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A COMPARATIVE PMR STUDY OF EXCHANGE REACTIONS IN ORGANO-MERCURY, -TIN AND -LEAD DERIVATIVES OF SOME THIOLS

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Summary

Metal—proton and metal—metal exchange reactions have been studied by PMR for thiophenol, 2-methylthiophenol, 2,6-dimethylthiophenol, benzyl mercaptan and their C_6H_5Hg, $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives in chlorobenzene and pyridine solutions. In chlorobenzene the metal—metal exchange has been found to proceed in many cases at a greater rate than the metal—proton type, the exchange mobility of hydrogen and organometallic groups in chlorobenzene increasing in the order $(C_6H_5)_3Sn < H < (C_6H_5)_3Pb < C_6H_5Hg$. In the case of the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ groups, pyridine accelerates the metal—proton exchange to a greater extent than the metal—metal exchange.

The influence of various factors on the exchange reactions has been studied. Analysis of the experimental findings and literature data has led to the conclusion that most probably the mechanism of the exchange reactions involves an associative pathway, the ease of exchange being mainly determined by the ability of the migrating group to form a cyclic transition state with delocalized bonds. The data on the exchange equilibria of the organometallic derivatives of 2-methylthiophenol and 2,6-dimethylthiophenol with thiophenol and its derivatives demonstrate that the C_6H_5HgS, $(C_6H_5)_3SnS$ and $(C_6H_5)_3PbS$ groups have equal steric requirements when involved in non-bonded interactions with *o*-methyl substituents.

Introduction

To obtain a better understanding of the nature of labile H—X bonds in XH acids (where X is N, O or S), as well as of labile M—X bonds in the corresponding organometallic derivatives of the type R_nMX (where R_nM represents a univalent organometallic group such as RHg, R_3Sn or R_3Pb) some valuable data can be obtained by investigating the reactivities of these compounds in the intermolecular exchange reactions of three various types, which include the hydrogen exchange, the exchange of hydrogen for an organometallic group and exchange of one organometallic group for another:

$$HX_1 + H^*X_2 \rightleftharpoons H^*X_1 + HX_2$$

$$HX_1 + R_nMX_2 \rightleftharpoons R_nMX_1 + HX_2$$

$$R_nMX_1 + R_nM^*X_2 \rightleftharpoons R_nM^*X_1 + R_nMX_2$$

$$[X_1 = X_2, X_1 \neq X_2, R_nM \neq R_nM^*]$$

In a previous work [1] we have investigated the relative reactivities of the H—N and Hg—N bonds in the exchange reactions of all three types, using as model systems *N*-methylbenzenesulphonamides and their phenylmercury derivatives. It has been found that the relative ease of proton—proton and metal—metal exchange involving the above NH acids and the corresponding phenylmercury derivatives depends on both their structure and the solvating power of the medium.

It appeared interesting to extend the comparison of the migrating abilities of hydrogen and univalent organometallic groups to the case of the H—S and M—S bonds. From a rather limited number of studies concerning the hydrogen lability in the SH-group of thiols it is known to be considerably smaller than the migrating ability of hydrogen in the OH-group of the corresponding oxygen analogues [2—5]. The data on the lability of M—S bonds in organo-mercury, -tin and -lead compounds also seem to be rather limited [6—7].

The present report concerns a comparative semiquantitative study of exchange reactions of the proton—proton, metal—proton and metal—metal types in some thiols and their organo-mercury, -tin and -lead derivatives, in which the thiols studied included thiophenol, 2-methylthiophenol, 2,6-dimethylthiophenol and benzyl mercaptan, whereas the univalent organometallic groups were represented by the C_6H_5Hg, $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ moieties:

$$HSR_1 + H^*SR_2 \rightleftharpoons H^*SR_1 + HSR_2$$

$$HSR_1 + R_nMSR_2 \rightleftharpoons R_nMSR_1 + HSR_2$$

$$R_nMSR_1 + R_nM^*SR_2 \rightleftharpoons R_nM^*SR_1 + R_nMSR_2$$

$$[R_1 = R_2, R_1 \neq R_2, R_nM = R_nM^*, R_nM \neq R_nM^*; R_1, R_2 = C_6H_5S, 2\text{-}CH_3C_6H_4S, 2,6\text{-}(CH_3)_2C_6H_3S, C_6H_5CH_2S; R_nM, R_nM^* = C_6H_5Hg, (C_6H_5)_3Sn, (C_6H_5)_3Pb]$$

The exchange reactions were investigated by PMR, using the common technique of recording the spectrum of a reaction mixture in dependence on temperature and concentration under the conditions of dynamic equilibrium. This technique was applied in studying the mixtures of 2-methylthiophenol, 2,6-dimethylthiophenol and benzyl mercaptan with their organometallic derivatives, as well as the mixtures of different organometallic derivatives of these thiols. However, in many cases the exchange proved to be slow on the PMR time scale and in this connection the spectra of some systems were studied also before the attainment of equilibrium. This method was used in studying the mixtures of organometallic derivatives of 2-methylthiophenol and 2,6-dimethylthiophenol with thiophenol and its derivatives. In this case the conclusions about the facility of exchange were based on the ease of the forward reactions.

Results

1. *Exchange reactions in the organometallic derivatives of thiophenols*

The exchange reactions involving 2-methylthiophenol, 2,6-dimethylthiophenol and their organometallic derivatives were studied mainly in chlorobenzene and pyridine solutions. The former solvent was taken as a sufficiently inert solvent with respect to specific solvation of the metal atom and the latter was used as a strongly coordinating solvent. The chemical shifts of the methyl group for solutions of the above compounds of 0.2 *M* concentration are listed in Table 1.

These data show that the shielding of the methyl group protons changes appreciably on substituting the HS proton by an organometallic group, and it is decreased in all the cases investigated. On the other hand, the chemical shift of the *o*-methyl group depends also on the nature of organometallic substituent, the shielding of the methyl protons in the derivatives of both thiophenols increasing in the order $C_6H_5Hg < (C_6H_5)_3Pb < (C_6H_5)_3Sn$. Thus, the observed differences in the shielding of the methyl group protons allowed, in principle, to study the exchange reactions of the following types:

$$HSR + R_nMS^*R \rightleftharpoons R_nMSR + HS^*R$$

$$R_nMSR + R_nM^*S^*R \rightleftharpoons R_nM^*SR + R_nMS^*R$$

$[R = 2\text{-}CH_3C_6H_4S,\ 2,6\text{-}(CH_3)_2C_6H_3S;\ R_nM \neq R_nM^* = C_6H_5Hg,\ (C_6H_5)_3Sn,$
$(C_6H_5)_3Pb]$

At the same time, the PMR spectra of the compounds under consideration could be also affected by the possible intramolecular dynamics involving the rotation of the corresponding groups about the aryl carbon—sulphur bond. To clear up this problem, the spectra of the individual compounds were examined in solution at low temperatures. It was found that in all cases lowering the temperature to −40° for chlorobenzene solutions and to −110° for solutions in a mixture of chloroform and methylene chloride (1/3 v/v) does not change

TABLE 1

CHEMICAL SHIFTS OF THE METHYL GROUP SIGNAL IN 0.2 *M* SOLUTIONS OF 2-METHYLTHIOPHENOL, 2,6-DIMETHYLTHIOPHENOL AND THEIR ORGANOMETALLIC DERIVATIVES (in Hz relative to TMS)

Compound	Solvent	
	C_6H_5Cl	C_5H_5N
$HSC_6H_4CH_3$-2	127.5	136.3
$C_6H_5HgSC_6H_4CH_3$-2	149.6	156.9
$(C_6H_5)_3SnSC_6H_4CH_3$-2	136.3	140.0
$(C_6H_5)_3PbSC_6H_4CH_3$-2[a]	139.8	143.2
$HSC_6H_3(CH_3)_2$-2,6	130.5	139.1
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	156.7	162.6
$(C_6H_5)_3SnSC_6H_3(CH_3)_2$-2,6	137.9	142.5
$(C_6H_5)_3PbSC_6H_3(CH_3)_2$-2,6[a]	142.7	147.1

[a] The ^{207}Pb satellites with $J(^{207}Pb—H)$ 3 to 4 Hz are observed.

perceptibly the width of the methyl group signal. This seems to indicate that the intramolecular rotation in the thiophenols and their organometallic derivatives studied is probably fast on the PMR time scale and can be excluded from further considerations.

In Table 2 are presented the chemical shifts of the methyl group protons in solutions of equimolar mixtures of different compounds with 0.2 *M* concentration of each component. From these data it is readily seen that the spectra of mixtures of thiophenols with their organometallic derivatives in chlorobenzene solution exhibit two methyl group signals, the chemical shifts of these resonances coinciding within the experimental error with those of the individual compounds. Raising the temperature to 100° did not lead to the broadening of these signals. Similarly, the chemical shifts of the methyl protons in the mixtures of different organometallic derivatives scarcely differ from those of the starting reactants. Thus, if in these systems the metal—proton and metal—metal exchange reactions occur, they are slow on the time scale of the measurement.

