tances in potassium iodate and iodine pentafluoride are assumed to be even approximately correct then it would seem evident that two cases must be distinguished. If a vacant orbital exists in the coördination polyhedron, the unshared pair may occupy that orbital and its effect on the iodine radius will be small and may be correlated with the formal charge on the central atom. If no such vacant orbital exists, then the extra electrons become an "inert pair" having no steric effect, but causing a relatively large increase in the iodine radius.

The Structure.—The coördination of oxygen and fluorine atoms about potassium is irregular but it is probable that the packing of the $IO_2F_2^-$ groups is the determining factor in the structure. The K–O and K–F contacts are: $O_I - K = 2.75$, 2.76 Å.; $O_{II} - K = 2.63, 3.03$ Å.; $F_I - K = 2.64$, 3.06 Å.; $F_{II} - K = 2.74, 3.04$ Å.

The interatomic distances which are less than 3.50 Å. between oxygen and fluorine atoms of different anion groups are: $F_I - F_{II} = 2.77, 3.23$ Å.; $F_I - O_{II} = 3.40$ Å.; $F_{II} - O_I = 3.24$ Å.

There are, in addition, two distances between iodine atoms and oxygen atoms in different $IO_2F_2^-$ groups that are shorter than three Ångströms: $I-O_I = 2.82$ Å.; $I-O_{II} = 2.88$ Å.

The similarity between this structure and that reported for potassium iodate may be seen if one considers an altered KIO_2F_2 in which the I–O contacts just mentioned are made real bonds so that each oxygen atom is shared between two iodine atoms. If, then, the iodine atoms and bonds to oxygen atoms are placed in the x–z plane, then

this plane will be identical with a plane $z = 0$ for the potassium iodate structure. In this altered structure the I–F bonds will be in a vertical position along the lines $x = z = 0$, etc. If now one atom of oxygen is substituted for two atoms of fluorine and this atom shared between two iodine atoms the structure would become the cubic structure attributed to potassium iodate. It is suggested that the similarity, although not very great, is sufficient to cause the orientation effects observed on photographs of KIO_2F_2 in which some of the salt had hydrolyzed. The powder lines had quite definite maxima at positions corresponding to the equator and layer lines for potassium iodate oriented with the cube edges parallel to the orthorhombic axes of KIO_2F_2.

Summary

From a determination of the crystal structure of KIO_2F_2 it has been found that the $IO_2F_2^-$ group is composed of an iodine atom forming bonds at approximately 100° with two oxygen atoms, and perpendicular to the plane of these three atoms, two opposed bonds at 180° to fluorine. The configuration may perhaps best be thought of as that of a trigonal bipyramid in which one of the three equivalent orbitals is occupied by an unshared electron pair. The interatomic distances in the ion were found to be: $I - O = 1.93 \pm 0.05$ Å.; $I - F = 2.00$ Å. ± 0.05 Å. The O–I–O bond angle $= 100 \pm 10°$. The influence of the unshared pair on the bond distance is discussed.

The Redistribution Reaction. VIII. The Relative Affinity of Mercury and Lead for Methyl and Ethyl Radicals

BY GEORGE CALINGAERT, HAROLD SOROOS AND GEORGE W. THOMSON

Previous papers[1,2] of this series have described the redistribution reaction for the interchange of alkyl radicals in alkyl compounds of lead, tin, silicon, or mercury. Redistribution of alkyl groups is not confined to systems containing a single metal, but under suitable conditions can take place between compounds of more than one metal. This was illustrated in the first paper[1]

of this series by an analytical distillation[3] curve for the reaction product of tetramethyltin with tetraethyllead, which indicated the presence of all ten possible R_4M compounds.

The fact that the equilibrium composition of a redistributed mixture corresponds to a random distribution of all the organic radicals present indicates that the relative affinity of a given radical for a given metal is independent of the

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

(2) Calingaert, Beatty and Soroos, *ibid.*, **62**, 1099 (1940); Calingaert, Soroos and Hnizda. *ibid.*. **62**, 1107 (1940).

(3) Calingaert, Beatty and Neal, *ibid.*, **61**, 2755 (1939).

nature of the other radicals attached to the metal. When two metals, for example mercury and lead, are present in the system, the same should still hold true for each metal separately, but it does not follow that the different radicals, for example methyl and ethyl, should be divided equally between the two metals. If the affinity of the methyl radicals, relative to that of the ethyl radicals, is greater for mercury than for lead, then the R_2Hg compounds will contain a greater proportion of methyl than the R_4Pb compounds. Based on the law of mass action, this difference in relative affinity can be expressed by a "relative affinity constant," K, whose value is given by $K = [\text{Me-Hg}][\text{Et-Pb}]/[\text{Et-Hg}][\text{Me-Pb}]$, where the brackets denote the proportions of the four different R-M bonds in the total product.

