IR-SPECTROSCOPIC INVESTIGATION OF EXCHANGE EQUILIBRIA IN SUBSTITUTED PHENOLS AND THEIR ORGANOMERCURY AND ORGANOTIN DERIVATIVES

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At the present time, the kinetics of the exchange processes associated with the migration of hydrogen or deuterium in OH-, NH-, and HS-acids [1], as well as exchanges in organic compounds of mercury and tin, proceeding with cleavage of metal–heteroatom bonds, has been studied in rather great detail [2, 3]. Considerably less attention has been paid to the study of exchange equilibria (with cleavage of the M–X bond, where X = OR, NR, SR). The exchange equilibria of the type $R_nMX + HY_n \rightleftarrows HX + R_nMY$, with the participation of RHg and R_3Sn groups, have practically not been investigated, although a number of communications have recently appeared on exchange equilibria of the M–M type [4, 5].

Within the framework of a study of the comparative ability for intramolecular coordination, characteristic of univalent organometallic groups, containing heavy nontransition metals, it was of interest to use a study of exchange equilibria of the metal–proton type

$$C_6H_5HgOAr + HOAr^* \rightleftarrows HOAr + C_6H_5HgOAr^*$$
$$(C_6H_5)_3SnOAr + HOAr^* \rightleftarrows HOAr + (C_6H_5)_3SnOAr^*$$

for a comparison of the strength of chelate rings in orthosubstituted phenols and their C_6H_5Hg and $(C_6H_5)_3Sn$ derivatives. The intramolecular hydrogen bond (IMHB) in o-substituted phenols was investigated in rather great detail [6], whereas the study of intramolecular coordination (IMC) in C_6H_5Hg derivatives of o-substituted phenols and thiophenols was begun comparatively recently [7, 8]. Earlier it was concluded that in organometallic derivatives of o-halophenols and thiophenols the C_6H_5Hg group forms a stronger intramolecular coordination bond (IMCB) than the $(C_6H_5)_3Sn$ group and the hydrogen atom. In addition, it has recently been suggested that there is no chelation in methylmercury derivatives of o-substituted phenols and thiophenols [9].

In this work a series of equilibria of the metal–proton type was studied by the method of IR spectroscopy on such model compounds as p-nitrophenol, some 2,6-dihalosubstituted phenols, and their C_6H_5Hg and $(C_6H_5)_3Sn$ derivatives. The existence of exchange equilibria in systems of the type of an organometallic p-nitrophenolate – substituted phenol was established according to the absorption band of the OH group in the IR spectra of the reaction mixtures. A prerequisite for this was a difference in the position of the band of the OH group in the spectra of p- or m- and 2,6-dihalosubstituted phenols.

The IR spectrum of a mixture of equivalent amounts of phenylmercury p-nitrophenolate and 2,6-dichlorophenol contains two bands of the OH group (solution in $CHCl_3$), one of which belongs to the initial 2,6-dichlorophenol, and the second to p-nitrophenol. The ratio of the intensities of the bands of the OH group does not change with time, and the same ratio is reached when diphenylmercury 2,6-dichlorophenolate and p-nitrophenol are introduced into the reaction. Consequently, in solution an exchange reaction $C_6H_5HgOC_6H_4NO_2\text{-}4 + HOC_6H_3Cl_2 \rightleftarrows HOC_6H_4NO_2\text{-}4 + C_6H_5HgOC_6H_3Cl_2$ occurs, with a rapidly established equilibrium.

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Measurement of the optical densities of the bands of the OH group permits a determination of the equilibrium constant K. An analogous phenomenon was also observed for other systems, for which the values of K are cited in Table 1.

