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Summary

A number of new functional derivatives as well as substitution products of 5-methyl-thiazoline-*m*-cresol have been described.

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

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

BY GEORGE CALINGAERT, HAROLD SOROOS AND HYMIN SHAPIRO

A previous paper[1] of this series has described the redistribution reaction for the interchange of alkyl radicals in alkyl compounds of lead and mercury. In this work, it was shown that mixtures of: (1) dimethylmercury and tetraethyllead and (2) diethylmercury and tetramethyllead, each system containing 50% methyl radicals and 50% lead bonds, undergo redistribution and yield the same equilibrium mixture, in which the mercury shows a greater relative affinity than lead for methyl with respect to ethyl radicals. This difference was expressed by a "relative affinity constant."

$$K = \frac{(\text{Me-Hg})(\text{Et-Pb})}{(\text{Et-Hg})(\text{Me-Pb})}$$

In order to show that this relative affinity constant is a true equilibrium constant whose value, at a given temperature, is independent of the relative proportions of methyl and ethyl radicals, and of lead and mercury bonds, we have checked the value of K, previously determined, by effecting redistribution in a lead alkyl–mercury alkyl system containing different relative proportions of methyl and ethyl radicals and of lead and mercury bonds. Thus, in the present study, a mixture of 60 mole per cent. dimethyldiethyllead and 40 mole per cent. dimethylmercury, a system containing 62.5% methyl radicals and 75% lead bonds, with aluminum chloride as the catalyst, underwent redistribution at 80° in five hours to give a random equilibrium mixture for which the value of the relative affinity constant, K, was found to be 3.4. This value of K is in good agreement with the previously determined value of 4.5 ± 0.4, considering the sensitivity of the constant to slight differences or errors in determining the composition of the product.[2]

The results are given in Tables I and II, and the distillation curve for the reaction products is shown in Fig. 1. The data show that: (1) the

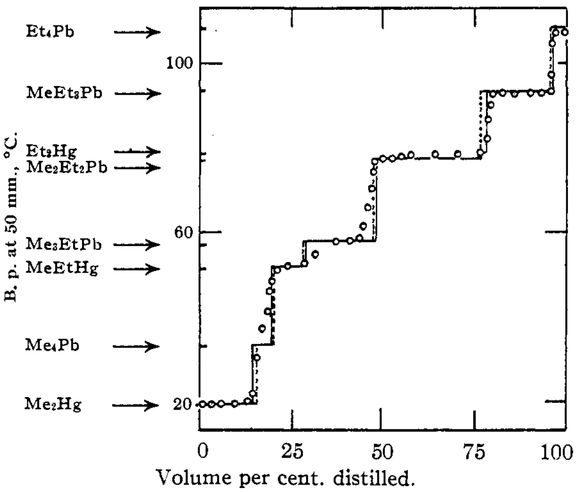

Fig. 1.—Distillation of reaction product from Me_2Hg + Me_2Et_2Pb: solid line calculated for a random equilibrium mixture, with 60% Me radicals, 75% RPb bonds and K = 3.4; broken line calculated for the same mixture with K = 4.55.

recovery of each metal was satisfactory, considering the difficulty of preventing small handling losses, resulting during extraction of the catalyst, filtration, and transfer of material; there was no appreciable decomposition. Also, the per cent. methyl in the product equalled that of

(1) Calingaert, Soroos and Thomson, THIS JOURNAL, **62**, 1542 (1940).

(2) For an example of this sensitivity, assuming 60% methyl radicals and 75% lead bonds, a variation of per cent. methyl in R_2Hg in the product from 79.4 to 83.0, changes the value of K from (0.197)(0.351)/(0.051)(0.401) = 3.4 to (0.206)(0.360)/(0.042)(0.392) = 4.5, or 32%. The small difference in the composition of the product required to effect this change in the value of K is also shown graphically in Fig. 1.