The above example is particularly suitable for experimental study, first, since it includes two dissimilar metals of different valence, for each of which alone the redistribution reaction is known[2] to occur readily, giving random equilibrium mixtures, and, second, since its reaction product is of such nature as to facilitate an accurate analysis.[3] Accordingly, two tests were made, one with a mixture of tetramethyllead and diethylmercury, the other with tetraethyllead and dimethylmercury, each mixture containing equal proportions of methyl and ethyl radicals, and equivalent amounts of mercury and lead. Both mixtures, with aluminum chloride as the catalyst, underwent redistribution at 80° in five hours. The results are given in Tables I–III, and the distillation curves for the reaction products are shown in Fig. 1.

The data show that: (1) the recovery of each metal was quantitative, exclusive of handling losses resulting from filtration and transfer of

TABLE I

REDISTRIBUTION OF TETRAMETHYLLEAD AND DIETHYLMERCURY: DISTILLATION AND ANALYTICAL DATA

	Fraction	B. p. (50 mm.) up to	Lead Content			Mercury Content			
No.	Wt., g.		Wt. %	Wt., g.	Mmoles.	Wt. %	Wt., g.	Mmoles.	Composition assumed from b. p.
1	91.72	31.5	0.315	0.288	1.39	85.51	78.430	390.96	Me$_4$Pb; Me$_2$Hg
2	9.27	50.5	4.06	0.376	1.81	78.05	7.235	36.07	Me$_4$Pb; MeEtHg
3	96.76	54.0	5.855	5.665	27.34	74.16	71.757	357.69	Me$_3$EtPb; MeEtHg
4	12.45	75.0	19.45	2.422	11.69	58.20	7.246	36.12	Me$_2$Et$_2$Pb; MeEtHg; Me$_3$EtPb; Et$_2$Hg^a
5	53.83	78.5	45.95	24.735	119.37	26.62	14.330	71.43	Me$_2$Et$_2$Pb; Et$_2$Hg
6	43.58	94.0	65.34	28.475	137.42	2.02	0.880	4.39	Me$_2$Et$_2$Pb; MeEt$_3$Pb; Et$_2$Hg^b
7	23.53	99.5	66.42	15.629	75.43	0.28	0.0659	0.33	MeEt$_3$Pb; Et$_4$Pb; Et$_2$Hg^b
8	24.61	..	62.81	15.458	74.60	0.135	0.0332	0.16	Et$_4$Pb; Et$_2$Hg
9	Column washings			0.027	0.13				Et$_4$Pb
	Total				449.18			897.15	

^{a} Estimated composition for each metal is 50% of each of the two alkyls present. ^{b} Composition determined assuming that the fraction is 100% metal alkyl.

TABLE II

REDISTRIBUTION OF TETRAETHYLLEAD AND DIMETHYLMERCURY: DISTILLATION AND ANALYTICAL DATA

	Fraction	B. p. (50 mm.) up to	Lead Content			Mercury content			
No.	Wt., g.		Wt. %	Wt., g.	Mmoles.	Wt. %	Wt., g.	Mmoles.	Composition assumed from b. p.
1	92.20	21.0	0.14	0.129	0.62	83.283	76.787	382.77	Me$_2$Hg; Me$_4$Pb
2	19.80	49.0	1.81	0.358	1.73	82.83	16.400	81.75	Me$_2$Hg; MeEtHg; Me$_4$Pb; Me$_3$EtPb^{a,b}
3	101.86	57.5	5.795	5.903	28.49	75.085	76.482	381.25	MeEtHg; Me$_3$EtPb
4	5.53	76.0	27.40	1.515	7.31	49.35	2.729	13.60	MeEtHg; Et$_2$Hg; Me$_3$EtPb; Me$_2$Et$_2$Pb^{a,b}
5	55.19	80.4	43.17	23.826	114.98	30.087	16.605	82.77	Et$_2$Hg; Me$_2$Et$_2$Pb
6	5.34	93.0	61.63	3.291	15.88	7.775	0.415	2.07	Et$_2$Hg; Me$_2$Et$_2$Pb; MeEt$_3$Pb^b
7	52.36	95.3	66.445	34.791	167.90	0.375	.196	0.98	Me$_2$Et$_2$Pb; MeEt$_3$Pb
8	36.22	109.0	64.525	23.371	112.79	0.15	.054	0.27	MeEt$_3$Pb; Et$_4$Pb
9	Column washings			2.16	10.42				Et$_4$Pb
	Total				460.12			945.46	

^{a} Estimated composition for lead alkyl is 50% of each of the two present. ^{b} Composition determined assuming that the fraction is 100% metal alkyl.

