STUDY OF EXCHANGE PROCESSES IN ORGANOMETALLIC DERIVATIVES [Hg, Sn, Pb, Sb(III), Sb(V)] OF CERTAIN THIOPHENOLS BY THE PMR METHOD

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In an investigation of exchange processes in organometallic (OM) derivatives of certain substituted phenols by the PMR method [1] it was shown that the OM groups are arranged in the following series with respect to increasing ability for reactions of intermolecular exchange (IME) and for intramolecular coordination: $R_3Sn < R_3Pb < RHg$, $R = C_6H_5$.

Such parallelism in the behavior of groups of the R_nM type is apparently evidence of a significant role of their coordination capacity in the formation of cyclic transition states:



In turn the coordination ability of the R_nM group is associated with the presence, as well as with the geometry of the vacant orbitals of the metal atom, which is determined by its position in the periodic system.

We were interested in comparing the behavior of the OM groups studied with the analogs, containing atoms of heavy transition metals from other groups of the periodic system, in particular, Sb(III) and Sb(V).

In this work, for a comparison of the migration ability of the diphenyl antimony group with other R_nM groups, we studied exchange reactions of the metal-metal and metal-proton types in the interaction of diphenylantimony 2,6-dimethylthiophenolate with thiophenol (TP) or its OM derivatives in chlorobenzene (CB)

 $R_{2}SbS \longrightarrow + XSAr \rightleftharpoons R_{2}SbSAr + X - S \longrightarrow CH_{3}$ $CH_{3} \qquad \qquad CH_{3}$ $K = HgR, SnR_{3}, H; R = C_{3}H_{3}$ (1)

Here, just as earlier [1], we recorded the time corresponding to 100% conversion of the initial reagents (Table 1). A comparison of the data of Table 1 with the results obtained in [1] permitted us to conclude that the $(C_6H_5)_2Sb$ group resembles the $(C_6H_5)_3Pb$ group in its ability for IME in OM derivatives of TP, so that the series can be supplemented: $R_3Sn < R_3Pb \approx R_2Sb < RHg$, $R = C_6H_5$.

The greater migration ability of the C_6H_5Hg group in comparison with the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ group was explained by its greater ability to form cyclic associates [1], which finds analogy in the fact that the first of the groups gives stronger intramolecular coordination bonds than the last two [2].

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TABLE 1. Time Corresponding to 10% Degree of Conversion in Reaction (I)

Exchangin	g group	t _{0,1}	
X²	X ¹		
SbR2 SbR2 SbR2	SnR₃ H HgR	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	

*In C_6H_5Cl the concentration of each of the reagents is 0.1 M.

The lower migration ability of the $(C_{6}H_{5})_{2}Sb$ group in comparison with the $C_{6}H_{5}Hg$ group, found in this work, is analogous to the fact that in OM derivatives of o-TP the diphenyl antimony group gives weaker chelate rings than the phenylmercury group [3]. It should be noted that the drawing of such analogies between the ability of the OM group to form cyclic associates and intramolecular coordination and its mobility in IME reactions is possible only if weakly polarized metal—heteroatom bonds, close in their polarity, are compared (Hg—X, Pb—X, Sn—X, Sb(III)—X). If, however, a group whose bond to the heteroatom is strongly polarized participates in the exchange reaction, then its ability for IME may vary greatly on account of an increase in the electrophilicity of the anionic residue X and, correspondingly, the nucleophilicity of the metal atom. In this case de-

viations from direct correlation between the ability of the OM group for intramolecular coordination and the IME reaction may be observed. An example of a univalent OM group, forming a strongly polarized M-S bond, is the $(C_6H_5)_4$ Sb group [4]. To determine its comparative ability for IME, we studied several reactions of the M-M and M-H type in chloroform:

In the PMR spectrum of a mixture of tetraphenylantimony 2-methylthiophenolate with 2-methylthiophenol or with phenylmercury 2-methylthiophenolate, a narrow single signal of the o-CH₃ group is observed, with a chemical shift intermediate between the chemical shifts of the methyl groups of the corresponding individual compounds (Table 2). Thus, M-M and M-H exchange in these systems is rapid in the time scale of PMR. At the same time, in a mixture of tetraphenylantimony 2-methylthiophenolate with triphenyltin 2-methylthiophenolate, as well as a mixture of 2-methylthiophenol with phenolmercury 2-methylthiophenolate, the exchange is slow, and two narrow signals from the individual compounds are observed in the spectrum. In the PMR spectrum of a mixture of tetraphenylantimony 2-methylthiphenolate with triphenyllead 2-methylthophenolate two signals of the CH₃ groups are also observed; however, these signals are appreciably broadened ($\Delta \nu_{1/2}$ of one of them is ~7 Hz).