TABLE I

REDISTRIBUTION OF DIMETHYLDIETHYLLEAD AND DIMETHYLMERCURY: DISTILLATION AND ANALYTICAL DATA

Fraction No.	Fraction Wt., g.	B. p. (50 mm.) up to	Lead content Wt. %	Lead content Wt., g.	Lead content Mmoles	Mercury content Wt. %	Mercury content Wt., g.	Mercury content Mmoles	Composition assumed from b. p.
1	...	17.0	...	0.048	0.18	....	6.45	27.96	Me_2Hg, Me_4Pb
2	98.20	37.3	6.52	6.40	30.90	78.52	77.11	384.36	Me_2Hg, MeEtHg, Me_4Pb
3[a]	10.23	49.7	45.37	4.64	22.40	32.93	3.37	16.79	Me_2Hg, MeEtHg, Me_4Pb, Me_3EtPb
4	87.64	61.6	52.70	46.19	222.90	23.31	20.42	101.79	MeEtHg, Me_3EtPb
5[b]	7.17	74.3	70.19	5.03	24.29	2.65	0.19	0.95	MeEtHg, Et_2Hg, Me_3EtPb, Me_2Et_2Pb
6	93.44	80.4	68.89	43.71	310.65	1.20	1.12	5.59	Et_2Hg, Me_2Et_2Pb, $MeEt_3Pb$
7	6.63	93.0	68.76	4.55	22.00	0.051	0.003	0.02	Et_2Hg, Me_2Et_2Pb, $MeEt_3Pb$
8	46.21	95.1	67.06	30.99	149.54	.070	.032	.16	Et_2Hg, Me_2Et_2Pb, $MeEt_3Pb$
9	1.83	104.8	66.33	1.21	5.86	.154	.003	.01	Et_2Hg, $MeEt_3Pb$, Et_4Pb
10	7.05	...	64.27	4.53	21.87	.067	.004	.02	Et_2Hg, $MeEt_3Pb$, Et_4Pb
Collected Washings				1.321	6.37	....	.011	.05	Et_2Hg, Et_4Pb
					816.96			537.70	

[a] Estimated composition for lead alkyls is 50% Me_4Pb and 50% Me_3EtPb. [b] Estimated composition for mercury alkyls is 50% MeEtHg and 50% Et_2Hg.

TABLE II

DISTRIBUTION OF METHYL AND ETHYL BETWEEN LEAD AND MERCURY IN REACTION PRODUCTS

Compound	Millimoles	Mole per cent. Found	Mole per cent. Calcd.[a]	Over-all, %
Me_4Pb	42.28	5.18	8.06	3.12
Me_3EtPb	251.43	30.78	28.27	18.56
Me_2Et_2Pb	321.65	39.37	37.18	23.74
$MeEt_3Pb$	174.43	21.35	21.73	12.88
Et_4Pb	27.16	3.32	4.76	2.01
Total	816.95	100.00	100.00	60.31
			% Me =	53.28
Me_2Hg	322.56	59.99	63.06	23.81
MeEtHg	208.81	38.83	32.70	15.41
Et_2Hg	6.32	1.18	4.24	0.47
Total	537.69	100.00	100.00	39.69
			% Me =	79.41

[a] Calculated[3] from % Me found. Total millimoles Pb-Hg, 1354.64. Total millimoles Me-Et, 4343.18. Over-all % Me = 59.75%; % R-Hg bonds = 24.76. K = 3.4.

the input, within experimental error. (2) For each metal, the alkyls in the product constitute a random distribution mixture. Thus, the five R_4Pb alkyls are found in proportions agreeing with those calculated for a random distribution mixture containing 53.3% methyl radicals; likewise, the distribution of the three R_2Hg alkyls is in agreement with that calculated for a mixture containing 79.4% methyl radicals. Moreover, the distribution of the lead and mercury alkyls is in agreement with that calculated for random distribution on the basis of 60 over-all per cent. methyl radicals, 75% lead bonds and K = 3.4, as shown in Fig. 1. (3) The per cent. methyl (79.4) in the mercury alkyls was about 50% greater than that in the lead alkyls (53.3), corresponding to a marked difference in relative affinity of mercury and lead for methyl with respect to ethyl radicals.

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

Experimental

Dimethyldiethyllead and Dimethylmercury.—Redistribution was effected between 255.0 g. (0.863 mole) of dimethyldiethyllead and 132.7 g. (0.576 mole) of dimethylmercury, in the presence of 2.0 g. (0.015 mole) of aluminum chloride. The method of carrying out the reaction, and of fractionating and analyzing the products was essentially the same as previously described.[1]

Summary

A mixture of dimethyldiethyllead and dimethylmercury containing 62.5% methyl radicals and 75% lead bonds undergoes redistribution to yield a random equilibrium mixture, for which the value of the "relative affinity constant," K, is in good agreement with that previously determined for lead alkyl–mercury alkyl systems, containing 50% each of methyl radicals and lead bonds, indicating that the value of K is independent of the relative proportions of methyl and ethyl radicals and of lead and mercury bonds.

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