On the basis of data on metal–proton type exchanges, we can calculate the values of K for exchanges of the M–M type. Thus, if K_1 and K_2 are known for the exchange reactions

$$R_nMA + HB \rightleftarrows HA + R_nMB \qquad (K_1)$$

$$R_nM^*A + HB \rightleftarrows HA + R_nM^*B \qquad (K_2)$$

then the equilibrium constant K_3 for the exchange reaction

$$R_nMA + R_nM^*B \rightleftarrows R_nM^*A + R_nMB \qquad (K_3)$$

can be expressed in terms of the constants K_1 and K_2:

$$K_3 = K_1/K_2$$

The calculated K for exchange equilibria of the M–M type are cited in Table 2. In general the position of equilibrium should depend on the polar effect of the substituent in the aromatic ring of the phenol, steric hindrances created by σ-substituents, and the IMCB.

From Table 1 it is evident that the polar effects of substituents from the p-position have a significant influence on the position of equilibrium in exchange of the metal–proton type, and electron-acceptor substituents shift the equilibrium in the direction of an organometallic derivative of the substituted phenol. In contrast to this, in an exchange of the M–M type, p-substituents produce little change in K.

The equilibrium constant K for the exchange reactions $R_nMA + HB \rightleftarrows HA + R_nMB$ can be expressed in terms of the dissociation constant of the acids and their organometallic derivatives

$$K = K_{HB} \cdot K_{MA}/K_{HA} \cdot K_{MB}$$

Considering that the potentially possible dissociation of M–O and H–O bonds should be increased by the introduction of electron acceptor substituents, we should conclude that the introduction of electron-acceptor substituents destabilizes the H–O bond to a greater degree than the Sn–O and Hg–O bonds. For an exchange of the M–M type, we can write an analogous expression for K:

$$R_nMA + R_nM^*B \rightleftarrows R_nM^*A + R_nMB$$

$$K = K_{M^*B} \cdot K_{MA}/K_{M^*A} \cdot K_{MB}$$

In accord with this, the small change in K of exchange of the M–M type under the influence of electron-acceptor substituents indicates a comparable destabilization of the Sn–O and Hg–O bonds under the influence of groups of this kind. In accord with the data for exchange equilibria in substituted thiophenols and their organometallic derivatives [10], the steric requirements of the $(C_6H_5)_3Sn$ and C_6H_5Hg groups in o-methylsubstituted organometallicthiophenolates are close. It can be assumed that in derivatives of o-substituted phenols, studied in this work, the steric requirements of the $(C_6H_5)_3Sn$ and C_6H_5Hg groups will also be close. Taking this circumstance and the negligible influence of the polar effects of substituents on the position of the equilibrium for an exchange of the M–M type into consideration, we might expect that in the case of the influence only of polar and steric factors, the position of the equilibrium for the exchange of phenylmercury p-nitrophenolate with o-substituted triphenyltin phenolates will correspond to a statistical distribution of the organomercury groups among the aroxyl radicals. However, the data of Table 2 show that actually the equilibria are strongly shifted in the direction of the formation of phenylmercury derivatives of o-halophenols.

The observed phenomenon may be caused stronger by a coordination bond of the phenylmercury group with the o-halogen than for the triphenyltin group, whereupon the differences in the strength of the coordination bonds increase in the sequence from Cl to Br and I. The results obtained show that in the case of IMC in organometallic derivatives of o-substituted phenols, the C_6H_5Hg group behaves as a relatively milder Lewis acid than the $(C_6H_5)_3Sn$ group.

TABLE 1. Equilibrium Constants in Chloroform at 20° for the Exchange Reactions of $C_6H_5HgOC_6H_4NO_2$-4, $(C_6H_5)_3SnOC_6H_4NO_2$-4, $(C_6H_5)_3SnOC_6H_4COCH_3$-4, $(C_6H_5)_3SnOC_6H_2Cl_2$-2, 6-NO_2-4 with Substituted Phenols

