NMR STUDY OF EXCHANGE EQUILIBRIA IN SOME THIOLS AND THEIR ORGANOMETALLIC DERIVATIVES (Hg, Sn, Pb)

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As was shown in a previous paper [1], exchange reactions of the metal—proton and metal—metal type, in solutions of mixtures of thiophenols and their organometallic derivatives in chlorobenzene, are slow on the NMR time scale. This circumstance made it possible to study exchange equilibria of the metal—proton and metal—metal type on the example of the reaction of thiophenol or its organometallic derivatives with either 2-methyl- or 2,6-dimethylthiophenol (I) derivatives.

$$C_6H_5SX^1 + 2\text{-}CH_3C_6H_4SX^2 \rightleftarrows C_6H_5SX^2 + 2\text{-}CH_3C_6H_4SX^1 \tag{1}$$

$$C_6H_5SX^1 + 2,6\text{-}(CH_3)_2C_6H_3SX^2 \rightleftarrows C_6H_5SX^2 + 2,6\text{-}(CH_3)_2C_6H_3CX^1 \tag{2}$$

$$X^1 \neq X^2 = H,\ C_6H_5Hg,\ (C_6H_5)_3Sn,\ (C_6H_5)_3Pb$$

The theory was expressed that a shift of the equilibrium position from the statistical position, which is observed for exchanges of the metal—proton type, and its shift toward the formation of the thiophenol organometallic derivatives, are associated with steric factors, which are caused by the greater space requirements of monovalent organometallic groupings when compared with the space requirements of the hydrogen atom. However, the position of the equilibrium in systems of this type can also be affected by the electronic effects of the substituents in the aryl radical attached to the sulfur atom, in particular the + I effect of the o-methyl groups. In addition, in systems with o substituents, which contain an unshared electron pair, the position of the equilibrium can depend not only on the polar and steric effects of the substituents, but also on the relative intensity of the intramolecular coordination interactions of the organometallic groupings and the hydrogen atom with the o substituents.

A study of the position of the exchange equilibria of the metal—proton and metal—metal type will probably permit comparing the relative strength of the intramolecular coordination bond (ICB) in o-substituted thiophenols and their organometallic derivatives. In this connection the equilibrium constants (K) of the exchange reactions of differently substituted thiophenols or their organometallic derivatives with the (I) derivatives were studied in the present paper.

$$ArSX^1 + 2,6\text{-}(CH_3)_2C_6H_3SX^2 \overset{K}{\rightleftarrows} ArSX^2 + 2,6\text{-}(CH_3)_2C_6H_3SX^1 \tag{3}$$

$$X^1 \neq X^2 = H,\ C_6H_5Hg,\ (C_6H_5)_3Sn,\ (C_6H_5)_3Pb$$

Since some of the organometallic derivatives of the substituted thiophenols proved to be difficultly soluble in chlorobenzene, we selected chloroform as the solvent. The NMR spectra of the mixtures of (I) with its organometallic derivatives, and also of the mixtures of different organometallic derivatives of (I), contain at ~20°C two signals of the o-CH_3 groups, the position of which corresponds to the pure compounds.* This testifies to the fact that in these systems in chloroform, the same as in chlorobenzene, exchanges of the metal—proton and metal—metal type are slow on the NMR time scale. The indicated circumstance, and also the quite great difference in the shielding of the signals of the methyl groups in (I) and its organometallic derivatives, made it possible to study the exchange equilibria (3) in chloroform in detail.

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* The δ_{CH_3} for $2,6\text{-}(CH_3)_2C_6H_3SX$ in 0.2 M solutions in $CHCl_3$ at 60 MHz is respectively 141.7, 158.1, 135.5, and 138.6 Hz [X = H, HgC_6H_5, $Sn(C_6H_5)_3$, and $Pb(C_6H_5)_3$].

