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Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV, N. S. VYAZANKIN,

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Abstract

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Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV, N. S. VYAZANKIN,
Yu. I. DERGUNOV, and O. S. D' YACHKOVSKAYA

ON SOME CASES OF THE RADICAL REDISTRIBUTION REACTION IN ORGANIC COMPOUNDS OF LEAD, TIN, AND SILICON

As is known, heating an unsymmetrical organometallic compound of the type $R_3R'Pb$ with catalytic amounts of aluminum chloride leads to redistribution of radicals (^{1}). As a result, a dynamic equilibrium is established and a mixture of all possible combinations of tetraalkyl derivatives of the corresponding metal is formed.

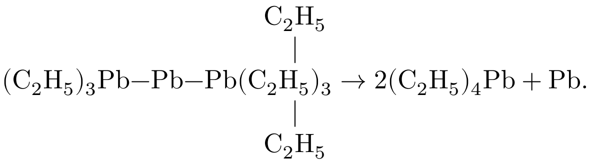
It seemed of interest to investigate such cases of the reaction under discussion in which the equilibrium state is disturbed, as a result of which the ratios between the reaction products differ sharply from those usually observed. Such cases, in our opinion, include the disproportionation of hexaethyldiplumbane and hexaethyldistannane under the influence of catalytic additions of aluminum chloride and similar substances.

It is known that redistribution of radicals in a symmetrical compound of the type tetraethyltin does not lead to the formation of new substances. Consequently, the very fact of the change of hexaethyldimetals under the action of a catalyst indicates their "unsymmetrical" character. Such a conclusion is legitimate, since any of the metal atoms in these compounds is bonded to three ethyl radicals and one triethylmetal radical, for example: $(C_2H_5)_3SnR$, where $R = (C_2H_5)_3Sn$.

If it is assumed that both kinds of radicals participate equally readily in the redistribution reaction, then, according to the literature data, in its course a mixture of the following compounds should be formed: $(C_2H_5)_4Sn$ (I), $(C_2H_5)_3SnR$ (II), $(C_2H_5)_2SnR_2$ (III), $C_2H_5SnR_3$ (IV), and SnR_4 (V).

It is easy to see that this basic reaction already leads to the formation of rather complex molecules, since in compounds (III), (IV), and (V) there are chains consisting respectively of three, four, and five metal atoms.

However, unlike the classical redistribution reactions, the given mixture will not be at equilibrium, since (III), (IV), and (V) are not "symmetrical" compounds. Thus, for example, (III) may be regarded as $(C_2H_5)_3SnR'$, where $R' = (C_2H_5)_2Sn - Sn(C_2H_5)_3$. Consequently, it is theoretically probable that (III), (IV), and (V) will enter into side reactions of radical redistribution, in the course of which, along with tetraethyltin, a series of substances with still longer and more branched chains of metal atoms will arise. The mixture of compounds (I)–(V) will not be at equilibrium also because, along with the complication of the molecules, their decomposition should occur, since chains of metal atoms are very unstable. In the case of organolead compounds, already a substance of type (III) should be extremely unstable even at room temperature:



$$(\mathrm{C_2H_5})_3\mathrm{Pb{-}Pb{-}Pb(C_2H_5)_3} \text{ (with } \mathrm{C_2H_5} \text{ above and below the central Pb)} \rightarrow 2(\mathrm{C_2H_5})_4\mathrm{Pb} + \mathrm{Pb}. \qquad \text{(A)}$$

For organotin compounds, depending on the temperature conditions, the formation of more or less long chains of tin atoms is possible. However, in this case as well, at comparatively low temperatures, decomposition of the complicated molecules with liberation of metal should be observed.

In accordance with the ideas expressed, it was found that the introduction into hexaethyldiplumbane of 2-3 wt.% aluminum chloride or other catalysts of radical redistribution (triethyllead bromide, diethyltin dibromide) sharply lowers the stability of the product and changes the mechanism of its decomposition.

Thus, for example, pure hexaethyldiplumbane decomposes completely, without access of air, at 105° in 5 hours (^{2}):

$$(\mathrm{C_2H_5})_6\mathrm{Pb_2} \rightarrow (\mathrm{C_2H_5})_4\mathrm{Pb} + \mathrm{Pb} + 2\mathrm{C_2H_5}. \qquad (\;)$$

The same product in the presence of 1.0-1.5% $\mathrm{AlCl_3}$ disproportionates completely at room temperature in 2–3 hours according to the equation:

$$2(\mathrm{C_2H_5})_6\mathrm{Pb_2} \rightarrow 3(\mathrm{C_2H_5})_4\mathrm{Pb} + \mathrm{Pb}. \qquad (\;)$$

Additions of aluminum chloride have an analogous effect on hexaethyldistannane. In this case the pure product begins to decompose according to equation ( ) at temperatures of 260-265°. In the presence of catalyst (2-3%), disproportionation of the substance according to equation ( ) is already observed at 70–75°.

By spectrophotometric means we have shown that decomposition of hexaethyldiplumbane (^{2}) and hexaethyldistannane according to equation ( ) proceeds with the intermediate formation of diethyllead or diethyltin. In the disproportionation of hexaethyldiplumbane according to equation ( ), we were unable to prove the presence of intermediate reaction products. On the contrary, in the disproportionation of hexaethyldistannane under mild conditions (70–75°), the formation of intermediate substances can be established from the appearance of an intense cherry-red coloration and the subsequent separation of the reaction mixture into layers. Analysis of the upper colorless layer shows that it consists mainly of tetraethyltin. Analysis of the separated heavy, viscous liquid, colored dark red, indicates that in composition it corresponds to diethyltin: $[Sn(C_2H_5)_2]_n$. Chlorine analysis established a uniform distribution of the catalyst in the upper and lower layers.