The existence of exchange reactions of the above types in chlorobenzene solution was demonstrated by special experiments in which the organometallic derivatives of 2-methylthiophenol and 2,6-dimethylthiophenol were allowed to react with thiophenol and its organometallic derivatives by mixing them in 1/1 ratio in chlorobenzene solution. It was found that after some time a second methyl group signal appeared in the PMR spectrum of the reaction mixture, which corresponded to one of the products of the expected exchange reaction. This indicates the occurrence in these systems of exchange processes of the metal—proton and metal—metal types. It was established that the exchange reactions are reversible, because the same equilibrium state was attained from both possible pairs of reactants, and thus they can be represented by the following equations:

$$R_nMSAr + HSC_6H_5 \rightleftharpoons HSAr + R_nMSC_6H_5$$

$$R_nMSAr + R_nM^*SC_6H_5 \rightleftharpoons R_nM^*SAr + R_nMSC_6H_5$$

$$[Ar = 2\text{-}CH_3C_6H_4,\ 2,6\text{-}(CH_3)_2C_6H_3$$
$$R_nM \neq R_nM^* = C_6H_5Hg,\ (C_6H_5)_3Sn,\ (C_6H_5)_3Pb]$$

Consequently, such exchange reactions are slow only on the PMR time scale and proceed with finite rates at the room temperature.

To follow the exchange processes in the above systems, the PMR spectra of the reaction mixtures were observed as a function of the time elapsed after mixing the reactant solutions. By measuring the relative intensity of the methyl group signal belonging to one of the reaction products, the time within which 10% of the starting compounds had reacted ($t_{0.1}$) was determined and taken as a semiquantitative criterion of the ease of exchange. The validity of using this criterion as a measure of facility of the forward exchange reaction for the systems investigated in our case can be substantiated by the following considerations.

In the course of the present study it was found that the $t_{0.1}$ values for exchange reactions of the metal—proton and metal—metal types depend upon the concentration of each reactant, which suggested that these reactions might be

TABLE 2

CHEMICAL SHIFTS OF THE METHYL GROUP SIGNALS FOR 0.2 *M* SOLUTIONS OF EQUIMOLAR MIXTURES OF 2-METHYLTHIOPHENOL AND 2,6-DIMETHYLTHIOPHENOL WITH THEIR ORGANOMETALLIC DERIVATIVES AND THE LIMITING VALUES OF THE PRE-EXCHANGE LIFE-TIMES

Reactants		Solvent			
		C_6H_5Cl		C_5H_5N	
		$\delta(CH_3)$ (Hz)	τ_a (sec)	$\delta(CH_3)$ (Hz)	τ_a (sec)
$HSC_6H_4CH_3$-2	+ $C_6H_5HgSC_6H_4CH_3$-2	127.2 150.0	> 0.20	147.0	< 0.022
$HSC_6H_4CH_3$-2	+ $(C_6H_5)_3SnSC_6H_4CH_3$-2	127.1 136.1	> 0.51	138.2	< 0.12
$HSC_6H_4CH_3$-2	+ $(C_6H_5)_3PbSC_6H_4CH_3$-2	127.2 139.4	> 0.37	139.9	< 0.065
$(C_6H_5)_3SnSC_6H_4CH_3$-2	+ $C_6H_5HgSC_6H_4CH_3$-2	136.1 149.8	> 0.34	139.8 157.1	> 0.27
$C_6H_5HgSC_6H_4CH_3$-2	+ $(C_6H_5)_3PbSC_6H_4CH_3$-2	149.7 139.4	> 0.46	156.2 143.2	> 0.33
$(C_6H_5)_3SnSC_6H_4CH_3$-2	+ $(C_6H_5)_3PbSC_6H_4CH_3$-2	135.8 139.4	> 1.28	139.9 143.6	> 1.40
$HSC_6H_3(CH_3)_2$-2,6	+ $C_6H_5HgSC_6H_3(CH_3)_2$-2,6	130.1 155.8	> 0.17	151.1	< 0.019
$HSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_3SnSC_6H_3(CH_3)_2$-2,6	130.6 138.4	> 0.61	138.9 141.8	> 1.32
$HSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_3PbSC_6H_3(CH_3)_2$-2,6	130.2 142.7	> 0.37	139.4 146.8	> 0.56
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_3SnSC_6H_3(CH_3)_2$-2,6	156.9 138.2	> 0.24	163.0 142.3	> 0.21
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_3PbSC_6H_3(CH_3)_2$-2,6	156.9 143.2	> 0.33	162.9 147.2	> 0.29
$(C_6H_5)_3SnSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_3PbSC_6H_3(CH_3)_2$-2,6	138.7 143.6	> 0.94	142.9 147.1	> 0.98

overall second-order. If we consider a second-order reversible reaction:

$$A + B \underset{k_b}{\overset{k_f}{\rightleftarrows}} C + D$$

under the initial conditions:

$t_0 = 0,\ [A]_0 = a,\ [B]_0 = b,\ [C]_0 = [D]_0 = 0$

and using the notations:

$[A] = a - x,\ [B] = b - x,\ [C] = [D] = x$

then the rate of the forward reaction can be represented [8] by

$$\frac{dx}{dt} = k_f(a-x)(b-x) - k_b x^2$$

or

$$\frac{dx}{dt} = k_f [ab - (a+b)x + (1 - \frac{1}{K})x^2] \qquad \text{where } K = \frac{k_f}{k_b}$$

If K is not considerably smaller than unity, then for small degrees of transformation with $x \leqslant 0.1a$ the latter term may be safely neglected, which leads to

$$\frac{dx}{dt} = k_f [ab - (a+b)x]$$

Further, using the approximation of graphical differentiation [9], which in our case introduces a relative error not greater than 0.5%, we may write:

$$\frac{\Delta x}{\Delta t} = \left(\frac{dx}{dt}\right)_{\Delta x/2}$$

Combining the two expressions we obtain:

$$\frac{\Delta x}{\Delta t} = k_f [ab - 0.5(a+b)\Delta x]$$

In our case $\Delta x = 0.1a$ and $\Delta t = t_{0.1}$ which corresponds to the 10% transformation of the starting reactant and yields the expression:

$$\frac{1}{t_{0.1}} = 10k_f [b - 0.05(a+b)]$$

On the basis of the latter expression it can be shown that for two experiments with the same initial concentrations $a_1 = a_2$ and different initial concentrations $b_1 \neq b_2$ the following relation should be valid:

$$\frac{t_{0.1(1)}}{t_{0.2(2)}} = [b_2 - 0.05(a_2 + b_2)]/[b_1 - 0.05(a_1 + b_1)]$$

TABLE 3

CONCENTRATION DEPENDENCE OF $t_{0.1}$ VALUES FOR SOME EXCHANGE REACTIONS OF THE METAL—PROTON AND METAL—METAL TYPES IN C_6H_5Cl[a]

Reactants and initial concentrations (*M*)			$t_{0.1}$ (min)
$(C_6H_5)_3SnSC_6H_4CH_3$-2	+	HSC_6H_5	
0.10		0.10	410 ± 50
0.10		0.20	200 ± 15
0.10		0.93	46 ± 5
$(C_6H_5)_3SnSC_6H_5$	+	$HSC_6H_4CH_3$-2	
0.10		0.10	780 ± 120
0.23		0.11	480 ± 30
0.47		0.11	180 ± 30
$(C_6H_5)_3SnSC_6H_4CH_3$-2	+	$(C_6H_5)_3PbSC_6H_5$	
0.10		0.10	25 ± 7
0.10		0.20	11 ± 4

[a] The reactions were run in argon.

which can be substituted by a simpler one:

$$t_{0.1(1)}/t_{0.1(2)} \approx b_2/b_1$$

with an error not greater than 10%, if $a \leqslant b$. From Table 3 it can be seen that the $t_{0.1}$ values for some representative metal—proton and metal—metal exchange reactions are in fact approximately inversely proportional to the concentration of each reactant. This indicates that these exchange reactions are apparently overall second-order, being first-order with respect to each reactant.

Further, employing the above expression for $1/t_{0.1}$, it can be shown that for two reversible second-order reactions with equal initial concentrations of the reactants and equilibrium constants not greatly different from unity the following relationship should be valid:

$$t_{0.1(1)}/t_{0.1(2)} \approx k_{f(2)}/k_{f(1)}$$

In this expression the main error will be determined by the error in the evaluation of $t_{0.1}$, due to limitations of the PMR technique in studying the kinetics of reversible reactions under non-equilibrium conditions.

