another kind, are interchanged between all the central groups present. This process, which is termed the "Redistribution Reaction," takes place smoothly at low temperatures in the liquid phase under the influence of a catalyst. The yield is quantitative, and the composition of the resultant mixture can be calculated from that of the reactants on the basis of a random distribution of the interchanged radicals or atoms: this reaction product is therefore termed a "Random Equilibrium Mixture." The reaction presents interesting possibilities for theoretical investigation into the nature and behavior of covalent bonds and the mechanism and kinetics of their reactions; also, the reaction provides novel methods of preparation of various organic compounds.