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TABLE 1. Equilibrium Constants (K) for Exchanges of Metal —Proton and Metal—Metal Type in Substituted Thiophenols and Their Organometallalic Derivatives in the System 2,6-$(CH_3)_2C_6H_3SY$ + ArSY

Aromatic substituent Ar	X + Y					
	C_6H_5Hg + + H	$(C_6H_5)_3Pb$+ + H	$(C_6H_5)_3Sn$ + H	C_6H_5Hg + + $(C_6H_5)_3Sn$	C_6H_5Hg + + $(C_6H_5)_3Pb$	$(C_6H_5)_3Pb$ + + $(C_6H_5)_3Sn$
C_6H_5	4,4	5,0	4,7	0,77	1,0	1,1
		4,4*	5,7*			0,77*
2-FC_6H_4	7,9	3,3*	4,2*	1,9	2,4	0,77*
2-ClC_6H_4	4,1	2,2	1,7			1,4
		2,3*	1,4*	3,7	2,3	1,6*
2-BrC_6H_4	5,2	1,5*	1,0*	5,0	3,5	1,4*
2-$NO_2C_6H_4$	0,77	0,71*	0,33*	2,3	1,1	2,1*
2-$CH_3OOCC_6H_4$	0,42	0,12*	0,10*	4,4	3,6	1,2*
2-$CH_3OC_6H_4$	21,0	2,7*	2,8*	7,5	7,8	1,0*
3-ClC_6H_4	4,6	6,4*	5,1*	0,91	0,71	1,3*
4-$N(CH_3)_2C_6H_4$	6,0	6,6*	7,8*	0,77	0,91	0,83
2,6-$Cl_2C_6H_3$	3,6	2,3	0,83	5,9	2,1	2,8
		1,7*	0,61*			2,8*

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*The K values were found by calculation (see Experimental).

A comparison of the K values, obtained for systems that comprise the thiophenol, (I), and their organometallic derivatives, in chlorobenzene [1] with the K values for the same systems in chloroform (Table 1) reveals that the transition from chlorobenzene to chloroform has little effect on the position of the equilibrium, which in the case of exchange of the metal—metal type is close to the statistical value, while for the metal—proton exchange it is shifted toward the formation of the organometallic derivatives of the thiophenol, in which connection K lies in the range between 4 and 5. As follows from Table 2, the insertion of the electron-donor p-$N(CH_3)_2$ group into the thiophenol ring had practically no effect on the position of the equilibrium for exchanges of the metal—metal type, while it causes the equilibrium of the metal —proton type to shift slightly toward the formation of the p-dimethylaminothiophenol organometallic derivatives. The insertion of an electron-acceptor substituent like m-Cl essentially does not change the position of the equilibrium for all of the studied types of exchange.

The obtained results indicate that the polar effects of the substituents have little effect on the position of the equilibrium, but still these effects should be taken into consideration when making a more rigorous analysis. As an acceptable alternative for estimating the electronic effect of an o substituent, in subsequent discussion we will employ the data given in [2], which were obtained when an NMR study was made of the substituted phenols as analogs of thiophenols in DMSO. Taking into account the fact that a $N(CH_3)_2$ group in the p position causes a greater electronic effect than two o-CH_3 groups [2], it may be assumed that a deviation of the equilibrium from the statistical value for exchange of the metal—proton type (1) and (2) (X^1 = H, X^2 = MR_n) is caused mainly not by the electron-donor effect of the methyl groups, but rather by the different space requirements of the hydrogen atom, on the one hand, and the monovalent organometallic groupings MR_n, on the other hand.

The insertion of substituents, which have unshared electron pairs, ortho to the SH and SMR_n groupings, in many cases leads to a noticeable change in the position of the equilibrium when compared with the equilibrium involving the unsubstituted thiophenol and its organometallic derivatives. Here the K values are quite dependent on the nature of both the migrating groups and the o substituent (see Table 1), in which connection the latter in the character of their effect on the equilibrium position can be divided into two groups.

Systems with the first group of o substituents (halogen and OCH_3) have the following characteristics. In the cases of exchanging the phenylmercury grouping by the triphenyltin and triphenyllead groupings the equilibrium is shifted toward the formation of the organomercury derivative with o substituents. For exchanges of the metal—proton type the equilibrium in most cases is shifted toward the organometallic derivative with o substituents, in which connection the shift increases notcieably when going from exchanges involving the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ (the K values change from 1.0 to 4.2) to exchanges involving the C_6H_5Hg group (K varies from 4.1 to 21.0).