Comparing the lifetimes of the exchanging particles obtained (see Table 2), we can conclude that the $(C_6H_5)_4Sb$ group is most labile in reactions of IME in OM derivatives of TP, of all the univalent OM groups in the heavy nontransition metals studied thus far. Thus, with respect to relative migration ability, the R_nM groups in these reactions in chloroform are arranged in the series: $R_3Sn < R_3Pb < RHg < P_4Sb$, $R = C_6H_5$.

The results obtained show that in chloroform, just as in CB [1], the order of relative migration ability of the R_3Sn , R_3Pb , and RHg groups is the same. Moreover, it has been shown that this order is unchanged in the transition from 2-methylthiophenyl derivatives to 2,6-dimethylthiophenol derivatives [1]. Assuming an analogy for other OM groups as well, on the basis of the results of this work it can be assumed

TABLE 2. Chemical Shifts of the Protons of the Methyl Groups and Boundary Lifetimes of the Exchanging Particles in a Reaction of Intermolecular Exchange (2) $(\delta, Hz, from TMS)$

Exchanging groups	δ _{CH3} , in mixture	δ_{CH_3} of individual compounds	τ, sec*
$SbR_4 + HgR$	130,8	108,5 (SbR ₄) $154,0$ (H α B)	<0,011
HgR + H	150,9	151,0 (HgR)	>0,41
$SbR_4 + H$	124,9	103, 5 (H) $108, 5 (SbR_4)$ 139, 9 (H)	<0,015
$SbR_4 + PbR_3$	109,7	103, 5 (B) $108, 5 (SbR_4)$ $136, 2 (PbR_4)$	0,053
$SbR_4 + SnR_3$	104,1 108,0 134,0	108,5 (SbR ₄) 134,3 (SnR ₃)	>0,18

* In chloroform, concentration of each of the reagents 0.1 M.

TABLE 3. Constants of Exchange Equilibria (3)*

Substituent	K
C ₆ H ₅ $4-(CH_3)_2NC_6H_4$ $3-CIC_6H_4$ $2-FC_6H_4$ $2-CIC_6H_4$ $2-CH_3OC_6H_4$ $3,5-CI_2C_6H_3$ 	$\begin{array}{c} 4,4\\ 2,2\\ 100\\ 15,0\\ 23,0\\ 1,9\\ >100\\ \end{array}$

TABLE 4. Calculated Constants of Exchange Equilibria and Polar Constants of Substituents in the Thiophenol Ring [5, 6] $C_6H_5SbR_4$ + $ArSSnR_3 \approx C_6H_5SSnR_3$ + $ArSSbR_4$

Substituent	K .	ø
C6H5 2-CH3C6H4 4-N(CH3)2C6H4 3-ClC3H4 3,5-Cl2C6H3 2-ClC6H4 2-FC6H4 2-CH2C6H4	$\begin{array}{c c} 1,00\\ 0,25\\ 0,50\\ 23\\ >23\\ 5,20\\ 3,4\\ 0,40\\ \end{array}$	$\begin{array}{c} 0,0\\0,13\\0,6\\ 0,37\\ 0,74\\ 0,50\\ 0,29\\ -0.37\end{array}$

that in relatively inert solvents of the type of chloroform and CB, the migration ability of the univalent OM groups containing heavy metals studied increases in the series: $R_3Sn < R_3Pb = R_2Sb < RHg < R_4Sb$; $R = C_6H_5$.