Inspection of Table 4 shows that in the case of the metal—proton exchange the ease of exchange depends markedly upon the nature of organometallic group, the differences in the exchange rate being quite large. Thus, in the exchange of the C_6H_5Hg group for hydrogen the equilibrium is attained within the time less than that required for recording the PMR spectrum after mixing the

TABLE 4

VALUES OF $t_{0.1}$ AND EQUILIBRIUM CONSTANTS FOR THE EXCHANGE REACTIONS OF ORGANOMETALLIC DERIVATIVES OF 2-METHYLTHIOPHENOL AND 2,6-DIMETHYLTHIOPHENOL WITH THIOPHENOL AND ITS DERIVATIVES[a]

Reactants		Solvent	$t_{0.1}$	K
$C_6H_5HgSC_6H_4CH_3$-2	+ HSC_6H_5	C_6H_5Cl	< 50 sec[b]	2.0
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	+ HSC_6H_5	C_6H_5Cl	< 50 sec[b]	4.0
$(C_6H_5)_3PbSC_6H_4CH_3$-2	+ HSC_6H_5	C_6H_5Cl	210 ± 30 sec	2.0
$(C_6H_5)_3PbSC_6H_3(CH_3)_2$-2,6	+ HSC_6H_5	C_6H_5Cl	390 ± 30 sec	4.0
$(C_6H_5)_3PbSC_6H_3(CH_3)_2$-2,6	+ HSC_6H_5	C_5H_5N	< 50 sec[b]	4.0
$(C_6H_5)_3SnSC_6H_4CH_3$-2	+ HSC_6H_5	C_6H_5Cl	410 ± 50 min	2.5
$(C_6H_5)_3SnSC_6H_3(CH_3)_2$-2,6	+ HSC_6H_5	C_6H_5Cl	29 ± 1 hr	4.8
$(C_6H_5)_3SnSC_6H_4CH_3$-2	+ $C_6H_5HgSC_6H_5$	C_6H_5Cl	< 50 sec[b]	1.0
$(C_6H_5)_3SnSC_6H_3(CH_3)_2$-2,6	+ $C_6H_5HgSC_6H_5$	C_6H_5Cl	< 50 sec	1.2
$(C_6H_5)_3SnSC_6H_3(CH_3)_2$-2,6	+ $C_6H_5HgSC_6H_5$	C_5H_5N	< 50 sec[b]	1.0
$(C_6H_5)_3PbSC_6H_4CH_3$-2	+ $C_6H_5HgSC_6H_5$	C_6H_5Cl	< 50 sec[b]	1.2
$(C_6H_5)_3PbSC_6H_3(CH_3)_2$-2,6	+ $C_6H_5HgSC_6H_5$	C_6H_5Cl	< 50 sec[b]	1.2
$(C_6H_5)_3PbSC_6H_3(CH_3)_2$-2,6	+ $C_6H_5HgSC_6H_5$	C_5H_5N	< 50 sec[b]	1.0
$(C_6H_5)_3PbSC_6H_4CH_3$-2	+ $(C_6H_5)_3SnSC_6H_5$	C_6H_5Cl	20 ± 10 min	1.0
$(C_6H_5)_3PbSC_6H_4CH_3$-2	+ $(C_6H_5)_3SnSC_6H_5$	C_5H_5N	< 50 sec[b]	1.0
$(C_6H_5)_3SnSC_6H_4CH_3$-2	+ $(C_6H_5)_3PbSC_6H_5$	C_6H_5Cl	25 ± 7 min	1.0
$(C_6H_5)_3SnSC_6H_4CH_3$-2	+ $(C_6H_5)_3PbSC_6H_5$	C_5H_5N	< 50 sec[b]	1.0
$(C_6H_5)_3SnSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_3PbSC_6H_5$	C_6H_5Cl	45 ± 15 min	1.0
$(C_6H_5)_3SnSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_3PbSC_6H_5$	C_5H_5N	< 50 sec[b]	1.0

[a] The initial concentration of each reactant was 0.1 *M*. [b] The equilibrium had been attained by the time the spectrum was recorded.

reactant solutions. In contrast, with the systems involving the $(C_6H_5)_3Pb$ and especially $(C_6H_5)_3Sn$ groups the $t_{0.1}$ values amount to several minutes and, respectively, several hours. These data indicate that, depending on the nature of organometallic group, the facility of exchange of the metal—proton type increases in the order $(C_6H_5)_3Sn < (C_6H_5)_3Pb < C_6H_5Hg$.

In considering the exchange of one organometallic group for another, it should be noted that the exchange of the $(C_6H_5)_3Sn$ group for other organometallic groups and of the $(C_6H_5)_3Pb$ group for C_6H_5Hg proceeds more readily than their exchange for hydrogen. These observations are inconsistent with the purely mechanistic ideas about the facility of such exchange reactions. With respect to the influence of the nature of organometallic group and introduction of the second *o*-methyl group upon the exchange rate, the results for the metal—metal exchange correspond to the data for the metal—proton exchange. Thus, the $(C_6H_5)_3Sn$ group is exchanged more readily for the C_6H_5Hg group than for $(C_6H_5)_3Pb$, and the exchange of $(C_6H_5)_3PbSC_6H_5$ proceeds more rapidly with the triphenyltin derivative of 2-methylthiphenol than with that of 2,6-dimethylthiophenol.

From Table 4 it may be noted that the exchange of the $(C_6H_5)_3Pb$ group for $(C_6H_5)_3Sn$ occurs in chlorobenzene at a slower rate than its exchange for hydrogen. Consequently, in this case the lability of the metal—sulphur bond turns out to be lower than that of the H—S bond. Comparison of this result with the preceding data leads to the conclusion that with respect to their exchange mobility in inert solvents hydrogen and the organometallic groups investigated form the sequence $(C_6H_5)_3Sn < H < (C_6H_5)_3Pb < C_6H_5Hg$, when bonded to the sulphur atom.

It seemed of interest to examine how the rate of exchange processes would be affected on passing from the inert to coordinating solvent, the latter being represented in our case by pyridine. From Table 2 it can be seen that in the spectra of pyridine solutions of mixtures of 2-methylthiophenol with its organometallic derivatives only a single sharp signal of the methyl group is observed, which appears at the average position between the methyl group signals in the spectra of the individual compounds. The same is true for the mixture of 2,6-dimethylthiophenol with its phenylmercury derivative. It was found that decreasing the temperature to —40° does not affect the pattern of the spectra for any of these systems. Thus, in these cases a change in solvent from chlorobenzene to pyridine accelerates considerably the metal—proton exchange reactions on the PMR time scale.

In contrast, the spectra of mixtures of 2,6-dimethylthiophenol with its $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives in pyridine exhibit two sharp methyl group resonances, their chemical shifts coinciding within the experimental error with the chemical shifts in the solutions of individual compounds. It was found that the spectra do not change their appearance on increasing the temperature to 110°. The observed absence of exchange processes on the PMR time scale in the above systems, in contrast to the fast exchange in the mixtures of 2-methylthiophenol with its derivatives, apparently demonstrates the retarding influence of steric hindrance on the exchange rate. At the same time, the data of Table 4 show that the change in solvent from chlorobenzene to pyridine actually accelerates the exchange of the $(C_6H_5)_3Pb$ group for hydrogen, but evidently insufficiently to cause the collapse of the methyl peaks in the spectrum of the mixture of 2,6-dimethylthiophenol with its $(C_6H_5)_3Pb$ derivative. Finally, the results obtained for the mixtures of 2,6-dimethylthiophenol with its organometallic derivatives indicate that the exchange lability of the C_6H_5Hg group in the metal—proton exchange in pyridine is greater than those of the $(C_6H_5)_3Pb$ and $(C_6H_5)_3Sn$ groups.

Inspection of the data in Table 2 for the spectra of mixtures of different organometallic derivatives of 2-methylthiophenol and 2,6-dimethylthiophenol in pyridine shows that in no case does the change in solvent from chlorobenzene accelerate the metal—metal exchange on the time scale of the measurement. At the same time, some interesting regularities can be established by comparing the facility of the metal—proton and metal—metal exchanges in chlorobenzene and pyridine. Thus, an analysis of the limiting values of the pre-exchange life-times τ_a (Table 2) for the corresponding pairs of compounds allows the conclusion to be made that the following relationships for the rates of exchange processes involving 2-methylthiophenol and its organometallic derivatives are valid in pyridine: $C_6H_5Hg + (C_6H_5)_3Sn < C_6H_5Hg + H$; $(C_6H_5)_3Sn + C_6H_5Hg <$ $(C_6H_5)_3Sn + H$; $C_6H_5Hg + (C_6H_5)_3Pb < C_6H_5Hg + H$; $(C_6H_5)_3Pb + C_6H_5Hg <$ $(C_6H_5)_3Pb + H$; $(C_6H_5)_3Sn + (C_6H_5)_3Pb < (C_6H_5)_3Sn + H$; $(C_6H_5)_3Pb + (C_6H_5)_3Sn <$ $(C_6H_5)_3Pb + H$.

Consequently, in all the cases investigated the exchange of an organometallic group for another in pyridine proceeds more slowly than its exchange for hydrogen. On the other hand, from Table 4 it appears that in chlorobenzene the following relations hold for the rates of exchange reactions involving thiophenol and the organometallic derivatives of 2-methylthiophenol: $(C_6H_5)_3Sn + C_6H_5Hg >$ $(C_6H_5)_3Sn + H$; $(C_6H_5)_3Pb + C_6H_5Hg > (C_6H_5)_3Pb + H$; $(C_6H_5)_3Pb + (C_6H_5)_3Sn <$ $(C_6H_5)_3Pb + H$; $(C_6H_5)_3Sn + (C_6H_5)_3Pb > (C_6H_5)_3Sn + H$.