In the case of metal—metal exchanges for systems with the second type of substituents (o-NO_2 and o-$COOCH_3$) the same rules are observed as for the systems with o halogens and the o-CH_3 group: the equilibrium is shifted toward the formation of the organomercury derivative with the o substituent, whereas for exchanges of the metal—proton type the equilibrium is shifted noticeably toward the formation of the o substituted thiophenol ($K < 1$).

The groupings C_6H_5HgS, $(C_6H_5)_3SnS$, and $(C_6H_5)_3PbS$ have practically the same steric requirements when they take part in nonvalent interactions with o-CH_3 groups [1]. As was indicated above, substituents in the aromatic ring that contains the sulfur atom have little effect on the position of the exchange equilibrium of the metal—metal type. As a result, it may be assumed that in the case of systems involving the derivatives of o-substituted thiophenols the observed shift in the position of the equilibrium for this type of exchange is caused mainly by the difference in the strength of the ICB of the monovalent organometallic groupings with an o substituent.

The advanced postulation can be considered to be sufficiently rigorous only for systems with o-substituents whose effective size does not exceed the effective size of the methyl group. Such substituents are the halogen atoms and probably the OCH_3 group, since the o-substituted anisoles exist mainly in the s-trans conformation [3]. In contrast to this the geometry of the nitro and carbomethoxy groups differs sharply from the geometry of the CH_3 group, as a consequence of which the C_6H_5Hg, $(C_6H_5)_3Sn$, and $(C_6H_5)_3Pb$ groupings can have different space requirements toward the indicated substituents and those with a similar geometry.

From the data in Table 1 it follows that in the case of such substituents as halogens and OCH_3, the investigated groups can be arranged in the following order when based on the increase in their coordination capacity: $(C_6H_5)_3Sn < (C_6H_5)_3Pb < C_6H_5Hg$. This conclusion is in agreement with the data obtained in [4] on the basis of studying the chemical shifts of fluorine in 2,6-dibromo-4-fluorothiophenol derivatives, and also with the results of studying 2,6-dichlorothiophenol and its organometallic derivatives by the NQR method [5].

It should be mentioned that the obtained results fail to give any information on either the existence or absence of an ICB in the case of the triphenyltin derivatives of o substituted thiophenols. A study of this problem will be made in further studies of the exchange equilibria involving such groupings as $(C_6H_5)_3C$, which are incapable of specific, not van der Waals interactions with an o substituent.

In connection with the mentioned characteristics of the o-nitro and o-carbomethoxy groups when discussing the chelate rings formed by organometallic groupings it is only possible to compare their relative strength, which includes both the bonding and nonbonding interactions and increases in the order: $(C_6H_5)_3Sn < (C_6H_5)_3Pb < C_6H_5Hg$. The greater coordination capacity of the C_6H_5Hg grouping when compared with the other groupings is apparently explained by the conformity of the geometry of the ICB in the organomercury derivatives of the o substituted thiophenols with the geometry characteristic for the tricoordinated mercury atom, and a nonconformity of the optimum geometry of the pentacoordinated metal atom in the case of the organotin groupings [6].

When discussing the equilibrium position for exchange of the metal—proton type in systems that contain an o substituent with an unshared electron pair it is necessary to take into account the differences in the space requirements of the hydrogen atom and the monovalent organometallic groupings. Taking into consideration the approximately additive effect of the o-CH_3 groups on the equilibrium position when going from 2-methylthiophenol derivatives to the (I) derivatives, it may be assumed, in the absence of intramolecular coordination, that $K \cong 2$ when groupings, close in size to the CH_3 group, are inserted in the o position of the thiophenol. Substantial deviation from this value for systems involving o-halo- and o-methoxy-substituted thiophenols is mainly associated with a difference in the strength of the intramolecular hydrogen bond (IMHB) of the SH proton with the o substituent and the ICB involving the metal atom.