It should be emphasized that the phenomenon of separation into layers has nothing in common with resin-formation processes, since after the separation the lower layer is observed to decompose with formation of metallic tin and tetraethyltin. Both the analytical data and the fact of separation into layers indicate that, in the course of disproportionation of hexaethyldistannane under the action of $AlCl_3$, high-molecular intermediate substances are formed, which agrees with the ideas set forth above concerning the mechanism of this reaction.

In the case considered, the disturbance of the equilibrium state occurs through the participation of the reaction products in side processes leading to the formation of unstable compounds. Another case is also possible—when one or several reaction products are stable toward the action of the catalyst.

In 1934 it was established that between $(C_2H_5)_4Pb$ and $(C_2H_5)_3PbCl$ there occurs an exchange of a chlorine atom for an ethyl radical (^{3}). It was shown that the equilibrium state is established in one day, and that the catalyst of the process is triethyllead chloride itself.

It was natural to suppose that the same exchange process, but without formation of an equilibrium mixture, should be observed in the interaction of tetraethyl derivatives of lead, tin, and silicon with alkyl halides in the presence of small additions of catalysts for the radical redistribution reaction. For example:

$$R_4Sn + R'Cl \xrightarrow[AlCl_3]{2\text{–}3\%} R_3SnCl + R{-}R'. \qquad (\,)$$

The possibility of processes of this kind followed from the work of Skoldinov and Kocheshkov (4) on the interaction of tetraphenyl- and tetraethyltin with acid chlorides and carbon tetrachloride, and also from Russell' s work on the dealkylation of tetraethylsilane by methyl bromide (5). In both cases the authors used amounts of aluminum chloride equimolar with the halogen derivatives.

We have found that rapid addition of 0.1 mole of dry isopropyl chloride to a mixture of 0.1 mole of tetraethylsilane and 0.3 g of $AlCl_3$ causes a spontaneous reaction. Additional boiling of the mixture for 2 hours leads to the formation of triethylchlorosilane. Yield 71.3% of theory; b.p. 143-145°; n_D^{20} 1.4316. The reaction proceeds smoothly and can be used for preparative purposes. The structure of triethylchlorosilane was confirmed by conversion into hexaethyldisilane (6).

The interaction of tetraethyltin with benzyl chloride proceeds just as vigorously. In this case, even under mild conditions, a side condensation reaction of benzyl chloride takes place under the influence of aluminum chloride (7). Successful interaction of isopropyl chloride with tetraethyltin, hexaethyldistannane, and triethyltin chloride is observed only in the presence of small amounts of benzene —a solvent that accelerates reactions of this type (8). In the case of hexaethyldistannane, disproportionation according to equation ( ) proceeds in parallel with the exchange process. We were unable to carry out an exchange reaction between isopropyl chloride and tetraethyllead. The experimental results are summarized in Table 1.

Table 1

No.	Sn-organic compound, moles	alkyl halide, moles	benzene, ml	$AlCl_3$, g	substance	b.p., °C	n_D^{20}	m.p., °C	yield, %
1	$(C_2H_5)_4Sn$, 0.10	iso-C_3H_7Cl, 0.10		0.28	$(C_2H_5)_4Sn$	175-176	1.4728	–	–
2	$(C_2H_5)_4Sn$, 0.05	iso-C_3H_7Cl, 0.05	1.9	0.160	$(C_2H_5)_3SnCl$	203-208	1.5035	–	68.3
3	$(C_2H_5)_4Sn$, 0.05	$C_6H_5CH_2Cl$, 0.05		0.22	$(C_2H_5)_3SnCl$	204-210	1.5043	–	73.0
4	$(C_2H_5)_4Sn$, 0.02	CCl_4, 0.02		0.50	$(C_2H_5)_3SnCl$	205-208	1.5047	–	53.6
4	$(C_2H_5)_4Sn$, 0.02	CCl_4, 0.02		0.50	$(C_2H_5)_2SnCl_2$	–		83-84	10.0
5	$(C_2H_5)_4Sn$, 0.05	iso-C_3H_7Cl, 0.10	1.9	0.31	$(C_2H_5)_3SnCl$	204-210	–	–	54.8
5	$(C_2H_5)_4Sn$, 0.05	iso-C_3H_7Cl, 0.10	1.9	0.31	$(C_2H_5)_2SnCl_2$	–		82-83	31.4
6	$(C_2H_5)_3SnCl$ 0.05	iso-C_3H_7Cl, 0.05	2.0	0.25	$(C_2H_5)_2SnCl_2$	–		82-83	35.5
7	$(C_2H_5)_6Sn_2$, 0.019	iso-C_3H_7Cl, 0.019	1.0	0.14	$(C_2H_5)_3SnCl$	203-209	1.5039	–	55.5
7	$(C_2H_5)_6Sn_2$, 0.019	iso-C_3H_7Cl, 0.019	1.0	0.14	$(C_2H_5)_4Sn$	175-178	1.4743	–	22.5

Note. The reaction mixture was heated as follows: Nos. 1, 2, 5, 6—to boiling for 2-3 hours; No. 4—in a boiling water bath in an evacuated ampoule for 16 hours; No. 7—in an evacuated ampoule at 70-80° for 48 hours; No. 3—addition of $C_6H_5CH_2Cl$ dropwise to the cooled aqueous mixture, then storage at room temperature for 12 hours.

Scientific Research Institute of Chemistry
at Gorky State University
named after N. I. Lobachevsky

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Note: Figure translations are in progress. See original paper for figures.