

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL GASOLINE CORPORATION]

The Redistribution Reaction. II. The Analysis of Metal Alkyl Mixtures and the Confirmation of Random Distribution

BY GEORGE CALINGAERT, HAROLD A. BEATTY AND HERBERT R. NEAL

In the previous paper of this series¹ it was stated that the analysis of mixtures of organo-metallic compounds which had undergone the redistribution reaction showed that the composition of the product obtained corresponded to a random distribution of the interchanged radicals. The present paper describes the analytical method used for the volatile metal alkyls, including a test of its accuracy, and gives a quantitative demonstration of this random distribution. The corresponding analytical methods and results obtained for organo-metallic halide mixtures will be given in a subsequent paper.

The Accuracy of Analysis.—From an estimation of the precision of the various analytical observations and of other sources of error, it was concluded that the absolute accuracy obtainable for a mixture of volatile metal alkyls should be close to 1% for each constituent. This conclusion was tested as follows. Two different mixtures of the five methyl and ethyl tetraalkyllead compounds were prepared—one containing about equal amounts of each compound, the other having about the composition of a random equilibrium mixture containing equal proportions of methyl and ethyl radicals. These mixtures were made up by one experimenter, by volume, from the pure individual compounds, and the volumetric summation was checked by comparison of the total net weight with that calculated from the densities of the compounds. The entire mixtures were each analyzed by another experimenter, using the procedure described below. The results, given in Table I, confirm the predicted accuracy, and indicate that the errors are independent of the volatility or concentration of the constituent; the standard deviation between the taken and observed values for the entire group of ten values was 0.6%, and the maximum deviation was 0.7%.

Confirmation of Random Distribution.—Most of the data suitable for comparison with the compositions predicted for random distribution were obtained for mixtures of the methyl and ethyl tetraalkyllead compounds. The data in Table

| Compound | Volume, ml. | | Taken | Volume, % | | Error |
|--|-------------|-------|-------|-----------|-------|-------|
| | Taken | Found | | Found | Found | |
| Test no. 1 | | | | | | |
| Me ₄ Pb | 13.00 | 12.3 | 20.60 | 19.9 | | -0.7 |
| Me ₃ EtPb | 12.49 | 12.7 | 19.79 | 20.5 | | .7 |
| Me ₂ Et ₂ Pb | 12.00 | 12.1 | 19.01 | 19.6 | | .6 |
| MeEt ₃ Pb | 12.30 | 12.0 | 19.49 | 19.4 | | -.1 |
| Et ₄ Pb | 13.32 | 12.7 | 21.11 | 20.5 | | -.6 |
| Total | 63.11 | 61.8 | | | | |
| Weight, g., calcd., 114.04; found, 114.01 | | | | | | |
| Test no. 2 | | | | | | |
| Me ₄ Pb | 2.90 | 2.5 | 4.77 | 4.15 | | -0.6 |
| Me ₃ EtPb | 14.51 | 14.8 | 23.86 | 24.6 | | .7 |
| Me ₂ Et ₂ Pb | 23.80 | 23.4 | 39.14 | 38.85 | | -.3 |
| MeEt ₃ Pb | 15.00 | 14.5 | 24.67 | 24.1 | | -.6 |
| Et ₄ Pb | 4.60 | 5.0 | 7.56 | 8.3 | | .7 |
| Total | 60.81 | 60.2 | | | | |
| Weight, g., calcd., 108.96; found, 108.98. | | | | | | |

II were selected as the best of a large number of analyses of these mixtures, the basis of the selection being solely the appearance of the plotted distillation curve together with freedom from known unusual sources of error or other complications. Of this group so selected, one analysis was discarded as being statistically out of line with the remainder.