It should be mentioned that the existing literature data on the IR and NMR spectra of o substituted thiophenols testify to the presence of an IMHB in these compounds, in particular in the compounds that contain halogens and the nitro group in the o position [7, 8].

Interesting data were obtained when the exchange equilibria were studied for the o-Br derivatives of the thiophenol (see Table 1). Taking into account the fact that the van der Waals radius of the Br atom is approximately equal to the van der Waals radius of the CH_3 group [9], it may be concluded that the ICB of the o-bromo atom with the mercury atom is stronger than the IMHB, while the latter in turn is more stable than the coordination bonds involving the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ groupings. As a result, in the case of systems involving the organometallic derivatives of the o-Br derivatives of the thiophenol the organometallic groupings and the hydrogen atom can be arranged in the following order of increase in the strength of their ICB with an o halogen: $(C_6H_5)_3Sn < (C_6H_5)_3Pb < H < C_6H_5Hg$.

TABLE 2. Analysis Results and Melting Points of Organometallic Derivatives of Thiophenols

Compound	T, mp, °C	Found/calculated, %	
		C	H
$C_6H_5HgSC_6H_4Cl$-2	128—129	$\frac{33,90}{34,16}$	$\frac{2,39}{2,13}$
$(C_6H_5)_3PbSC_6H_4Cl$-2	82—84	$\frac{49,60}{49,52}$	$\frac{3,30}{3,29}$
$(C_6H_5)_3SnSC_6H_4Cl$-2	60—61	$\frac{58,66}{58,40}$	$\frac{4,02}{3,88}$
$C_6H_5HgSC_6H_4Br$-2	151—154	$\frac{30,97}{30,94}$	$\frac{2,16}{1,95}$
$(C_6H_5)_3PbSC_6H_4Br$-2	81—83	$\frac{46,35}{46,00}$	$\frac{3,60}{3,06}$
$(C_6H_5)_3SnSC_6H_4Br$-2	68—70	$\frac{53,13}{53,57}$	$\frac{3,86}{3,56}$
$C_6H_5HgSC_6H_4N(CH_3)_2$-4	146—149	$\frac{39,14}{39,07}$	$\frac{3,61}{3,49}$
$(C_6H_5)_3PbSC_6H_4N(CH_3)_2$-4	97—98	$\frac{52,75}{52,88}$	$\frac{4,31}{4,24}$
$(C_6H_5)_3SnSC_6H_4N(CH_3)_2$-4	118—119	$\frac{62,00}{62,15}$	$\frac{5,30}{4,98}$
$C_6H_5HgSC_6H_4NO_2$-2	139—140	$\frac{33,28}{33,37}$	$\frac{2,68}{2,10}$
$(C_6H_5)_3PbSC_6H_4NO_2$-2	108—110	$\frac{48,87}{48,63}$	$\frac{3,38}{3,23}$
$(C_6H_5)_3SnSC_6H_4NO_2$-2	113—115	$\frac{57,33}{57,17}$	$\frac{4,26}{3,80}$
$C_6H_5HgSC_6H_4Cl$-3	140—141	$\frac{34,27}{34,20}$	$\frac{2,28}{2,15}$
$(C_6H_5)_3PbSC_6H_4Cl$-3	90—91	$\frac{50,00}{49,51}$	$\frac{3,44}{3,29}$
$(C_6H_5)_3SnSC_6H_4Cl$-3	84—85	$\frac{58,22}{58,39}$	$\frac{4,14}{3,88}$
$C_6H_5HgSC_6H_4COOCH_3$-2	88—90	$\frac{37.91}{37,79}$	$\frac{2,73}{2.72}$
$(C_6H_5)_3PbSC_6H_4COOCH_3$	56—58	$\frac{52,06}{51,55}$	$\frac{3,88}{3,66}$
$(C_6H_5)_3SnSC_6H_4COOCH_3$-2	58—59	$\frac{60,40}{60,38}$	$\frac{3,94}{4,29}$
$C_6H_5HgSC_6H_4OCH_3$-2	112—113	$\frac{37,25}{37,45}$	$\frac{3,09}{2,90}$
$(C_6H_5)_3PbSC_6H_4OCH_3$-2	101—102	$\frac{51,94}{51,97}$	$\frac{3,85}{3,84}$
$(C_6H_5)_3SnSC_6H_4OCH_3$-2	93—95	$\frac{61,24}{61,38}$	$\frac{4.55}{4,53}$
$C_6H_5HgSC_6H_4F$-2	81—83	$\frac{35,31}{35,60}$	$\frac{2,38}{2,24}$
$(C_6H_5)_3PbSC_6H_4F$-2	89—91	$\frac{51,39}{50,96}$	$\frac{3,52}{3,39}$
$(C_6H_5)_3SnSC_6H_4F$-2	81—83	$\frac{60,31}{60,41}$	$\frac{4,00}{4,01}$