Substituted phenol	K
$C_6H_5HgOC_6H_4NO_2$-4	
$HOC_6H_2(C(CH_3)_3)_2$-2,6-CH_3-4	0,0
$HOC_6H_2Cl_2$-2,6-CH_3-4	1,36±0,08
$HOC_6H_3Cl_2$-2,6	1,56±0,4
$HOC_6H_2Cl_2$-2,6-I-4	2,38±0,4
$HOC_6H_2Cl_2$-2,6-F-4	1,62±0,07
$HOC_6H_2Br_2$-2,6-F-4	2,88±0,19
$HOC_6H_2I_2$-2,6-F-4	8,40±0,20
$HOC_6H_2Cl_2$-2,6-NO_2-4	21,10±0,62
$HOC_6H_2Br_2$-2,6-NO_2-4	24,60±0,08
$HOC_6H_2I_2$-2,6-NO_2-4	76,9±0,8
$HOC_6H_4NO_2$-2	0
$(C_6H_5)_3SnOC_6H_4NO_2$-4	
$HOC_6H_2Cl_2$-2,6-CH_3-4	0,10±0,01
$HOC_6H_3Cl_2$-2,6	0,14±0,01
$HOC_6H_2Cl_2$-2,6-F-4	0,15±0,01
$HOC_6H_2Br_2$-2,6-F-4	0,10±0,01
$HOC_6H_2I_2$-2,6-F-4	0,04±0,06
$HOC_6H_2Cl_2$-2,6-NO_2-4	1,74±0,05
$HOC_6H_2Br_2$-2,6-NO_2-4	0,90±0,05
$HOC_6H_2I_2$-2,6-NO_2 -4	0,34±0,03
HOC_6H_3F-4-NO_2-2	0,00
HOC_6H_2F-4-$(NO_2)_2$-2,6	0,00
HOC_6H_3F-4-CHO-2	0,00
HOC_6H_2F-4-$(CHO)_2$-2,6	0,00
$(C_6H_5)_3SnOC_6H_4COCH_3$-4	
$HOC_6H_2Cl_2$-2,6-F-4	0,66±0,03
$HOC_6H_2Br_2$-2,6-F-4	0,35±0,04
$HOC_6H_2I_2$-2,6-F-4	0,22±0,05
$HOC_6H_2Cl_2$-2,6-NO_2-4	5,60±0,23
$(C_6H_5)_3SnOC_6H_2Cl_2$-2,6-NO_2-4	
HOC_6H_5	0,007±0,004
HOC_6H_4F-4	0,008±0,002
HOC_6H_4Cl-4	0,07±0,01
$HOC_6H_4COCH_3$-4	0,18±0,02
$HOC_6H_4NO_2$-4	0,55±0,04
$HOC_6H_2Br_2$-3,5-F-4	0,28±0,04

Analyzing the results for exchanges of the metal–proton type with the participation of $(C_6H_5)_3Sn$, we should note that on the basis of the values of K of exchange of triphenyltin p-nitrophenolates and 2,6-dichloro-4-nitrophenolate with substituted phenols, we can also calculate K of the exchange of triphenyltin phenolate with substituted phenols. Thus, the values of K of the two reactions of exchange

$$R_nMA_1 + HA_2 \rightleftarrows HA_1 + R_nMA_2 \qquad (K_1)$$

$$R_nMA_1 + HA_3 \rightleftarrows HA_1 + R_nMA_3 \qquad (K_2)$$

permits us to find K for the third reaction

$$R_nMA_2 + HA_3 \rightleftarrows R_nMA_3 + HA_2 \qquad (K_3)$$

from the expression $K_3 = K_2/K_1$. The corresponding constants are cited in Table 3. As can be seen, the introduction of two chlorine atoms into the 2- and 6-positions has approximately the same influence on the value of K (K = 11) as the introduction of chlorine into the p-position (K = 10), while on the basis of the summary electron acceptor effect of two chlorines from the o-position [11] we might have expected a substantially larger increase in K. The observed difference evidently is due to the lower strength of the five-membered chelate ring formed by the $(C_6H_5)_3Sn$ group in comparison with the ring in the IMHC. The decrease in the value of K in the sequence from 2,6-dichloro-4-fluorophenol to 2,6-dibromo- and diiododerivatives, despite a certain increase in the electron-acceptor effect of the