The mole fraction of methyl and ethyl radicals in the mixture is denoted, respectively, by r and $(1 - r)$. The value of r was, in many cases, not known in advance; accordingly, it was calculated in each case from the result of the analysis by means of the equation

$$r = [\text{Me}_4\text{Pb}] + 0.75[\text{Me}_3\text{EtPb}] + 0.5[\text{Me}_2\text{Et}_2\text{Pb}] + 0.25[\text{MeEt}_3\text{Pb}]$$

where the brackets denote the concentration in mole fraction. The predicted mole fractions of the five tetraalkyllead compounds are

$$\begin{array}{ccccc} \text{Me}_4\text{Pb} & \text{Me}_3\text{EtPb} & \text{Me}_2\text{Et}_2\text{Pb} & \text{MeEt}_3\text{Pb} & \text{Et}_4\text{Pb} \\ r^4 & 4r^3(1-r) & 6r^2(1-r)^2 & 4r(1-r)^3 & (1-r)^4 \end{array}$$

Inspection of the differences shown in Table II indicates that, like those in Table I, they are scattered at random and do not appear to be a function of the compounds or of their concentrations or of r , the mole fraction of methyl radicals. Moreover, there is no statistically

(1) Calingaert and Beatty, *THIS JOURNAL*, 61, 2748 (1939).

TABLE II
 ANALYSIS OF RANDOM EQUILIBRIUM MIXTURES FOR METHYL-ETHYLLEAD ALKYLs

| r | Me ₂ Pb | | | Me ₂ EtPb | | | Composition, mole per cent. | | | | | | | | |
|---------------|--------------------|--------|-------|----------------------|--------|-------|------------------------------------|------|-------|----------------------|------|-------|--------------------|------|------|
| | Found | Calcd. | Diff. | Found | Calcd. | Diff. | Me ₂ Et ₂ Pb | | | MeEt ₃ Pb | | | Et ₄ Pb | | |
| 0.205 | 0.0 | 0.2 | -0.2 | 2.8 | 2.7 | +0.1 | 16.1 | 15.9 | +0.2 | 41.3 | 41.2 | +0.1 | 39.8 | 40.0 | -0.2 |
| .258 | .2 | .4 | -.2 | 4.7 | 5.1 | -.4 | 22.5 | 22.0 | + .5 | 43.4 | 42.2 | +1.2 | 29.2 | 30.3 | -1.1 |
| .325 | .8 | 1.1 | -.3 | 8.7 | 9.3 | -.6 | 29.5 | 28.9 | + .6 | 41.6 | 40.0 | +1.6 | 19.4 | 20.7 | -1.3 |
| .329 | 1.5 | 1.2 | + .3 | 8.8 | 9.5 | -.7 | 29.5 | 29.2 | + .3 | 40.2 | 39.8 | +0.4 | 20.0 | 20.3 | -0.3 |
| .340 | 1.7 | 1.3 | + .4 | 9.3 | 10.4 | -1.1 | 31.1 | 30.2 | + .9 | 39.0 | 39.1 | -.1 | 18.9 | 19.0 | -.1 |
| .463 | 5.3 | 4.6 | + .6 | 20.2 | 21.3 | -1.1 | 37.6 | 37.1 | + .5 | 28.6 | 28.7 | -.1 | 8.4 | 8.3 | + .1 |
| .667 | 19.2 | 19.8 | -.6 | 40.7 | 39.5 | +1.2 | 29.1 | 29.6 | -.5 | 9.8 | 9.9 | -.1 | 1.2 ^a | 1.2 | 0 |
| .737 | 29.3 | 29.5 | -.2 | 42.5 | 42.1 | +0.4 | 22.5 | 22.5 | 0 | 5.2 | 5.4 | -.2 | 0.5 ^a | 0.5 | 0 |
| Mean | | | -.025 | | | -.275 | | | + .31 | | | + .35 | | | -.36 |
| Standard dev. | | | .44 | | | .85 | | | .54 | | | .72 | | | .66 |

^a Estimated from the total of MeEt₃Pb + Et₄Pb.

significant difference between the results given in Tables I and II. It appears, therefore, that the differences in Table II can be ascribed solely to experimental error. In contrast to these small differences are the large effects resulting from a change in the relative proportions of methyl and ethyl radicals, as can be seen by

 TABLE III
 ANALYSIS OF RANDOM EQUILIBRIUM MIXTURES FOR OTHER SYSTEMS

The mole fraction of the first of the two radicals cited is denoted by r . The data are given in mole per cent.