To obtain quantitative data on the comparative ability of univalent organoantimony groups of the type of $(C_{6}H_{5})_{4}Sb$ for intramolecular coordination with an o-substituent, we studied the exchange equilibria of the M-M type in chloroform, with the reaction

$$\begin{array}{c} -\text{SSb}R_4 + \text{ArSSn}R_3 \neq & -\text{SSn}R_3 + \text{ArSSb}R_4 \\ \text{CH}_3 & \text{CH}_3 \\ \text{R} = C_6 H_4 \end{array}$$

$$\begin{array}{c} (3) \\ \end{array}$$

as an example. The selection of the $(C_6H_5)_3$ Sn group as a partner is due to the fact that at $X^1 = SbR_4$ and $X^2 = SnR_3$, the exchange reaction (2) proves to be slow in the time scale of PMR.

Equilibrium is established immediately after the chloroform solutions of the initial compounds are poured together, and its position does not depend on which of the two possible pairs of reagents is the initial one. Just as in our previous studies, an attempt was made to evaluate the influence of various factors on the position of equilibrium of the reactions under consideration by an analysis of the equilibrium constants (Table 3).

In the interpretation of the data obtained, indeterminacies arose, due in all probability, to the existence of a strongly polarized M—S bond in $(C_{6}H_{5})_{4}$ Sb derivatives of TP. Thus, the introduction of an electron donor group $N(CH_{3})_{2}$ into the p-position of the TP ring leads to destabilization of tetraphenylantimony thiophenolate and, correspondingly to a shift of equilibrium in the direction of the formation of the o-meth-ylthiophenolate of tetraphenylantimony. The replacement of hydrogen in the thiophenyl ring by electron donor substituents m-Cl and m,m-Cl₂, on the contrary, substantially stabilizes the corresponding tetraphenyl antimony derivatives.

In contrast to the statistical nature of the analogous exchange equilibria with the participation of other OM groups [1], the equilibrium (3) for the reaction of tetraphenylantimony o-methylthiophenolate with triphenyltin thiophenolate is substantially shifted in the direction of the formation of triphenyltin o-methylthiophenolate.

Considering that the stronger electron donor group $p-N(CH_3)_2$ [5, 6] has less of an influence on the position of equilibrium, this circumstance is evidence of the substantially greater space requirements of the substituents $(C_6H_5)_4SbS$ in comparison with the $(C_6H_5)_3SnS$, C_6H_5HgS , $(C_6H_5)_3PbS$, and $(C_6H_5)_2SbS$ group in the case when they enter into nonvalence interactions with the o-CH₃ group.

The observed difference in the space requirements of the MO groups in the systems studied is probably due to the fact that in the R_nMS group [M = Hg, Sn, Pb, Sb(III)], steric hindrances are caused chiefly by contact between the metal atom and the o-CH₃ group, whereas in the $(C_6H_5)_4SbS$ group a significant role is also played by nonvalence interactions between the o-CH₃ and the equatorial phenyl substituents [7]. Thus, in contrast to exchange reactions of the M-M type, in derivatives of TP in which other OM groups participate, the position of equilibrium for reactions including the $(C_6H_5)_4Sb$ group depends on the polar and steric effects of the substituents. To simplify the analysis of the results obtained, the equilibrium constants were calculated from the values of the experimental equilibrium constants (see Table 3) for systems not containing $o-CH_3$ groups (Table 4). As it follows from these data, the introduction of electron acceptor substituents into the TP ring leads to stabilization of substituted tetraphenylantimony thiophenolate; moreover, with increasing acceptor properties of the substituent, the equilibrium is shifted in the direction of the formation of the corresponding antimony compounds.

On the basis of this, and also on the basis of a comparison of the values of σ characterizing the polar effects of substituents on the o-, m-, and p-positions in substituted phenols [5, 6], we might expect that the values of the equilibrium constants for reactions in which o-Cl- and o-F-substituted triphenyltin thiophenolates participate will be close to two. However, the experimental values prove to be substantially smaller. Consequently, in this case the electron acceptor effect of the o-substituent is to a substantial degree balanced by the oppositely directed net effect of the steric hindrances and coordination interactions; moreover, it is impossible to isolate and evaluate the contribution of each of them.