A consideration of the above relations permits us to reveal the following regularities. The exchange of the $(C_6H_5)_3Pb$ group for $(C_6H_5)_3Sn$ occurs at a slower rate than its exchange for hydrogen both in pyridine and chlorobenzene. At the same time, the exchanges of the $(C_6H_5)_3Sn$ group for other organometallic groups and of the $(C_6H_5)_3Pb$ group for C_6H_5Hg proceeds in chlorobenzene more readily than their exchanges for hydrogen, whereas in pyridine the opposite is the case. These results might be due to the fact that either pyridine retards the metal—metal exchange or accelerates it less strongly than the metal—proton exchange. From Table 4 it can be noted that the change in solvent from chlorobenzene to pyridine actually facilitates the exchange reactions of the $(C_6H_5)_3Sn$ derivatives of 2-methylthiophenol and 2,6-dimethylthiophenol with $(C_6H_5)_3PbSC_6H_5$. On this basis it may be concluded that at least in the case of the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ groups the change in the relative ease of metal—metal and metal—proton exchanges on transfer from chlorobenzene to pyridine arises from the fact that the coordinating solvent accelerates the exchange of the organometallic group for hydrogen to a greater extent than its exchange for another organometallic group.

Thus far we have discussed the influence of various factors upon the ease of metal—metal and metal—proton exchange. Now it seems appropriate to consider the position of equilibrium in the exchange reactions of the organometallic derivatives of 2-methylthiophenol and 2,6-dimethylthiophenol with thiophenol and its derivatives. The equilibrium constants can be easily determined in most cases due to the slowness of the exchange processes on the PMR time scale, and thus the possibility exists of measuring the integral intensities of the methyl group signals for one of the starting reactants and one of the exchange reaction products.

From Table 4 it can be seen that for the exchange reactions involving thiophenol the equilibrium is shifted in favour of its organometallic derivatives. It is of considerable interest that the equilibrium constants do not differ very much from unity even in the exchange of the organometallic derivatives of 2,6-dimethylthiophenol with thiophenol. For the exchanges of the organometallic derivatives of 2-methylthiophenol and 2,6-dimethylthiophenol with those of thiophenol, the equilibrium constants are practically equal to unity in all the cases investigated. The values of equilibrium constants do not change on transfer from chlorobenzene to pyridine for both metal—proton and metal—metal exchanges.

2. *Exchange reactions in the organometallic derivatives of benzyl mercaptan*

In order to compare the exchanges of the proton—proton, metal—proton and metal—metal types, we have examined the PMR spectra of benzyl mercaptan and its organometallic derivatives. In chlorobenzene solutions of 0.4 *M* concentration the spin—spin coupling of the CH_2 group protons with the ^1H, ^{207}Pb and $^{117/119}Sn$ nuclei of the SH, $(C_6H_5)_3Pb$ and $(C_6H_5)_3Sn$ groups was found. The chemical shifts of the CH_2 group protons and the values of spin—spin coupling constants are listed in Table 5. Further, it was found that the solution spectra of mixtures of benzyl mercaptan with its organometallic derivatives and of different organometallic derivatives in chlorobenzene exhibit a superposition of the CH_2 group signals corresponding to those of individual compounds. Increasing the temperature to 110° does not produce any broadening of the CH_2 group resonances in the spectra of 0.4 *M* solutions of individual compounds and their mixtures in chlorobenzene. These results demonstrate that for benzyl mercaptan and its organo-tin and -lead derivatives the exchange reactions of all three types are too slow in chlorobenzene on the PMR time scale to be studied by conventional NMR methods. These observations are consistent with published data for benzyl mercaptan [2], as well as those for the $(CH_3)_3Sn$ and $(CH_3)_3Pb$ derivatives of methanethiol [7].

In the spectra of pyridine solutions of benzyl mercaptan and its organo-tin and -lead derivatives (Table 5) a reduction in the spin—spin coupling constants J(HS—CH) and J(MS—CH) compared to those in chlorobenzene is observed. These results are in line with the ideas [10] concerning the solvation mechanism of organic derivatives of non-transition metals. If the compounds containing the C—M—X moiety (where X = Cl, O, N, S and represents the first heteroatom of an electron-accepting ligand) are dissolved in donor solvents, redistribution of electron density in the metal bonds occurs. As a result, the *s*-character of the metal orbitals in the C—M bonds increases and in the M—X bonds decreases. With the compounds investigated, a decrease in the amount of *s*-character of the metal orbitals in the M—S bonds on solvation leads to a reduction in the J(MS—CH) values. At the same time, the line widths of the CH_2 group resonances for all the compounds remain in pyridine the same as in chlorobenzene and do not change

TABLE 5

PARAMETERS OF PMR SPECTRA FOR 0.4 *M* SOLUTIONS OF BENZYL MERCAPTAN AND ITS ORGANOMETALLIC DERIVATIVES

Compound	Solvent	$\delta(CH_2)^a$ (Hz)	J(M/H—SCH) (Hz)
$HSCH_2C_6H_5$	C_6H_5Cl	208.1	7.6
	C_5H_5N	216.6	7.3
$C_6H_5HgSCH_2C_6H_5$	C_6H_5Cl	244.7	—
	C_5H_5N	255.3	—
$(C_6H_5)_3SnSCH_2C_6H_5$	C_6H_5Cl	225.6	37.1
	C_5H_5N	234.7	34.5
$(C_6H_5)_3PbSCH_2C_6H_5$	C_6H_5Cl	240.4	59.9
	C_5H_5N	247.4	53.1

[a] Relative to TMS.

on raising the temperature to 110° for 0.4 *M* solutions, indicating the slow exchange on the PMR time scale.

In contrast to benzyl mercaptan and its organo-tin and -lead derivatives, the (^{199}HgS—CH) spin—spin coupling satellites in phenylmercury benzyl mercaptide are observed neither in chlorobenzene nor in pyridine at 0.4 *M* concentration, the CH_2 group singlet showing no broadening on cooling the solution to −40° in chlorobenzene and to −110° in a mixture of chloroform and methylene chloride (1/3 v/v). These observations suggest a fast exchange involving the C_6H_5Hg group and indicate that the Hg—S bond in $C_6H_5HgSCH_2C_6H_5$ turns out to be more exchange-labile than the H—S, Pb—S and Sn—S bonds in benzyl mercaptan and its organometallic derivatives in these proton—proton and metal—metal exchange processes.

Discussion

In turning to a more detailed consideration of the results obtained, it is first necessary to propose a reasonable mechanism for the exchange reactions which takes into account the fact that in some cases metal—metal exchange proceeds more readily than metal—proton or proton—proton. In principle, three types of reaction pathways are possible for the exchanges studied, the first of which involves a radical-chain mechanism:

$$HSR + X^{\cdot} \rightarrow HX + {}^{\cdot}SR \qquad R_nMSR^{*} + {}^{\cdot}SR \rightarrow R_nMSR + {}^{\cdot}SR^{*}$$
$$R_nMSR + X^{\cdot} \rightarrow R_nMX + {}^{\cdot}SR \qquad R_nM^{*}SR^{*} + {}^{\cdot}SR \rightarrow R_nM^{*}SR + {}^{\cdot}SR^{*}$$

The second possible pathway involves initial dissociation of the reactant to ions:

$$HSR \rightarrow H^{+} + {}^{-}SR \qquad R_nMSR \rightarrow R_nM^{+} + {}^{-}SR \qquad R_nM^{*}SR^{*} \rightarrow R_nM^{*+} + {}^{-}SR^{*}$$

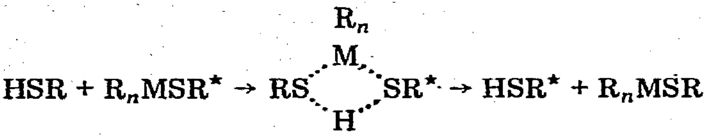
followed by either a rapid recombination reaction:

$$H^{+} + {}^{-}SR^{*} \rightarrow HSR^{*} \qquad R_nM^{+} + {}^{-}SR^{*} \rightarrow R_nMSR^{*}$$

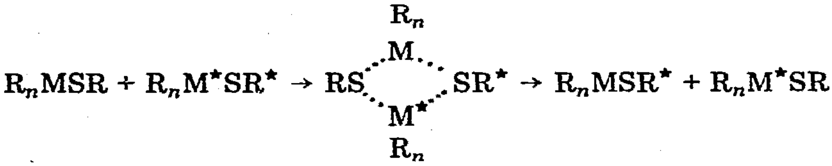
or an attack upon the undissociated molecule of the second reactant:

$$HSR + {}^{-}SR^{*} \rightarrow HSR^{*} + {}^{-}SR \qquad R_nMSR + {}^{-}SR^{*} \rightarrow R_nMSR^{*} + {}^{-}SR$$

Finally, the third possibility represents the reaction proceeding through a cyclic (in the simplest form four-membered) transition state:



$$HSR + R_nMSR^{*} \rightarrow RS\overset{\overset{R_n}{M}}{\underset{H}{\cdots\cdots}}SR^{*} \rightarrow HSR^{*} + R_nMSR$$



$$R_nMSR + R_nM^{*}SR^{*} \rightarrow RS\overset{\overset{R_n}{M}}{\underset{\underset{R_n}{M^{*}}}{\cdots\cdots}}SR^{*} \rightarrow R_nMSR^{*} + R_nM^{*}SR$$

Most published data suggest that the exchange reactions of the proton—proton [11] and metal—metal [12] type take place through the formation of a cyclic activated complex both in inert and solvating media. At the same time, the exchange of thiophenol with diphenyl disulphide occurs by a free radical mechanism, being catalyzed by atmospheric oxygen [13]. Similarly, a free radical mechanism has been proved for the reaction of thiophenol with the aryl compounds of antimony and bismuth [14], and radical substitution at the metal atom seems to be rather common for organometallic compounds of non-transition metals [15]. Finally, the exchange reactions of the metal—metal type occurring through an ionization step are known [16]. These facts mean that all possible mechanisms have to be considered.