When discussing exchange of the metal—proton type in systems involving other o-halo-substituted thiophenols and o-methoxythiophenol, and taking into account the fact that the van der Waals radii of fluorine, chlorine, and oxygen are somewhat smaller than the radius of the CH_3 group, it may also be concluded that the ICB involving the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ groups and the hydrogen atom is less stable than the ICB involving the C_6H_5Hg group. This result is in agreement with the previously obtained data on the greater strength of the ICB in the phenylmercury derivatives of 2,6-dihalo-substituted thiophenols when compared with the IMHB in the latter [4, 5].

When discussing exchange of the metal—proton type, involving o-nitrothiophenol and o-carbomethoxythiophenol, it should be mentioned that in this case the observed shift of the equilibrium toward the o-substituted thiophenol can be caused, at least partially, by the steric effect of the o substituent. At the same time, the assumption that only nonvalent interactions between the organometallic groupings and the discussed substituents are present in these systems must be excluded on the basis of the data for systems involving 2-methoxy-thiophenol. It is known that an IMHB with the NO_2 and $OCOOCH_3$ groups exists in o-substituted thiophenols [7, 8]. In combination with the obtained data (see Table 1), the indicated considerations make it possible to conclude that in systems with o-NO_2 and o-$COOCH_3$ substituents the stability of the chelate ring involving the hydrogen atom is greater than that of the rings involving monovalent organometallic groupings.

In summary, it may be said that for thiophenols and their organometallic derivatives, the same as for benzenesulfonyl-o-toluidide derivatives [10], the five-membered chelate rings involving the phenylmercury grouping are more stable than the corresponding rings involving hydrogen, whereas in the case of the six-membered rings the reverse is true. In contrast to this, for the triphenyltin or triphenyllead groupings, both the five- and the six-membered chelate rings prove to be less stable than the chelate rings with the IMHB.

From the data in Table 1 it also follows that in the case of systems that contain 2,6-dichlorothiophenol and (or) its organometallic derivatives the same rules regarding the relative stability of the chelate rings, formed by an o halogen with monovalent organometallic groupings and the hydrogen atom, are retained as for the corresponding systems that contain 2-chlorothiophenol and its organometallic derivatives.

In the present paper we also studied the effect of temperature on the equilibrium position for exchanges of the metal—proton and metal—metal type in chloroform. It proved that in the range from —50 to 50° a change in the temperature has no effect on the equilibrium position for the reactions of phenylmercury 2,6-dimethylthiophenolate with either the triphenyltin thiophenolate or o-chlorothiophenolate. These results indicate that differences in the relative space requirements of the C_6H_5Hg and $(C_6H_5)_3Sn$ groupings cannot be detected in the investigated temperature range. In addition, under the selected conditions the difference in the stability of the chelate rings involving these groupings and the chlorine atom remains unchanged.

While studying the exchanges of thiophenol with phenylmercury 2-methylthiophenolate or with phenylmercury 2,6-dimethylthiophenolate it was found that a temperature reduction from 50 to —50° leads to an increase in K, respectively, from 2.0 to 7.1, and from 4.0 to 34. The heats of these reactions in the indicated temperature range are, respectively, —1.8 ± 0.2 and —3.1 ± 0.3 kcal/mole. The observed phenomenon is apparently caused by an enhanced destabilization of the phenylmercury derivatives of 2-methylthiophenol and (I) when the temperature is lowered when compared with the thiophenol derivatives, in which connection this destabilization is manifested to a greater degree in the latter case than in the former.