Therefore, on the basis of the data obtained, we can only conclude that in OM derivatives of TP, potential five-membered chelate rings with the participation of the $(C_6H_5)_3$ Sn groups are evidently stronger than potential chelate rings with the participation of the $(C_6H_5)_4$ Sb group.

EXPERIMENTAL

The PMR spectra were taken on a Perkin Elmer R-12 spectrometer (60 MHz) at 34°. The chemical shifts were measured using the technique of the side band from TMS as an internal standard with an accuracy of ± 0.3 Hz. The lifetime $\tau_{\rm A}$ of the exchanging particles was calculated according to approximate formulas [8].

The equilibrium constants K were found by integrating the signals of the o-methyl groups of one of the reaction products and one of the initial compounds, accuracy of determination $\pm 10\%$. The equilibrium constants cited in Table 4 were obtained by calculation from the experimental constant on the basis of simple calculations, which showed that in general, if the equilibrium constants K₁ and K₂ for the reactions

$$MA + M^{\bullet}B \stackrel{K_{1}}{\leftarrow} M^{\bullet}A + MB$$
$$M \neq M'$$
$$MC + M^{\bullet}B \stackrel{K_{2}}{\leftarrow} MB + M^{\bullet}C$$

are known, then the equilibrium constant K₃ for the reaction

$$MA + M^*C \gtrsim M^*A + MC$$

is found from the relationship $K_3 = K_2/K_1$. The synthesis of substituted triphenyltin thiophenolates will be described later.

Diphenylantimony thiophenolates were produced by the action of diphenylantimony acetate on the sodium salt of the corresponding thiophenols in abs. alcohol. Tetraphenylantimony thiophenolates were produced by the action of tetraphenylantimony methylate on the corresponding thiophenol in benzene. The melting points and results of analysis of the organoantimony compounds used in this work, as well as investigated previously [3], are cited in Table 5. 3,5-Dichlorothiophenol was produced from 3,5-dichlorophenylmagnesium bromide and sulfur in abs. ether (see Table 5). Below are cited typical examples of synthesis of the compounds studied.

Diphenylantimony m-Chlorothiophenolate. To a hot solution of 1.8 g (0.005 mole) diphenylantimony acetate in 20 ml abs. alcohol was added 0.83 g (0.005 mole) sodium m-chlorothiophenolate in 20 ml of the same solvent. The reaction mixture was heated to boiling, the solvent removed under vacuum, the oily residue washed with water, dissolved in ether, and the ether solution dried with Na_2SO_4 . After removal of the ether, the residue in the form of a yellow oil was freed of impurities by chromatography in a thick layer of neutral ammonium oxide (eluent petroleum ether). The light lemon-colored oil obtained (1.8 g, 86%) crystallized upon grinding, mp 42-43°. The remaining substituted diphenylantimony thiophenolates were produced analogously.

Tetraphenylantimony p-Dimethylaminothiophenolate. A mixture of 1.1 g (0.0025 mole) tetraphenylantimony methylate and 0.38 g (0.0025 mole) p-dimethylaminothiophenol in 25 ml abs. benzene was boiled with a reflux condenser, equipped with a calcium chloride tube, for 2 h. After removal of the solvent, we obtained 0.9 g (60%) of a bright-yellow precipitate, which after recrystallization from cyclohexane has bp 145-146°. The remaining substituted tetraphenylantimonythiophenolates were produced analogously.