TABLE III

COMPOSITION OF REACTION PRODUCTS

Compound	From Me$_4$Pb + Et$_2$Hg Milli-moles	Mole per cent. Found	Calcd.[a]	From Et$_4$Pb + Me$_2$Hg Milli-moles	Mole per cent. Found	Calcd.[a]
Me$_4$Pb	3.2	0.7	1.0	1.5	0.3	0.8
Me$_3$EtPb	33.2	7.4	8.9	33.0	7.2	7.8
Me$_2$Et$_2$Pb	130.7	29.1	28.3	126.4	27.5	26.8
MeEt$_3$Pb	199.8	44.5	40.3	199.7	43.4	41.0
Et$_4$Pb	82.3	18.3	21.5	99.5	21.6	23.6
Total	449.2	100.0	100.0	460.1	100.0	100.0
Me$_2$Hg	391.0	43.6	44.3	430.9	45.6	46.1
MeEtHg	411.8	45.9	44.5	422.0	44.6	43.6
Et$_2$Hg	94.4	10.5	11.2	92.6	9.8	10.3
Total	897.2	100.0	100.0	945.5	100.0	100.0
Methyl, %						
in R$_4$Pb		31.9			30.3	
in R$_2$Hg		66.5			67.9	
overall		49.2			49.3	
% R—Hg bonds		50.0			50.7	
Relative affinity constant K		4.2			4.9	

[a] Calculated[1] from % methyl found.

material, and there was no appreciable decomposition. Also, the over-all per cent. methyl in the product equalled that of the input, within experimental error. (2) The over-all equilibrium was completely attained, since the same product was obtained starting with either pair of metal alkyls. (3) Each metal yielded a random equilibrium mixture. (4) The per cent. methyl (67.2 ± 0.7) in the mercury alkyls was about twice that in the lead alkyls, corresponding to a marked difference in relative affinity of mercury
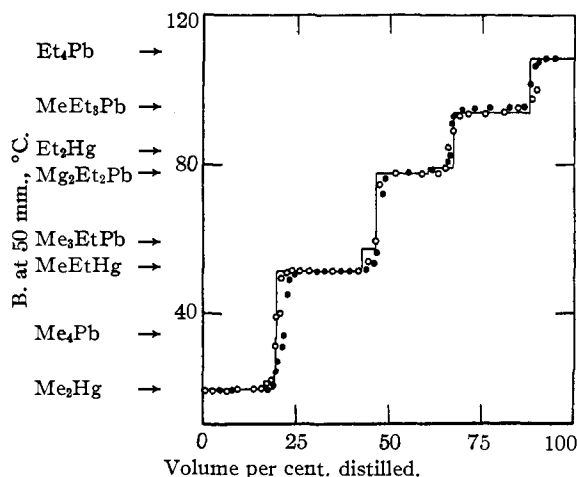

Fig. 1.—Distillation of reaction product from: ○— Me$_4$Pb + Et$_2$Hg; ●—Et$_4$Pb + Me$_2$Hg. Solid line calculated for random equilibrium mixtures, with 50.0% R-Hg and 50.0% R-Pb bonds, and with a total of 49.3% Me radicals, 33.3% Me-Hg and 16.0% Me-Pb,

and lead for methyl with respect to ethyl radicals. (5) The numerical values of K (as defined above) of 4.2 and 4.9 are in excellent agreement, in view of the sensitivity of the constant to slight differences in the composition of the product.

Investigations of this kind obviously can be extended to other systems containing two or more metals or other central atoms or groups which, individually, are known to undergo redistribution under the conditions used. The reaction was shown to occur between the methyl and ethyl compounds of lead and tin,[1] and quantitative experiments are in progress to determine the value of K.

A few related observations of the interchange of radicals between different RM compounds have been reported, although the existence of equilibria has nowhere been recognized. Schlenk and Holtz[4] prepared methyllithium and phenyllithium by treating ethyllithium with methylmercury and phenylmercury, respectively. Challenger and Ridgway[5] isolated di-α-naphthylmercury, diphenyl-α-naphthylbismuth, and triphenylbismuth from the reaction product obtained by heating a mixture of tri-α-naphthylbismuth and diphenylmercury at 200° for two hours. Evidence has been reported[6] indicating similar reactions between diphenylselenium and n-butyllithium, diphenylmercury and n-butylsodium, and between triarylbismuth compounds and n-butyllithium or n-butylsodium.

Accordingly, it appears that redistribution reactions like the one described in the present study may be expected to occur, under suitable experimental conditions, in a variety of other analogous systems. It is evident that the analysis of such equilibria as these furnishes a useful method for the determination of relative bond energies, in which the comparison is obtained from a single reaction process, under strict equilibrium conditions, and is uncomplicated by side or consecutive reactions. Investigation of the temperature coefficient of these energies is also facilitated, inasmuch as the equilibria for each metal taken alone are not affected by temperature, so far as has been observed.