In order to choose the most probable mechanism, we have studied in more detail the influence of various factors upon the ease of metal—proton and metal—metal exchange (Table 6). For the reaction between $(C_6H_5)_3PbSC_6H_3(CH_3)_2$-2,6 and $(C_6H_5)_3SnSC_6H_5$ it was found that the metal—metal exchange proceeds at the same rate both in air an under argon, and is not accelerated by UV irradiation. In contrast, metal—proton exchange occurs with greater ease in air than in argon, being considerably accelerated by UV irradiation. It is interesting to note that irradiation of thiophenol before reaction also increases the rate of exchange. On the other hand, metal—proton exchange is not inhibited by addition of phenothiazine, and is catalyzed by trifluoroacetic acid. These observations permit the following conclusions to be drawn.

The metal—metal exchange seems very unlikely to involve radical mechanism. The acceleration of the metal—proton exchange by UV irradiation indicates the possibility of the reaction proceeding by a radical pathway, since it is known [17—18] that photolysis of thiols leads to the formation of thiyl radicals. However, the acceleration of the exchange upon UV irradiation of thiophenol before the reaction is evidently not related to the radical mechanism, but is probably due to the catalytic effect of benzenesulphonic acid, which is formed by the oxidation of thiophenol by traces of oxygen upon irradiation [19]. This factor may be partly responsible for the acceleration of exchange upon irradiation of the reaction mixture.

TABLE 6

INFLUENCE OF EXPERIMENTAL CONDITIONS UPON $t_{0.1}$ VALUES FOR THE EXCHANGE REACTION OF TRIPHENYLTIN 2-METHYLTHIOPHENOXIDE WITH THIOPHENOL IN CHLOROBENZENE SOLUTION[a]

Experimental conditions	$t_{0.1}$
b,c,d	200 ± 15 min
b,c,d,e	215 ± 35 min
b,c,d,f	< 50 sec
b,c,d,g	< 20 min
b,c,d,h	30 ± 5 min
b,c,i	135 ± 15 min
b,i,j	100 ± 10 min
i,j,k	55 ± 5 min

[a] The initial concentrations of $(C_6H_5)_3SnSC_6H_4CH_3$-2 and C_6H_5SH were 0.1 and 0.2 *M* respectively. [b] Thiophenol was distilled in argon. [c] Chlorobenzene was distilled in argon. [d] The reaction was run in argon. [e] 2% *M* of phenothiazine was added. [f] 2% *M* of trifluoroacetic acid was added. [g] The reaction mixture was UV irradiated for 15 min. [h] The chlorobenzene solution of thiophenol was UV irradiated for 15 min before the reaction. [i] The reaction was run in air. [j] Chlorobenzene was distilled in air. [k] Thiophenol was distilled in air.

Further, in spite of some acceleration of the metal—proton exchange on transfer from argon to air, the free-radical reaction promoted by the traces of oxygen is apparently not the main pathway of the metal—proton exchange in an inert atmosphere. Thus, in accordance with previous data [13], the rate of the free-radical exchange between thiophenol and diphenyldisulphide is proportional to the square root of oxygen concentration. In our case polarographic determination of oxygen showed that the oxygen concentration increases by not less than two orders of magnitude on going from argon-saturated chlorobenzene to chlorobenzene saturated with air. This allowed a ten-fold enhancement in the exchange rate to be expected, whereas actually the rate increases only by a factor of two.

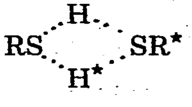
In the free-radical exchange [13] the rate is proportional to the square root of thiophenol concentration, while in our case the exchange reaction is of first-order in thiophenol. Finally, addition of phenothiazine, which is a powerful inhibitor of free-radical reactions involving thiophenol [20], practically does not affect the rate of the metal—proton exchange. Thus, on the basis of the above considerations, it seems proper to conclude that in an inert atmosphere and in the absence of UV radiation the radical mechanism is not the predominant pathway for the exchange of thiophenols with their organometallic derivatives. On the other hand, the dissociative mechanism of exchange seems also not to be operative.

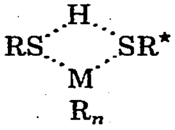
Thus, as mentioned above, the exchange reactions of the metal—proton and metal—metal types appear to be approximately second-order overall, being first-order in each of the reactants. This strongly indicates [21] that the reactions occur through an associative pathway, because for the reactions proceeding by a dissociative mechanism an overall first-order should be observed [16, 22]. Further, it is known from the literature [23,24] that even in such strongly solvating solvent as water the hydrogen exchange of carboxylic acids with this solvent proceeds through the formation of a cyclic transition state, rather than through a dissociative pathway. In chlorobenzene the ion formation should be still les probable than in the strong ion-solvating solvent. A similar situation occurs in the case of exchange reactions involving organometallic groups. Thus, it has been found [25] that in aqueous solution CH_3HgOH exchanges the OH group for other ligands through the S_N2 mechanism. Again, in chlorobenzene the dissociation of the metal—element bond should take place to a smaller extent than in water.

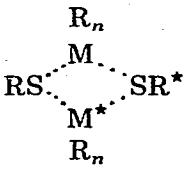
An additional argument in favour of the associative mechanism of exchange comes from the fact that the Hg—S bond turns out to be considerably more exchange-labile than the H—S bond, although the former dissociates less easily [26] than the latter [27]. In addition, the steric hindrance which increases in going from the derivatives of 2-methylthiophenol to those of 2,6-dimethylthiophenol, inhibits exchange, whereas it should facilitate exchange if there were a dissociative rate-determining step. Thus, the bulk of available evidence indicates that an associative mechanism is the most probable pathway for the metal—metal, metal—proton and proton—proton exchanges involving thiols and their organometallic derivatives.

Further, it should be noted that in the case of an associative mechanism, the number of molecules participating in the formation of the corresponding cyclic transition state remains generally unknown. Usually it is believed that the relevant data can be obtained from the order of the reaction, and thus the exchange reactions of organometallic compounds which have an overall second order and first order in each of the reactants are considered as a rule to be bimolecular and proceed through a four-membered cyclic transition state [21,28]. However, the order of a reaction may not coincide with its molecularity [8,29]. For instance, the formation of the generally accepted four-membered cyclic transition state in hydrogen exchange reactions has been questioned [11] as being energetically unfavourable.

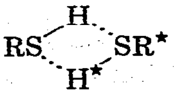
In the following discussion we shall assume for the sake of simplicity that the exchange reactions studied in this work proceed through the following four-membered cyclic transition states because the participation of larger cyclic activated complexes will not affect considerably the validity of our explanations.

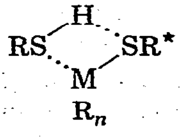


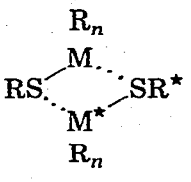




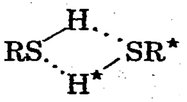
As can be seen from the above formulae, the structure of the transition states is close to that of the corresponding cyclic coordinate associates:

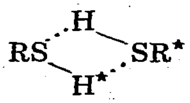




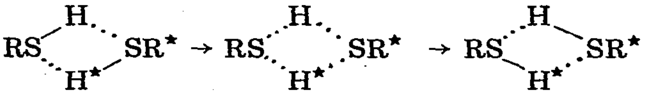


and represents an intermediate state of the relevant system between two possible associate structures which in the case of hydrogen exchange can be described by:





With the hydrogen exchange, the transition of the system from one of these states to the other requires the crossing of a potential barrier in the double-minimum potential energy curve [30,31] (Fig. 1) during the motion of the system along the one-dimensional reaction path, where the maximum of potential energy corresponds to the transition state with delocalized bonds.



It should be noted that in the case of the metal—metal exchange in some organometallic compounds the potential energy curve may have a different shape, a minimum, rather than a maximum, corresponding to the intermediate state with fully delocalized bonds [32]. According to the above considerations it can be expected that the ease of exchange will depend both on the rate of formation of the cyclic coordinated species and the ease of motion of the hydrogen or metal atom along the system of coordinate bonds. It is appropriate to discuss first the former of the above factors.