TABLE 2. Calculated K for Exchange Reactions of $C_6H_5HgOC_6H_4$-NO_2-4 with $(C_6H_5)_3SnOR$ (in chloroform, 20°)

R	K	R	K
C_6H_3Cl-2,6	11,1±2,9	$C_6H_2I_2$-2,6-F-4	210±6,4
$C_6H_2Cl_2$-2,6-CH_3-4	13,6±1,0	$C_6H_2Cl_2$-2,6-NO_2-4	12,2±0,6
$C_6H_2Cl_2$-2,6-F-4	10,1±0,6	$C_6H_2Br_2$-2,6-NO_2-4	27,0±1,5
$C_6H_2Br_2$-2,6-F-4	28,8±1,9	$C_6H_2I_2$-2,6-NO_2-4	226±22

TABLE 3. Calculated K for Exchange Reactions of $(C_6H_5)_3SnOC_6H_5$ with Substituted Phenols (in chloroform, 20°)

Substituted phenol	K	Substituted phenol	K
HOC_6H_4F-4	1,1±0,7	$HOC_6H_2Br_2$-2,6-F-4	7,9±5
HOC_6H_4Cl-4	10±6	$HOC_6H_2I_2$-2,6-F-4	3,2±2
$HOC_6H_4COCH_3$-4	26±15	HOC_6H_3F-4-NO_2-2	0,0
$HOC_6H_2Br_2$-3,5-F-4	40±24	HOC_6H_2F-4-$(NO_2)_2$-2,6	0,0
$HOC_6H_4NO_2$-4	79±45	HOC_6H_3F-4-CHO-2	0,0
$HOC_6H_3Cl_2$-2,6	11±7	HOC_6H_2F-4-$(CHO)_2$-2,6	0,0
$HOC_6H_2Cl_2$-2,6-F-4	12±7		

halogen [11], indicates a further increase in the difference in strength of the chelate rings formed by the $(C_6H_5)_3Sn$ group and the hydrogen atom.

An especially sharp difference in the strength of the chelate rings is observed for systems with the o-nitro and o-formyl groups. Considering the substantial electron acceptor effect of these substituents from the o-position, under the condition of the influence only of polar factors, we should have expected a sharp shift of the equilibrium to the right, while actually it is entirely shifted to the left. This can be explained only by an even larger difference in the strength of the six-membered chelate rings formed by the $(C_6H_5)_3Sn$ group and the hydrogen atom than for five-membered rings.

A different situation is observed for the exchange of phenylmercury p-nitrophenolate with 2,6-dihalophenols, where the equilibrium is shifted in the direction of the phenylmercury derivative of dihalophenol. A consideration of the summary polar effect of the substituents [11] shows that under the influence only of polar factors, the value of K should be close to one, while the greater steric requirements of the C_6H_5Hg group in comparison with the H atom [10] should make it less than one. The observed values of K indicate a greater strength of IMCB with the participation of a C_6H_5Hg group in comparison with IMCB in o-halophenols.

EXPERIMENTAL METHOD

Most of the substituted phenols were produced according to the well-known methods and characterized according to the melting points. The synthesis of 3,5-dibromo-4-fluorophenol and 2,6-diformyl-4-fluorophenol will be described later. Organometallic derivatives of phenols used in the study of exchange equilibria were produced by the action of phenylmercury hydroxide and triphenyltin hydroxide on the corresponding phenols and purified by recrystallization or reprecipitation. Phenolates and p-fluorophenolates of diphenylmercury [12, 13] and triphenyltin [13, 14], as well as triphenyltin p-nitrophenolate [14] and phenylmercury 2,6-dibromo-4-fluorophenolate [7] were described earlier. The melting points and data of analysis of the new compounds are cited in Table 4. Typical examples of the production of a number of organometallic phenolates are described below.