Experimental

Tetramethyllead and Diethylmercury.—To 1.83 g. (0.014 mole) of aluminum chloride contained in a small 3-

(4) Schlenk and Holtz, Ber., 50, 262 (1917).

(5) Challenger and Ridgway, J. Chem. Soc., 121, 104 (1922).

(6) Gilman and Bebb, THIS JOURNAL, 61, 109 (1939); Gilman, Yablunky and Svigoon, ibid., 61, 1170 (1939).

neck flask fitted with a dropping funnel, reflux condenser, and thermometer, was added a mixture of 134.9 g. (0.502 mole) of tetramethyllead and 253.7 g. (0.973 mole) of diethylmercury, while cooling the flask in ice water. An atmosphere of nitrogen was maintained within the system during the addition and for the duration of the experiment. The mixture was kept at 78–83° for four hours, after which it was cooled and allowed to stand at room temperature overnight. The catalyst was extracted by shaking with water; the oily layer was separated and shaken twice with concentrated ammonia solution and finally with distilled water. After filtration through paper to remove traces of water, the product was fractionated[3] through a column packed with glass helices. The metal alkyls distilled readily and without decomposition. The various fractions were analyzed for lead and mercury. Figure 1 shows the distillation curve, Table I the analyses, and Table III the composition of the product.

Tetraethyllead and Dimethylmercury.—The above experiment was repeated, starting with 2.0 g. (0.015 mole)

aluminum chloride, 233 g. (1.006 mole) dimethylmercury (which contained 0.001 mole tetramethyllead), and 162 g. (0.498 mole) tetraethyllead. The reaction time was five hours at 80°, and the product stood at room temperature over two nights. Subsequent handling was the same as above. The distillation curve, analyses, and composition of the product are given in Fig. 1 and Tables II and III, respectively.

Summary

Mixtures of diethylmercury with tetramethyllead, and of dimethylmercury with tetraethyllead, containing equal proportions of methyl and ethyl radicals and equivalent amounts of mercury and lead, undergo redistribution and yield the same random equilibrium mixture, in which the mercury shows a greater relative affinity than lead for methyl with respect to ethyl radicals.

DETROIT, MICHIGAN   RECEIVED OCTOBER 13, 1939

The Redistribution Reaction. IX. Redistribution of Halides and of Esters[1]

BY GEORGE CALINGAERT, HAROLD SOROOS, VINCENT HNIZDA AND HYMIN SHAPIRO

As stated in the first paper of this series,[2] the redistribution reaction is not confined to organo-metallic compounds, but also has been found to take place in two distinctly different fields, namely, aliphatic halides and esters. So far, the work in these and other fields has been merely exploratory, designed to furnish only a roughly quantitative measure of the occurrence or non-occurrence of redistribution. No attempt has been made to study the influence of the different reaction variables, such as the temperature and amount of catalyst, and no accurate material balances or measurements of the amount of side reaction with the catalyst have been obtained. Further experiments are in progress but, pending future publication of their results, the present paper completes the presentation of the experimental data previously cited.[2]

In the halides, redistribution was found to occur between ethylene dichloride and dibromide, between ethyl chloride and ethylene dibromide, and between ethyl bromide and ethylene dichloride, in each case using 1.5–3 mole per cent. aluminum chloride as the catalyst.

As shown in Fig. 1 and Table I, in the first of

(1) For paper VIII, see Calingaert, Soroos and Thomson, THIS JOURNAL, **62**, 1542 (1940).
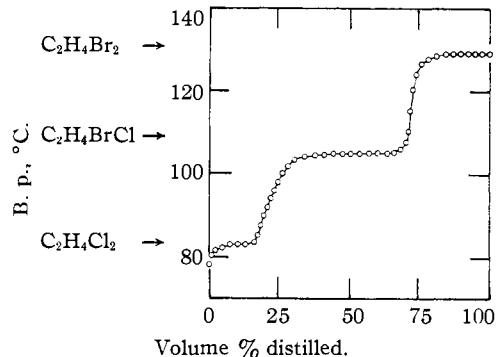
(2) Calingaert and Beatty, *ibid.*, **61**, 2748 (1939).

Fig. 1.—Distillation of the reaction product from $C_2H_4Br_2$ + $C_2H_4Cl_2$.

these reactions, between the two ethylene dihalides, the composition of the product corresponded within experimental error to a random distribution of the halogen atoms. In this one case, we found later that our result has been fully antici-

TABLE I

PRODUCTS FROM THE REDISTRIBUTION OF ETHYLENE DICHLORIDE WITH ETHYLENE DIBROMIDE

| | Composition, mole per cent. | |
	Found	Calcd.[2] for r^a = 0.467
$C_2H_4Cl_2$	23.0	21.8
C_2H_4ClBr	47.4	49.8
$C_2H_4Br_2$	29.6	28.4

[a] r is the atomic fraction of chloride found in the product.