A search of literature revealed a number of studies concerning the kinetics of hydrogen bond formation for the bonds O—H··O, N—H··O and N—H··S [33—37]. It has been found in all these cases that the formation of hydrogen-bonded associates is a diffusion-controlled reaction. Regretfully, there appears to be practically no information in the literature regarding the kinetics of association of inorganic or organometallic compounds, nor any on the formation of donor—acceptor complexes of inorganic or organometallic compounds in inert solvents. The single report of this kind seems to be the investigation of formation of BF_3 complexes with tertiary amines in the vapour phase [38] which also proved to be diffusion-controlled. On the basis of these results and because of the lack of the data bearing on the compounds studied in the present work or

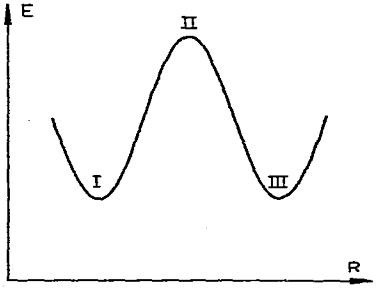
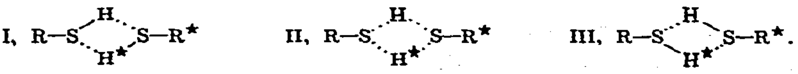
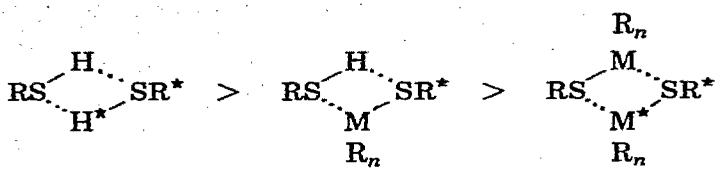


Fig. 1. Variation of the potential energy of the cyclic complex for the proton—proton exchange along the reaction path:

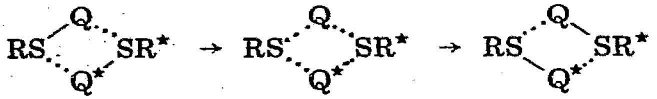


their analogues, it will be supposed in the following discussion that the association rate of thiols and their organometallic derivatives is also diffusion-controlled.

In this case, bearing in mind that the molecules of the organometallic derivatives are of greater size than those of the parent thiols, and taking into account the general regularities in the influence of molecular structure on the diffusion coefficients [39,40] we should expect that the formation rate of cyclic coordinated species will decrease in the sequence:

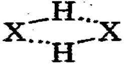


Thus the operation of this factor should have retarded the exchange reactions in going from the proton—proton exchange to those of the metal—proton and metal—metal types, if the formation of the coordinated species had been the rate-controlling step. This should have been paralleled by the influence of the more negative activation entropy for more complex molecules [8]. However, the greater ease of the metal—metal than metal—proton and proton—proton exchange found in a number of cases in the present work, and the fact that the rates of exchange processes of all types in the absence of catalysts are considerably smaller than those of the diffusion-controlled processes [11,12,41—43] suggests [44] that the rate-determining step in the exchange reactions involves a concerted transfer [31] of the hydrogen or metal atoms along the chain of coordinate bonds over the potential barrier associated with the formation of the transition state with delocalized bonds:



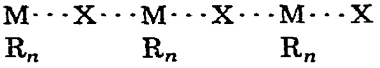
$[Q = Q^*,\ Q \neq Q^* = H,\ R_nM,\ R_nM^*]$

According to the transition state theory [8,29], the ease of such trasnfer will decrease, as the mass of the activated complex and the height of the potential energy barrier increase. The operation of the former factor should have retarded the process in passing from proton—proton to metal—proton and metal—metal exchange. However, taking into account the data obtained in the present investigation, it is reasonable to conclude that the height of potential barrier is the governing factor.

The problem of the nature and magnitude of the potential barrier in associated species has been studied most extensively for the hydrogen-bonded systems [30,45,46]. In contrast, comparatively little attention has been given to this problem in the coordination chemistry of organometallic compounds [32]. In general, for the hydrogen-bonded systems X—H··Y X—H··X  $X\overset{H}{\underset{H}{\rightleftharpoons}}X$ the height of the potential energy barrier separating the two minima is lowered with decreasing X··X distance and increasing energy of hydrogen bond. For very short $X\cdot\cdot X$ distances and very high hydrogen bond energies the potential energy curve may have a single minimum, which corresponds to the symmetrical location of the hydrogen atom between the two proton-accepting centres and leads to the formation of the system with fully delocalized bonds, $X\cdot\cdot H\cdot\cdot X$, in which the hydrogen atom encounters practically no potential barrier in moving from one X atom to the other. The systems of such type are exemplified by bifluoride ion and hydrogen chloride dihydrate [47,48]. The conditions which favour the formation of systems with delocalized hydrogen bonds include the similarity of the proton-accepting centres X and the presence of considerable positive charge on the hydrogen atom or considerable negative charge at the proton-accepting centre [49,50]. It should be noted that the absence of potential barrier in the case of hydrogen-bonded systems with delocalized bonds is the main cause of the rates of hydrogen exchange being often diffusion-controlled under the conditons of acid or base catalysis [51,52].

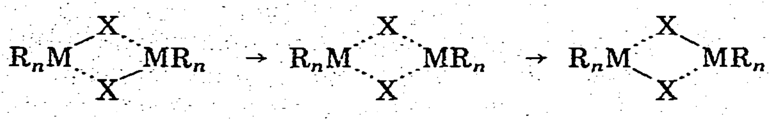
If neither from the two latter conditions is fulfilled, then even for compounds with like proton-accepting centres X the associates with undelocalized bonds and asymmetrical location of hydrogen are formed, as in the case of hydrogen-bonded associates of carboxylic acids [53,54]. Consequently, in most cases the potential energy curve for the hydrogen-bonded associates of the type $\mathrm{X}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\diamond}}\mathrm{X}$ will have two minima separated by a potential barrier [55], the height of which will decrease with decreasing difference in the lengths of the H—X and $H\cdot\cdot X$ bonds, being lowered as the structure of the coordinated species becomes closer to that with delocalized bonds. It should be mentioned that the tunnelling effect which may be involved in the crossing of the potential barrier by hydrogen atom, is not very probable for most systems, since the tunnelling rate is sufficiently high only with narrow potential barriers and short distances between the potential wells [56].

In turning to the consideration of the potential barriers in the systems with coordinate bonds involving metal atoms, it should be emphasized that with the same, not very strongly electron-accepting ligands, organotin and organomercury groups are often more capable of forming structures with delocalized bonds [57—59] (see below) than the hydrogen atom [54,59,60].

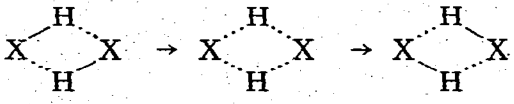


$$\underset{R_n}{M}\cdots X\cdots\underset{R_n}{M}\cdots X\cdots\underset{R_n}{M}\cdots X$$

In connection with the present study, it is interesting to note that phenylmercury thiocyanate exists in the solid state as a cyclic dimer with delocalized $Hg\cdots S$ bonds [61]. The above facts strongly suggest that for organometallic compounds the structure of cyclic associates $R_nM\overset{X}{\underset{X}{\diamond}}MR_n$ may be considerably more close to that of the transition state with delocalized bonds $R_nM\overset{X}{\underset{X}{\diamond}}MR_n$ than the structure of analogous hydrogen-bonded associates $X\overset{H}{\underset{H}{\diamond}}X$ to that of the corresponding activated complexes $X\overset{H}{\underset{H}{\diamond}}X$. In this case the potential barrier for the motion of the metal atoms along the chain of coordinate bonds:

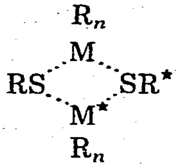


will be considerably lower than that for the proton motion along the chain of hydrogen bonds:

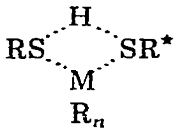


The ease of formation of the transition state with delocalized bonds will be the greater, the higher the affinity of the metal atom for the electron-donating centre in the X ligand and the larger its ability to participate in cyclic intermolecular coordination, being at the same time increased by partial positive charge on the metal atom and partial negative charge on the X ligand [28].

The general considerations presented above allow to explain quite reasonably the results obtained in the present investigation. Thus, in accordance with the literature data [62—66], thiols are very weakly associated, the energy of hydrogen bond being of the order of 1.2 kcal mol^{-1}. According to the regularities discussed above, the low energy of hydrogen bond should lead to a considerable height of the potential barrier for the motion of hydrogen atoms in the cyclic complex along the system of hydrogen bonds, which is reflected in the very low ability of the H—S bonds to undergo uncatalyzed exchange reactions [2]. The greater ease of the metal—metal exchange relative to that of metal and proton observed in some cases may be partly determined by geometric factors, which lead to the more ready formation of the transition state A than transition state B.