System: Me₄Sn + Et₄Sn; $r = 0.459$

| Compd. | Found | Calcd. | Diff. |
|------------------------------------|-------|--------|-------|
| Me ₄ Sn | | 4.4 | |
| Me ₃ EtSn | 24.6 | 20.9 | -0.7 |
| Me ₂ Et ₂ Sn | 38.4 | 37.0 | 1.4 |
| MeEt ₃ Sn | 28.6 | 29.1 | -0.5 |
| Et ₄ Sn | 8.4 | 8.6 | -.2 |

System: C₂H₄Cl₂ + C₂H₄Br₂; $r = 0.467$

| Compd. | Found | Calcd. | Diff. |
|---|-------|--------|-------|
| C ₂ H ₄ Cl ₂ | 23.0 | 21.8 | 1.2 |
| C ₂ H ₄ ClBr | 47.4 | 49.8 | -2.4 |
| C ₂ H ₄ Br ₂ | 29.6 | 28.4 | 1.2 |

System: Et₄Si + Pr₄Si; $r = 0.464$

| Compd. | Found | Calcd. | Diff. |
|------------------------------------|-------|--------|-------|
| Et ₄ Si | 4.5 | 4.6 | -0.1 |
| Et ₃ PrSi | 21.3 | 21.4 | -.1 |
| Et ₂ Pr ₂ Si | 39.6 | 37.1 | 2.5 |
| EtPr ₃ Si | 24.3 | 28.6 | -4.3 |
| Pr ₄ Si | 10.3 | 8.3 | 2.0 |

System: Me₂Hg + Et₂Hg; $r = 0.486$

| Compd. | Found | Calcd. | Diff. |
|--------------------|-------|--------|-------|
| Me ₂ Hg | 25.5 | 23.6 | 1.9 |
| MeEtHg | 46.1 | 50.0 | -3.9 |
| Et ₂ Hg | 28.4 | 26.4 | 2.0 |

System: CH₃COOMe + C₃H₇COOEt; [CH₃CO] = 0.50; [OMe] = 0.45^a

| Compd. | Found | Calcd. | Diff. |
|-------------------------------------|-------|--------|-------|
| CH ₃ COOMe | 25.4 | 22.5 | 2.9 |
| CH ₃ COOEt | 23.4 | 27.5 | -4.1 |
| C ₃ H ₇ COOMe | 22.7 | 22.5 | 0.2 |
| C ₃ H ₇ COOEt | 28.5 | 27.5 | 1.0 |

^a The [OEt] was augmented by the Al(OEt)₃ used as catalyst.

comparing the calculated compositions for different values of r in Table II, or by referring to Fig. 1 in the preceding paper.¹ The confirmation of the randomness of the redistribution, for this system of lead compounds at least, is evident.

Quantitative data for some of the other systems tested are given in Table III. These data were mostly of a somewhat lower order of analytical accuracy than those given above, and it is seen that the deviations from the predicted values are considerably greater. However, the deviations appear to be well scattered and random, and show no statistically significant trends, and it may justifiably be concluded that in these cases also there is no deviation from the random distribution outside of the experimental error in each.

Experimental Method and Procedure.—The relative proportions of the various metal alkyls present in a given mixture were determined by fractional vacuum distillation, after removal of the catalyst and halide salts (if any) by filtration and washing or extraction. Standard distillation practice was followed, with adaptations appropriate to the particular mixtures.

The equipment used, shown schematically in Fig. 1, comprised a small fractionating column, vacuum jacketed and electrically heated; a 100-ml. three-necked distilling flask, fitted with a nitrogen inlet tube and heated with an oil-bath; a still head, fitted with a thermometer, and partial or total condenser; a graduated receiver kept in a transparent Dewar-flask cooling bath; an additional trap kept in a dry-ice-bath; together with a vacuum pump, an adjustable mercury U-tube pressure regulator, manometers for normal and low pressures, a controlled nitrogen supply, and other usual accessory equipment.