	mp, °C	Found/calculated,%	
Compound		, C	H
(C ₅ H ₅) ₂ SbSC ₆ H ₃ (CH ₃) ₂ -2,6	88—89	$\frac{57,91}{58,14}$	$\frac{4,47}{4,64}$
(C6H5)2SbSC6H4OCH3-2	103—104	$\frac{54,71}{54,97}$	$\frac{4,23}{4,13}$
(C6H5)2SbSC6H4Br-2	Oíl*	$\tfrac{46,54}{46,59}$	$\frac{3,37}{3,04}$
(C ₆ H ₆) ₂ SbSC ₃ H ₄ F-2	5051	$\frac{53,39}{53,63}$	$\frac{3,27}{3,50}$
(C₅H₅)₂SbSC6H4NO2-2	Oil†	$\frac{50,47}{50,27}$	$\frac{3,56}{3,28}$
(C6H5)2SbSC6H4Cl-3	42-43	$\frac{51,31}{51,52}$	$\frac{3,18}{3,36}$
(C6H5)2SbSC6H4CH3-2	Oil*	$\frac{57,25}{57,48}$	$\frac{4,29}{4,29}$
$(C_6H_5)_2SbSC_6H_4N(CH_3)_2-4$	80-82	$\frac{56,35}{56,40}$	$\frac{4,67}{4,71}$
(C6H5)2SbSC6H2Cl2-3,5	40-42	$\frac{47,90}{47,61}$	$\frac{2,84}{2,89}$
(C6H5)4SbSC6H4CH3-2	131-132	$\frac{67,13}{67,29}$	$\frac{4,85}{4,92}$
(C6H5)4SbSC6H4OCH3-2	120-123	$\frac{65,18}{65,40}$	$\frac{5,01}{4,78}$
(C6H5)4SbSC6H4F-2	146—147	$\frac{64,17}{64,66}$	$\frac{4,37}{4,33}$
(C6H5)&SbSC6H3Cl2-3,5	153	$\frac{58,96}{59,23}$	$\frac{3,87}{3,81}$
(C₅H₅)₄SbSC₅H₄Cl-3	144—146	$\frac{62,78}{62,80}$	$\frac{4,28}{4,22}$
(CoH5)4SbSC6H4N(CH3)2-4	145—146	$\frac{66,02}{66,00}$	4,97 5,19
(C₅H₅)₄SbSC₅H₄Cl-2	39-41	$\frac{51,34}{51,52}$	$\frac{3,42}{3,36}$

TABLE 5. Melting Points and Results of Analysis of Substituted Diphenyl- and Tetraphenylantimonythiophenolates

*Rf in a mixture of petroleum ether + acetone (6:1) equal to 0.5. The same, 0.2.

<u>3,5-Dichlorothiophenol.</u> To a solution of 3,5-dichlorophenylmagnesium bromide, obtained from 28.6 g (0.13 mole) 3,5-dichlorobromobenzene in 80 ml of abs. ether and 3,24 g (0.135 mole) Mg in 30 ml abs. ether, a suspension of 4.16 g (0.13 mole) finely ground flowers of sulfur in 50 ml of the same solvent was cautiously added. In this case a change of the color of the reaction mass from dark red to yellow-brown and a substantial evolution of heat were observed. After boiling for 1.5 h, the reaction mixture was decomposed with cooling with highly dilute HCl, the organic layer removed, and the aqueous layer extracted twice with benzene. The thiophenol obtained was extracted with a dilute solution of alkali, precipitated with diluted HCl, reextracted with benzene, and dried with Na₂SO₄. After removal of the solvent, 6.7 g (32%) of 3,5-dichlorothiophenol was obtained, and after sublimation it had mp 53-54°. Found: C 40.02; H 2.25%.

CONCLUSIONS

1. Exchange reactions of diphenylantimony 2,6-dimethylthiophenolate with thiophenol and its $(C_6H_5)_3Sn$ and C_6H_5Hg -derivatives in chlorobenzene and the exchange of tetraphenylantimony 2-methylthiophenolate with 2-methylthiophenol and its C_6H_5Hg -, $(C_6H_5)_3Sn$ -, and $(C_6H_5)_3Pb$ -derivatives in chloroform were studied.

2. The migration ability of organometallic groups of the $R_n M$ type in derivatives of thiophenols in chlorobenzene and chloroform increases in the series: $(C_6H_5)_3Sn < (C_6H_5)_3Pb \approx (C_6H_5)_2Sb < C_6H_5Hg < (C_6H_5)_4Sb$.

3. The position of the exchange equilibria of tetraphenylantimony 2-methylthiophenolate with substituted tetraphenyltin thiophenolate depends greatly on the polar and steric effects of the substituents in the thiophenol ring.

4. The $(C_6H_5)_4$ SbS group possesses greater space requirements than the $(C_6H_5)_3$ SnS, C_6H_5 HgS, $(C_6H_5)_3$ PbS, and $(C_6H_5)_2$ SbS groups in uncoupled interactions with the o-CH₃ group.

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