The purity of organometallic derivatives was monitored according to the IR spectra. It was found that a number of organometallic phenolates contain an admixture of the corresponding phenol, which is not removed by repeated crystallization or reprecipitation. In view of this, in determining the constants of exchange equilibria, a correction was introduced for the impurity of phenol, the content of which was determined according to the intensity of the absorption of the band of the phenolic OH group in a solution of the corresponding phenolate.

TABLE 4. Melting Point and Data of Analysis for Substituted Phenylmercury and Triphenyltin Phenolates

Compound	Mp, °C (with dec.)	Found, %			Calculated, %		
		C	H	M(F)	C	H	M(F)
$C_6H_5HgOC_6H_4NO_2$-4	168—169	34,47	2,24	48,45	34,66	2,18	48,24
$C_6H_5HgOC_6H_2Cl_2$-2,6-NO_2-4	180—181	29,74	1,55	41,00	29,78	1,45	41,48
$C_6H_5HgOC_6H_2Br_2$-2,6-NO_2-4	177—178	25,27	1,28	34,35	25,10	1,22	34,39
$C_6H_5HgOC_6H_2I_2$-2,6-NO_2-4	186—187	21,86	1,16	29,75	21,58	1,04	30,06
$(C_6H_5)_3SnOC_6H_2Cl_2$-2,7-NO_2-4	155—156	51,63	3,09	21,35	51,83	3,06	21,36
$(C_6H_5)_3SnOC_6H_2Br_2$-2,6-NO_2-4	170—171	45,28	2,70	18,35	44,60	2,63	18,39
$(C_6H_5)_3SnOC_6H_2I_2$-2,6-NO_2-4	182—183	39,26	2,38	15,97	38,95	2,30	16,05
$(C_6H_5)_3SnOC_6H_4COCH_3$-4	132—133	64,81	4,63	24,54	64,53	4,54	24,54
$C_6H_5HgOC_6H_2Cl_2$-2,6-F-4	156—157	31,15	1,47	3,49	31,50	1,53	4,15
$C_6H_5HgOC_6H_2I_2$-2,6-F-4	136—137	22,33	1,07	3,08	22,50	1,09	2,96
$(C_6H_5)_3SnOC_6H_2Cl_2$-2,6-F-4	81—83	54,33	3,20	3,42	54,44	3,21	3,59
$(C_6H_5)_3SnOC_6H_2Br_2$-2,6-F-4	100—102	46,36	2,47	2,88	46,36	2,47	3,06
$(C_6H_5)_3SnOC_6H_2I_2$-2,6-F-4	121—123	40,46	2,42	2,54	40,40	2,38	2,66

The spectral measurements were performed on an R-20 spectrophotometer in the region of 3400-3680 cm^{-1} (LiF prism), spectral width 3.6 cm^{-1}. Chloroform purified according to the standard procedure and redistilled over P_2O_5 was used as the solvent. CCl_4 was also used for triphenyltin phenolates. The concentration of the investigated compounds was varied from $3 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ M, which guarantees the absence of autoassociation of the phenols. The equilibrium constants of the exchange reactions was calculated according to the equation

$$K=\frac{C_A-\frac{D_A}{\varepsilon\cdot d}}{\left[\frac{D_A}{\varepsilon\cdot d}\right]\left[C_B-\left(C_A-\frac{D_A}{\varepsilon\cdot d}\right)\right]}$$

for a band in the region of 3500-3530 cm^{-1}. In the reaction with phenylmercury phenolates, the bands 3530 and 3580 cm^{-1} overlap; therefore, for the refinement of D_A we used the method of [15].

In the determination of K, the exchange reactions in most cases were conducted in both directions.

Phenylmercury p-Nitrophenolate. To a hot solution of 1.5 g phenylmercury hydroxide in 40 ml methanol we added a hot solution of 0.7 g p-nitrophenol in 10 ml of CH_3OH. After evaporation of the solvent under vacuum, 1.9 g (92%) of light-yellow crystals was obtained, and they were recrystallized from a mixture of xylene and heptane.