The column, 32 cm. long and 14 mm. i. d., was packed with 4.76-mm. (³/₁₆-in.) filed aluminum balls.² The still head was designed to reduce the dead space to a minimum, using a partial condenser, but better results were obtained with only a slight increase in hold-up, by using a total con-

(2) This packing is prepared by rubbing the balls between 6-in. (15-cm.) circular flat steel files. It has a fairly low H. E. T. P., a very low hold-up, and high maximum throughput.

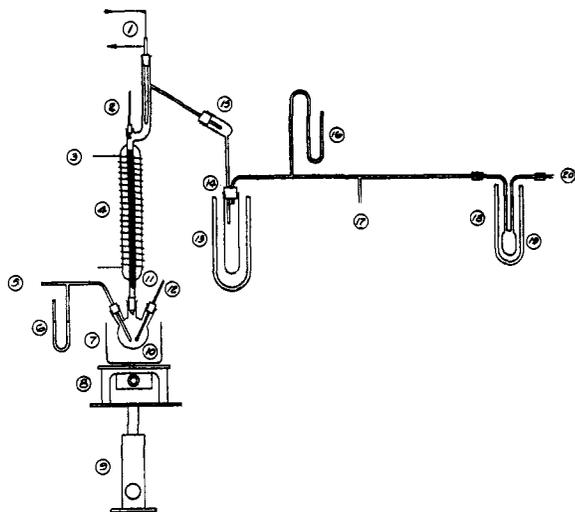


Fig. 1.—Distillation equipment: 1, condenser with regulated water flow; 2, thermometer, range 30–90°; 3, jacket heating wire; 4, evacuated glass jacket; 5, nitrogen inlet; 6, manometer; 7, oil-bath; 8, hot plate; 9, movable platform; 10, 100-ml. flask; 11, 14-mm. i. d. column with 32 cm. of filed aluminum ball packing; 12, thermometer; 13, unsilvered Dewar flask and bath at –30°; 14, 80-ml. graduated receiver; 15, adapter; 16, low-pressure manometer; 17, nitrogen inlet; 18, Dewar flask and bath at –75°; 19, trap; 20, line to pressure regulator, high-pressure manometer, and exhaust.

denser and controlling the delivery of product by the adjustment of a grooved stop-cock. Reflux ratios, and also the correct heating current for the column jacket, were estimated by counting drops. The graduated receiver was kept at about –30° in a trichloroethylene bath with dry-ice. All liquid volumes were corrected to 20° by an arbitrary temperature coefficient of 0.1% per degree. Since the temperature of observation, as well as the true temperature coefficient, was usually almost identical for all the distillate, this arbitrary procedure produced only negligible errors. The pressure was lowered at intervals during the progress of the distillation, and the temperature and level of the heating bath were adjusted, so as to maintain a temperature in the neighborhood of 50–75° at the still head, thus minimizing the thermal decomposition of the higher-boiling metal alkyls. The reflux ratio was maintained at about 5 to 1 over the flat portions of the distillation curves, and was increased to about 10 to 1 at the point of separation between compounds.

The observed temperatures at any given pressure were converted to a common basis of 50 mm. pressure. Inspec-

TABLE IV
VAPOR PRESSURES OF LEAD ALKYLs
 $\text{Log}_{10} P$ (mm. Hg) = $A - B/(t + 230)$; $t = ^\circ\text{C}$.

| Compound | A | B | t at 50 mm., $^\circ\text{C}$. |
|------------------------------------|--------|--------|-----------------------------------|
| Me ₄ Pb | 6.9381 | 1378.7 | 33.2 |
| Me ₃ EtPb | 7.2760 | 1602.5 | 57.3 |
| Me ₂ Et ₂ Pb | 7.5903 | 1810.7 | 77.4 |
| MeEt ₃ Pb | 7.8768 | 2000.5 | 93.8 |
| Et ₄ Pb | 8.1547 | 2184.6 | 108.4 |

tion of vapor pressure data for the five methyl and ethyl tetraalkyllead compounds, obtained from the literature and in this Laboratory, showed that the vapor pressures are given very accurately by the five equations in Table IV which have a common point of intersection³ at $\log P = 4.8566$ and $1/(t + 230) = 0.0015097$, where $t = ^\circ\text{C}$.