(A)



(B)

The bond lengths M—S and M*—S in A are more similar than M—S and H—S bonds lengths in B, which will result in the more effective orbital overlap in the activated complex for the metal—metal exchange.

Further, the greater exchange reactivities of the Hg—S and Pb—S bonds relative to those of the H—S and Sn—S bonds may be due to the greater polarity of the corresponding metal—sulphur bonds and greater coordinating ability of the C_6H_5Hg and $(C_6H_5)_3Pb$ groups with respect to the sulphur atom, which is consistent with mercury [67], and probably lead [68], being "soft" Lewis acids. In contrast, hydrogen and tin are usually classified as "hard" acids [67,68], which is reflected in the low affinities of hydrogen and R_3Sn-groups for sulphur [69,70]. The above considerations are supported by data for fluorine chemical shifts in *p*-fluorothiophenol and its organometallic derivatives in chlorobenzene and thiophan (Table 7). This shows that the polarities of the Hg—S and Pb—S bonds in chlorobenzene are larger than that of the Sn—S bond, while the tendency of the C_6H_5Hg group to coordinate to the sulphur atom is much greater than that of the SH, $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ groups.

TABLE 7

^{19}F CHEMICAL SHIFTS (ppm) RELATIVE TO INTERNAL FLUOROBENZENE

Compound	Solvent		
	C_6H_5Cl	C_4H_8S	C_5H_5N
HSC_6H_4F-4	3.7	4.0	4.5
$C_6H_5HgSC_6H_4F$-4	4.4	5.8	6.3
$(C_6H_5)_3SnSC_6H_4F$-4	3.0	3.2	3.5
$(C_6H_5)_3PbSC_6H_4F$-4	3.7	4.0	4.3

Further, X-ray examination of phenylmercury 2,6-dimethylthiophenoxide [71] has shown that in the crystal state this compound is associated with the formation of a four-membered coordinate cycle involving Hg—S and Hg· ·S bonds, the lengths of which are equal to 2.33 and 3.18 Å respectively. In contrast, there is no intermolecular coordination in the crystals of triphenyltin 2,4,6-trimethylthiophenoxide [72], and quantum chemical calculations have shown [73] that in the cyclic dimer of hydrogen sulphide the lengths of the H—S and H· ·S bonds are 1.48 and 2.75 Å. Assuming the same geometry of coordinated species in solution, it can be concluded from these data that for the formation of cyclic transition state with delocalized bonds the length of the H—S bond must be increased by 42%, whereas in the case of the Hg—S bond the corresponding increase in length will amount to 18% only.

The exceedingly high exchange lability of the C_6H_5HgS group is in agreement with the literature data on the fast exchange in methylmercury salts [74, 75] and arises probably from the fact that for the C_6H_5Hg group the high ability of the metal to coordinate to sulphur is combined with the approximate conformity of geometry of the four-membered cyclic transition state to the optimal orbital geometry of the three-coordinated mercury atom, which in the C_6H_5Hg group uses a 6*p*-unhybridized orbital to form a coordinate bond [76]. This situation is contrasted by the behaviour of the organo-tin and -lead groups of the R_3M type for which the preferred geometry of the pentacoordinated sp^3d-hybridized state requires the location of the more electron-accepting ligands on the axis of a trigonal bipyramid [77,78], which is not compatible with the geometry of the cyclic transition state. The indicated difference between the C_6H_5Hg group on the one hand, and $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ groups on the other, is reflected also in the greater ability of the former to participate in intramolecular coordination [79,80], the geometry of which is similar to that of cyclic activated complexes.

Finally, it might have been expected that the greater migrating ability of the C_6H_5Hg group than the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ groups arises from the fact that rotation of the former around the Hg—S bond produces smaller steric hindrance to the formation of the transition state than rotation of the latter two around the Sn—S and Pb—S bonds. However, on the basis of the data discussed below for the exchange equilibria involving the organometallic derivatives of thiophenol and 2,6-dimethylthiophenol, it appears probable that the above factor does not play a significant role in determining the relative ease of exchange of the organometallic groups.

Now we shall discuss the observation that pyridine accelerates the metal—proton exchange more than it does the metal—metal type. It appears probable that this results from the absence of low energy vacant orbitals on the hydrogen atom and their presence on the metal atom. Although it was not possible to determine the order of exchange reactions in pyridine solution, the results obtained earlier for the exchange of 2′,6′-dimethyl-4′-bromobenzenesulphonanilide with its phenylmercury derivative [81] lead one to expect that the overall second order is retained in pyridine, and exchange reactions proceed through the formation of cyclic transition state.

In principle [82], the formation of ion pairs of the type $C_6H_5S\cdots HNC_5H_5$ is possible for solutions of thiophenols in basic solvents such as pyridine. Thus, the equilibrium between a hydrogen-bonded complex and ion pair $AH\cdots B \rightleftharpoons A^-\cdots HB^+$ has been studied recently [83,84] and it has been established that proton transfer with formation of ion pair is favoured by increasing acidity of the acid and basicity of the base, as well as by the solvent polarity and hydrogen bond formation between the anion and solvent. At the same time, it is known [85] that no ion pairs are formed in pyridine solution of chloroacetic acid. Taking into account that thiophenol is considerably less acidic [86] than chloroacetic acid [87], we shall assume in the present discussion that in solutions of thiophenols in pyridine only hydrogen-bonded complexes of the type $C_6H_5SH\cdots NC_5H_5$ are formed.

Further, quantum chemical calculations have recently shown [88] that the interaction between the H—S bond and a donor of lone electron pair increases the partial positive charge on the hydrogen atom involved in hydrogen bonding. Accordingly, the formation of hydrogen bond between thiophenol and pyridine [89] will produce an additional polarization of the H—S bond and increase the partial positive charge on the hydrogen atom and partial negative charge on the sulphur atom, thereby enhancing the electron affinity of the former and nucleophilic power of the latter. The existence of complexes of the type $2B\cdot HA$ for stronger acids [90] suggests that the above factors may increase the ability of the H—S bond to form the cyclic transition state, despite the repulsion between the nitrogen and sulphur lone electron pairs.

Whereas with hydrogen bonding the electron charge transfer occurs into the partially-occupied 1*s* hydrogen orbital [91] or antibonding orbital of the H—X bond [92], the coordination of the organometallic group with a donor of lone electron pair involves the transfer of electron density into the metal vacant orbitals, apparently without formation of ions [93]. Consequently, pyridine will block to a smaller or greater extent the vacant metal orbitals, decreasing the partial positive charge on the metal atom [94] and reducing its coordinating ability. On the other hand, the fluorine chemical shifts for the organometallic derivatives of *p*-fluorothiophenol in pyridine (Table 7) indicate that the coordinating solvent enhances the polarity of the metal—sulphur bond, the partial negative charge on the sulphur atom increasing in pyridine solution in the order $(C_6H_5)_3SnS < (C_6H_5)_3PbS \approx HS < C_6H_5HgS$.

Due to the competition of two opposite factors, the ability of metal—sulphur bond to form the cyclic transition state can either increase or decrease in going from an inert to a coordinating solvent. Thus, it has been found earlier that pyridine accelerates exchange processes involving the metal—halogen bonds in trimethyltin halides [95], but slows down the metal—metal exchange in the C_6H_5Hg derivatives of *N*-methylbenzenesulphonamides [1]. As was found in the present work, the exchange ability of the C_6H_5Hg group in pyridine is smaller than that of hydrogen, in spite of the greater partial negative charge on the sulphur atom of the C_6H_5HgS group (Table 7), which is evidently due to the vacant metal orbitals being blocked by solvent molecules. In contrast, the acceleration of exchange of the $(C_6H_5)_3Sn$ group for $(C_6H_5)_3Pb$ in pyridine indicates facilitation of the transition state formation by the coordinating solvent and may be connected with the specificity of metal orbital geometry in the transition state in this case [95]. Finally, if the exchange reactions in coordinating solvents do involve ion pairs, then the differences in the influence of these solvents on the exchange lability and the ease of formation of ion pairs by hydrogen and organometallic groups must be again determined by the presence or absence of vacant orbitals [93].

In turning to a consideration of the factors affecting the equilibrium in the systems studied, it should be noted that the deviation of equilibrium from randomness for the metal—proton exchange is probably determined by steric factors, which result from the greater steric requirements of the organometallic groups compared to those of hydrogen. Taking into account the rather low potential barrier to the rotation of the HS group in thiophenol [96] and the approximately additive influence of the *o*-methyl group on the equilibrium constant, it may be concluded that the shift of equilibrium in favour of the organometallic derivatives of thiophenol is associated with the different inhibition of rotation of the R_nMS and HS groups around the C—S bond, rather than with the different degrees of twist of the HSC and MSC planes from coplanarity with the thiophenol ring. This effect may result from either the difference in the ranges of mainly free rotation for the R_nMS and HS groups, and/or the difference in the potential barrier to rotation produced by the *o*-methyl substituent. Thus, inspection of molecular models shows that the *o*-methyl group restricts the range of free rotation for the R_nMS group to a larger extent than for the HS group. On the other hand, *o*-methyl substituents should increase the barrier to internal rotation for the HS group to a smaller degree than for the R_nMS groups due to the greater overlap of Van der Waals envelopes in the eclipsed conformation in the latter case. At present it is not possible to evaluate the contributions of both factors by the methods of statistical thermodynamics [97], but it is obvious that *o*-methyl groups will destabilize the organometallic derivatives relative to the parent thiophenol.