EXPERIMENTAL METHOD

A Perkin—Elmer R-12 spectrometer (60 MHz) was used to measure the chemical shifts and study the exchange equilibria at 34°. The chemical shifts were determined with an accuracy of ±0.3 Hz. 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 starting compounds. The accuracy of the determination was K ± 10%.

The K values in Table 1 marked by an asterisk were obtained from the available K values on the assumption that K_1 and K_2 for the reactions

$$RA + R_1B \overset{K_1}{\rightleftarrows} RB + R_1A \ \text{и} \ RC + R_1B \overset{K_2}{\rightleftarrows} RB + R_1C$$

are known, and then the equilibrium constant of the reaction $RA + R_1C \overset{K_3}{\rightleftarrows} RC + R_1A$ is equal to K_2/K_1.

On the example of the exchange reactions of thiophenol and its organometallic derivatives with the (I) derivatives, for which the experimental K values were obtained for all of the possible combinations, it was shown that the calculated K values are in good agreement with the experimental values (see Table 1).

As supporting systems, whose K values were determined experimentally, we selected the exchange reactions of 2,6-dimethylthiophenylmercury with the substituted thiophenols and their $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives. For the other systems the K values were calculated. This choice was due to achieving the equilibrium state in the indicated systems before the start of taking the NMR spectra. For these systems the separation of the corresponding signals in the spectrum is quite large, which facilitates the integration. The remaining three possible systems do not have these advantages.

The organometallic derivatives of the substituted thiophenols were synthesized by treating the Na salts of the appropriate thiols in aqueous alcohol medium with phenylmercury acetate or with the triphenyltin and triphenyllead chlorides [1]. The melting points and analysis results are given in Table 2. The organometallic derivatives of 2,6-dichlorothiophenol were described previously [5].

CONCLUSIONS

1. The polar effects of the substituents in the thiophenol ring have little effect on the position of the exchange equilibria of the metal—proton and metal—metal type involving substituted thiophenols and their C_6H_5Hg, $(C_6H_5)_3Sn$, and $(C_6H_5)_3Pb$ derivatives.

2. Depending on the acceptor of the unshared electron pair, in o-substituted thiophenols and their organometallic derivatives the stability of the chelate rings in most cases increases in the order $(C_6H_5)_3Sn < (C_6H_5)_3Pb < H < C_6H_5Hg$ for five-membered rings, and in the sequence $(C_6H_5)_3Sn < (C_6H_5)_3Pb < C_6H_5Hg < H$ for six-membered rings.

LITERATURE CITED

1. D. N. Kravtsov, A. S. Peregudov, L. A. Fedorov, and E. M. Rokhlina, J. Organometal. Chem., 77, 199 (1974).
2. M. T. Tribble and J. G. Traynham, J. Am. Chem. Soc., 91, 379 (1969).
3. W. F. Anzilotti and B. C. Curran, J. Am. Chem. Soc., 65, 607 (1943).
4. D. N. Kravtsov, B. A. Kvasov, L. S. Golovchenko, E. M. Rokhlina, and E. I. Fedin, J. Organometal. Chem., 39, 107 (1972).
5. D. N. Kravtsov, G. K. Semin, A. P. Zhukov, T. A. Babushkina, E. M. Rokhlina, and A. N. Nesmeyanov, Teor. i Éksperim. Khim., 9, 513 (1973).
6. R. Hulme, J. Chem. Soc., C 1524 (1963).
7. A. E. Lutskii, A. K. Kul'chitskaya, E. M. Obukhova, S. A. Volchenok, and G. I. Sheremet'eva, Zh. Obshch. Khim., 36, 1577 (1966).
8. T. Kobayashi, A. Yamashita, and Y. Furuya, Bull. Chem. Soc. Japan, 44, 1858 (1971).
9. A. Bondi, J. Phys. Chem., 68, 441 (1964).
10. A. S. Peregudov, D. N. Kravtsov, and L. A. Fedorov, J. Organometal. Chem., 71, 347 (1974).