The assumption was made that any other similar metal alkyl (or mixture) would have a similar vapor pressure line passing through the same point of intersection. Accordingly a nomogram was constructed to give the temperature at 50 mm. pressure corresponding to any observed pressure and temperature.

The distillation data were plotted to give the volume of distillate corrected to 20° as a function of the temperature corrected to 50 mm. pressure. Good curves usually were obtained and the identity of the distillate over the various flat portions of the curve as a rule was defined beyond question by the nature of the materials taken for the reaction. In these cases the volume of each constituent in the distillate was estimated by dividing the distillation curve into segments at points halfway between the boiling points (at 50 mm.) of the various compounds. While such a method of division is theoretically not strictly accurate, the errors so introduced are very small, and the personal equation is eliminated.

In those cases where the composition of the distillate over each portion of the curve was not unequivocally known (for example, in the product from a mixture of tetramethyltin and tetraethyllead, or in cases where a solvent might also be present), the distillate was taken in separate cuts which were analyzed for the metals present by conventional methods. When most of the charge had been distilled, and no further fractionation was possible, the distillation was stopped, the column allowed to drain, and the volume of residue measured. This volume was taken to consist solely of the highest-boiling constituent, when no other than that one constituent was conceivably present; otherwise, it was taken to comprise all the possible remaining constituents.

From the volumes of the constituents and their known

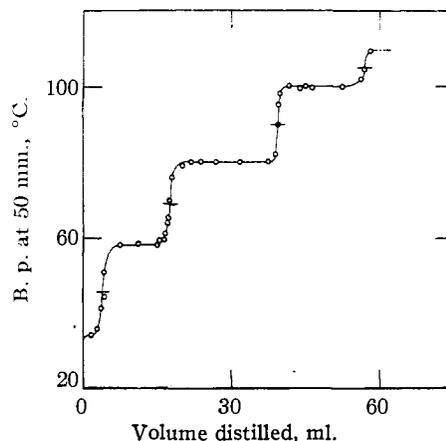


Fig. 2.—Typical distillation curve: —points of division between compounds; ---undistilled residue.

(3) Calingaert and Davis, *Ind. Eng. Chem.*, **17**, 1287 (1925).

densities and molecular weights, the mole fractions of each component of the metal alkyl portion of the product were calculated. In those relatively few cases where two or three components were expected to be present in the resi-