The random equilibrium in the case of the metal—metal exchange indicates that within the sensitivity level of the present approach the inhibition of internal rotation, and the steric requirements are almost equal for the C_6H_5HgS, $(C_6H_5)_3SnS$ and $(C_6H_5)_3PbS$ groups involved in non-bonded interactions with *o*-methyl substituents, which agrees with the data obtained previously [79]. This situation arises probably from the fact that, as evidenced by the inspection of molecular models and some X-ray data [70,71], the steric interactions of the organometallic group with the *o*-substituent are mainly determined by the contacts between the metal atom and the CH_3 group, in which the organic radicals on the metal do not participate. Finally, the absence of pyridine influence on the equilibrium constant in the exchange reactions of 2,6-dimethylthiophenol and its organometallic derivatives indicates that *o*-methyl substituents either do not inhibit the coordination of metal and hydrogen with the solvent, or inhibit the solvation regardless of the nature of the electron-accepting centre.

In conclusion, we mention that further studies on the exchange processes in the organo-mercury, -tin and -lead derivatives of substituted thiophenols now in progress should allow us to elucidate how polar substituent effects, steric hindrance and intramolecular coordination influence the exchange equilibria in these systems.

Experimental

General

The PMR spectra at various temperatures were recorded by a RYA-2305 spectrometer at 60 MHz. The proton chemical shifts were measured at 34° using a Hitachi—Perkin—Elmer R12 spectrometer operating at 60 MHz. TMS was used as an internal standard. The accuracy of the proton chemical shift values was not less than ± 0.3 Hz. The ^{19}F NMR spectra were taken at 34° on a Hitachi—Perkin—Elmer R20 spectrometer operating at 56.4 MHz, the measurements being performed on 0.2 *M* solutions. The use of the substitution method for the determination of fluorine chemical shifts relative to internal fluorobenzene has been described elsewhere [98]. The experimental error in the fluorine chemical shift did not exceed ± 0.1 ppm.

The limiting life-times of the species before exchange (τ_a) for the exchange reactions of 2-methylthiophenol and 2,6-dimethylthiophenol with their organometallic derivatives were calculated on the basis of the approximate formulae [99]. The expression $\tau_a < 0.45/\Delta\delta°$ was used in the case of fast exchange corresponding to the occurrence of a single methyl group signal in the spectrum of the reaction mixture, and $\tau_a > 4.5/\Delta\delta°$ was applied with the slow exchange indicated by the presence of two methyl group peaks ($\Delta\delta°$ being the signal separation in Hz in the absence of exchange). In order to determine the $t_{0.1}$ values, the PMR spectra of the reaction mixtures were recorded at different times after mixing the reactant solutions and were compared with the solution spectra of mixtures of the corresponding starting compound and reaction product tagged with the indicator *o*-methyl groups. The concentrations and mole ratios of the starting compound and reaction product in the above mixtures corresponded to those resulting in the reaction mixture at different degrees of transformation. The determination of each $t_{0.1}$ value was performed three times and the mean value was taken.

The exchange reactions of organometallic derivatives of 2-methylthiophenol and 2,6-dimethylthiophenol with thiophenol and its organometallic derivatives were run at 34 ± 1°. In running the exchange reactions of the metal—proton type in an inert atmosphere, the reactant solutions were prepared and mixed under argon, the NMR tubes and capillaries for transferring the solutions were flushed with argon, which was also used for deaeration of the solvents. A 200 W PRK-4 UV lamp was used for UV irradiation of the samples, which were placed in a stoppered quartz test-tube at a distance of 15 cm from the lamp, the necessary temperature being maintained during irradiation by cooling the sample with a ventilator.

TABLE 8

ANALYTICAL DATA AND MELTING POINTS FOR THE ORGANOMETALLIC DERIVATIVES OF 2-METHYLTHIOPHENOL AND 2,6-DIMETHYLTHIOPHENOL

Compound	M.p. (°C)	Analysis found (calcd.) (%)	
		C	H
$C_6H_5HgSC_6H_4CH_3$-2	111—112	38.72 (38.94)	2.97 (3.01)
$(C_6H_5)_3SnSC_6H_4CH_3$-2	65—66	63.27 (63.46)	5.12 (4.68)
$(C_6H_5)_3PbSC_6H_4CH_3$-2	63—65	53.42 (53.46)	3.93 (3.94)
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	109—110	40.55 (40.53)	3.33 (3.37)
$(C_6H_5)_3SnSC_6H_3(CH_3)_2$-2,6	107—108	64.09 (64.18)	4.97 (4.96)
$(C_6H_5)_3PbSC_6H_3(CH_3)_2$-2,6	100—102	54.34 (54.24)	4.24 (4.19)

The equilibrium constants were calculated from equilibrium concentrations of the reactants and products, which were obtained by integrating the methyl group signals for one of the reactants and one of the products after the attainment of equilibrium, the latter being approached by starting with both possible pairs of the reactants. The relative error in equilibrium constant did not exceed ± 15% in all the cases investigated.

The solvents were purified by conventional methods, chlorobenzene was distilled over phosphorus pentoxide before use, pyridine was dried and stored over molecular sieves (4 Å). Thiophenol (b.p. 168—169°, n_D^{20} 1.5881) and benzyl mercaptan (b.p. 194—195°, n_D^{20} 1.5730) were commercial products. 2-Methylthiophenol and 2,6-dimethylthiophenol were prepared from *o*-bromotoluene and 2,6-dimethylbromobenzene via the Grignard reagents. All thiols were distilled under argon before use, and their purity was found by the PMR spectra and GLC to be not less than 98%.

The organometallic thiophenoxides were prepared by the action or organometallic hydroxides upon the thiols or by the reaction of triphenyltin and triphenyllead chlorides and phenylmercury acetate with the sodium salts of the corresponding thiols and were purified by repeated recrystallization. The phenylmercury [100], triphenyltin [101,102] and triphenyllead derivatives [103] of thiophenol and benzyl mercaptan, previously reported in the literature, were characterized by their melting points. It was shown by special experiments that additional recrystallization of the organometallic derivatives of thiophenols studied did not affect the $t_{0.1}$ values for the exchange reactions. The melting points and analytical data for the new compounds are presented in Table 8. Melting points were obtained in capillaries and are uncorrected. The preparations of some compounds described below are illustrative of the experimental procedures used in the present investigation.

2,6-Dimethylthiophenol

To the Grignard reagent prepared from 22.0 g (0.12 mol) of 2,6-dimethylbromobenzene [104] and 3.0 g magnesium turnings in 100 ml of dry ether, was added with stirring 3.84 g of sulphur powder in small portions. After heating on a water bath for 30 min, the reaction mixture was cooled to room temperature and decomposed by the addition of 100 ml of 5% hydrochloric acid. The ether layer was separated and the aqueous layer was extracted with 50 ml of petroleum ether. The combined extracts were treated with 5% aqueous solution of NaOH. The aqueous layer was separated, acidified with 5% hydrochloric acid and extracted with petroleum ether. The organic layer was washed with water and dried over Na_2SO_4. On removal of the solvent the resulting product was distilled in vacuum under argon, giving 13.0 g (78%) of a colourless oil with b.p. 99°/20 mm (lit. [105] b.p. 84—85/10 mm), n_D^{20} 1.5742.

Triphenyllead 2,6-dimethylthiophenoxide

To a hot solution of 2.24 g (5 mmol) of triphenyllead hydroxide [106] in 150 ml of ethanol was added 0.69 g (5 mmol) of 2,6-dimethylthiophenol. The reaction mixture was evaporated in vacuum and the residue recrystallized from ethanol, affording 2.1 g (73%) of colourless crystals.

Triphenyltin 2,6-dimethylthiophenoxide

To a hot solution of 1.93 g (5 mmol) of triphenyltin chloride [107] in 100 ml of ethanol was added a solution of 0.20 g (5 mmol) of NaOH and 0.69 g (5 mmol) of 2,6-dimethylthiophenol in 10 ml of the same solvent. The solvent was removed in vacuum and the residue treated with water. The insoluble solid was filtered, washed with water, dried and recrystallized from methanol, yielding 1.6 g (66%) of colourless crystals.

Phenylmercury 2,6-dimethylthiophenoxide

A solution of 0.69 g (5 mmol) of 2,6-dimethylthiophenol and 0.20 g (5 mmol) of NaOH in 10 ml of ethanol was added to a hot solution of 1.68 g (5 mmol) of phenylmercury acetate [108] in 100 ml of the same solvent. The reaction mixture was evaporated under reduced pressure and the residue treated with water. The insoluble solid was filtered, washed with water, dried and recrystallized from cyclohexane, giving 1.3 g (63%) of colourless crystals.

Acknowledgements

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