Phenylmercury 2,6-Dichloro-4-nitrophenolate. To a hot solution of 0.7 g 2,6-dichloro-4-nitrophenol in 20 ml of methanol we added a hot solution of 0.99 g phenylmercury hydroxide in 30 ml of methanol. The precipitate that formed upon cooling was filtered off, washed with methanol, and dried. We obtained 1.5 g (90%) of yellow crystals, which was purified with reprecipitation from heptane from hot toluene.

Triphenyltin 2,6-Dichloro-4-nitrophenolate. To a hot solution of 0.54 g 2,6-dichloro-4-nitrophenol in 100 ml abs. benzene we added a hot solution of 1.0 g triphenyltin hydroxide in 50 ml abs. benzene. Benzene was distilled off to dryness on a water bath, then another 50 ml of abs. benzene was added, and the operation of distillation was repeated. The yellow oil remaining crystallized upon standing under vacuum, after which it was washed with hot heptane. Yield 1.4 g (97%) of the yellow powder.

CONCLUSIONS

1. Exchange equilibria of the metal—proton and metal—metal type were studied by the method of IR spectroscopy in a series of substituted phenols and their C_6H_5Hg and $(C_6H_5)_3Sn$ derivatives.

2. The polar effects of substituents in the phenol ring change the position of an equilibrium of the metal—proton type and practically do not influence an equilibrium of the metal—metal type.

3. Depending on the nature of the acceptor of the unshared electron pair, the strength of the intramolecular coordination bond with o-halogens increases in the series: $(C_6H_5)_3Sn < H < C_6H_5Hg$.

4. The C_6H_5Hg group is a milder Lewis acid than $(C_6H_5)_3Sn$.

5. The differences in the strength of the chelate rings with the participation of the $(C_6H_5)_3Sn$ group and the H-atom of hydrogen increases sharply for six-membered rings formed by NO_2 and CHO groups.

LITERATURE CITED

1. V. K. Pogorelyi and I. P. Gragerov, Uspekhi Khimii, 39, 1856 (1970).
2. L. L. Murrell and T. L. Brown, J. Organometal. Chem., 13, 301 (1968).
3. U. Folli, D. Jarossi, and F. Taddei, J. Chem. Soc. Perkin Trans., II, 1284 (1973).
4. R. J. Klyne and L. F. Sytsma, Inorg. Nucl. Chem. Letters, 8, 1 (1972).
5. D. A. Armitage and A. Farascoli, Inorg. Nucl. Chem. Letters, 9, 1225 (1973).
6. A. W. Baker and A. T. Shulgin, Canad. J. Chem., 43, 650 (1965).
7. A. N. Nesmeyanov, D. N. Kravtsov, É. I. Fedin, B. A. Kvasov, V. M. Pachevskaya, and L. S. Golovchenko, Dokl. Akad. Nauk SSSR, 183, 1098 (1968).
8. D. N. Kravtsov, B. A. Kvasov, L. S. Golovchenko, E. M. Rokhlina, and E. I. Fedin, J. Organometal. Chem., 39, 107 (1972).
9. R. J. Klyne and L. F. Sytsma, J. Organometal. Chem., 54, 15 (1973).
10. D. N. Kravtsov, A. S. Peregudov, E. M. Rokhlina, and L. A. Fedorov, J. Organometal. Chem., 77, 199 (1974).
11. M. T. Tribble and J. G. Traynham, J. Amer. Chem. Soc., 91, 379 (1969).
12. A. J. Bloodworth, J. Chem. Soc., C, 2051 (1970).
13. A. N. Nesmeyanov, D. N. Kravtsov, B. A. Kvasov, and E. M. Rokhlina, V. M. Pachevskaya, L. S. Golovchenko, and E. I. Fedin, J. Organometal. Chem., 38, 307 (1972).
14. J. D'Ans and H. Gold, Chem. Ber., 92, 3076 (1956).
15. Y. Kakiuti, T. Shimozawa, and R. Suzuki, J. Molec. Spectroscopy, 23, 388 (1967).