TABLE V
ANALYSIS OF A TETRAALKYLLEAD MIXTURE

| Pressure, mm. | Vapor temp. | | Distillate | |
|------------------|-------------|--------------------|-----------------------|----------------------|
| | Obsd. | Corr. to 50 mm. | Vol. obsd. at -30° | Vol. corr. to 20° |
| 60 | 38.5 | 34.8 | 1.5 | 1.5 |
| | 41.6 | 37.5 | 3.2 | 3.3 |
| | 45.4 | 41.8 | 3.6 | 3.7 |
| 33 | 40.0 | 49.0 | 4.2 | 4.4 |
| | 45.2 | 54.2 | 5.0 | 5.2 |
| | 46.5 | 55.9 | 5.5 | 5.7 |
| | 47.0 | 56.1 | 7.5 | 7.8 |
| 32 | 47.4 | 56.4 | 11.0 | 11.5 |
| | 47.2 | 57.0 | 13.0 | 13.6 |
| | 48.5 | 58.2 | 15.6 | 16.3 |
| | 53.0 | 63.0 | 16.3 | 17.1 |
| 11 | 36.6 | 67.0 | 17.0 | 17.8 |
| | 42.5 | 73.3 | 17.3 | 18.1 |
| | 45.5 | 76.5 | 19.2 | 20.1 |
| | 46.3 | 77.2 | 21.0 | 22.0 |
| | 46.0 | 77.0 | 26.0 | 27.3 |
| | 46.0 | 77.0 | 33.0 | 34.6 |
| | 46.0 | 77.0 | 36.0 | 37.8 |
| 5.5 | 50.5 | 81.3 | 37.8 | 39.6 |
| | 45.0 | 88.2 | 38.7 | 40.6 |
| | 49.4 | 93.0 | 39.5 | 41.4 |
| | 49.5 | 93.0 | 42.0 | 44.1 |
| | 49.5 | 93.0 | 44.3 | 46.5 |
| | 50.5 | 94.0 | 49.0 | 51.4 |
| | 50.4 | 94.0 | 52.6 | 55.2 |
| | 52.5 | 96.0 | 54.0 | 56.7 |
| 4.5 | 54.4 | 98.0 | 54.2 | 56.9 |
| | 59.4 | 103.2 | 54.5 | 57.2 |
| | 59.0 | 106.5 | 56.0 | 58.8 |

| Compound | Cut points, ml. | Vol., ml. | Milli- mole | Mole, % |
|------------------------------------|--------------------|--------------|----------------|------------|
| Solvent | 0 | | | |
| Me ₃ Pb | 1.5 | 2.7 | 20.1 | 5.5 |
| Me ₃ EtPb | 4.2 | 13.4 | 89.6 | 24.4 |
| Me ₂ Et ₂ Pb | 17.6 | 22.9 | 138.9 | 37.8 |
| MeEt ₃ Pb | 40.5 | 16.7 | 92.6 | 25.2 |
| Et ₄ Pb dist. | 57.2 | 5.1 | 26.1 | 7.1 |
| Et ₄ Pb residue | 59.8 | | | |
| | 62.3 | | | |

$$[\text{Me}] = 0.055 + (0.75 \times 0.244) + (0.5 \times 0.378) + (0.25 \times 0.252) = 0.490.$$

due, a reasonable estimate of each was made; inasmuch as the amounts of these involved were always small and their various molecular volumes did not differ greatly, this procedure introduced no significant uncertainty in computation of the total amount of each kind of metal and alkyl group present.

The observed and derived data and the distillation curve for a typical example of a satisfactory analysis of a mixture of the five methyl and ethyl tetraalkyllead compounds are given in Table V and Fig. 2.

Summary

The procedure used for the analysis of volatile metal alkyl mixtures by distillation is described, and is shown by tests to give results accurate to less than 1% of the total volume.

Analyses of a series of mixtures of methyl and ethyl lead alkyls which have undergone the redistribution reaction show, within this experimental error, exact agreement with the compositions predicted for random equilibrium mixtures; individual analyses for other systems are also in satisfactory accord with prediction.

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The Redistribution Reaction. III. Determination of a Material Balance

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The first paper¹ of this series reported, as a distinctive characteristic of the redistribution reaction, its essential freedom from side reactions and decomposition. This was evidenced, for many different systems, by the absence of gas evolution, precipitation, tar formation, or heat of reaction, and by satisfactory recoveries of material. To provide a quantitative measure of this, for one case at least, the present work was undertaken, and consisted in carrying out a representative redistribution reaction in the usual

manner, obtaining an accurate material balance, and testing for secondary products.

Such a determination can be made with a high degree of accuracy for a reaction involving tetraalkyllead compounds, since any side reactions will convert the lead to other forms, which can be separated readily from the tetraalkyllead compounds constituting the bulk of the reaction mass. Accordingly, a mixture of tetramethyl- and tetraethyllead was used for this test.

Table I gives the material balance on a lead basis for two tests in which a mixture of the two

(1) Calingaert and Beatty, *THIS JOURNAL*, **61**, 2748 (1939).