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A PMR STUDY OF EXCHANGE EQUILIBRIA BETWEEN THIOPHENOLS AND THEIR ORGANO-ANTIMONY AND -MERCURY DERIVATIVES

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Summary

The exchange reactions between substituted thiophenols and their $(C_6H_5)_2Sb$ and C_6H_5Hg derivatives are slow on the PMR time scale in chloroform. The corresponding equilibrium constants indicate that the strength of the virtually chelate rings involving the $(C_6H_5)_2Sb$ group is lower than those of the chelate rings involving the C_6H_5Hg group or hydrogen.

Results and discussion

The PMR spectrum of an equimolar mixture of $(C_6H_5)_2SbSC_6H_5$ (I) and $C_6H_5HgSC_6H_3(CH_3)_2$-2,6 (II) in $CHCl_3$ solution (0.1 *M* in each of the components) show two CH_3 group resonances, one of which (2.63 ppm downfield from TMS) corresponds to the starting compound (II) and the other (2.41 ppm downfield from TMS) to $(C_6H_5)_2SbSC_6H_3(CH_3)_2$-2,6, (III). These data show that in $CHCl_3$ solution a metal—metal exchange reaction of the type shown in eqn. (1) occurs. The exchange is slow on the PMR time scale. Equilibrium is established rapidly on mixing the reactant solutions, the same equilibrium position being attained in the reaction between (III) and $C_6H_5HgSC_6H_5$. Integration of the CH_3 group peaks of (II) and (III) in the spectra of the reaction mixtures made it possible to determine the equilibrium constants for the exchanges between $(C_6H_5)_2SbSAr$ and (II).

$$(C_6H_5)_2SbSC_6H_5 + C_6H_5HgSC_6H_3(CH_3)_2\text{-}2,6 \rightleftharpoons C_6H_5HgSC_6H_5 + (C_6H_5)_2SbSC_6H_3(CH_3)_2\text{-}2,6 \qquad (1)$$

As can be seen from Table 1, the equilibrium constant for the exchange reaction between (I) and (II) is equal to unity, showing that the steric requirements of the C_6H_5Hg and $(C_6H_5)_2Sb$ groups are practically the same in the systems studied. Introduction of 3-Cl or 4-$(CH_3)_2N$ substituents into the C_6H_5S moiety shifts the equilibrium only slightly. These results indicate that steric or

TABLE 1

EQUILIBRIUM CONSTANTS FOR THE EXCHANGE REACTIONS IN CHLOROFORM AT 34°

Reactants		K
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_2SbSC_6H_5$	1.0
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_2SbSC_6H_4Cl$-3	0.77
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_2SbSC_6H_4N(CH_3)_2$-4	0.59
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_2SbSC_6H_4OCH_3$-2	6.7
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_2SbSC_6H_4NO_2$-2	7.4
$C_6H_5HgSC_6H_3(CH_3)_2$-2,6	+ $(C_6H_5)_2SbSC_6H_4F$-2	2.6
$C_6H_5HgSC_6H_3(CH_3)_2$2,6	+ $(C_6H_5)_2SbSC_6H_4Cl$-2	2.4
$C_6H_5HgSC_6H_3(CH_3)_2$2,6	+ $(C_6H_5)_2SbSC_6H_4Br$-2	4.0
$(C_6H_5)_2SbSC_6H_3(CH_3)_2$-2,6	+ HSC_6H_5	3.9
$(C_6H_5)_2SbSC_6H_4CH_3$-2	+ HSC_6H_5	2.3
$(C_6H_5)_2SbSC_6H_3(CH_3)_2$-2,6	+ $HSC_6H_3Cl_2$-3,5	4.1
$(C_6H_5)_2SbSC_6H_3(CH_3)_2$-2,6	+ $HSC_6H_4N(CH_3)_2$-4	5.4
$(C_6H_5)_2SbSC_6H_3(CH_3)_2$-2,6	+ $HSC_6H_4OCH_3$-2	2.9
$(C_6H_5)_2SbSC_6H_3(CH_3)_2$-2,6	+ $HSC_6H_4NO_2$-2	0.49
$(C_6H_5)_2SbSC_6H_3(CH_3)_2$-2,6	+ HSC_6H_4F-2	1.4
$(C_6H_5)_2SbSC_6H_3(CH_3)_2$-2,6	+ HSC_6H_4Cl-2	1.1
$(C_6H_5)_2SbSC_6H_3(CH_3)_2$-2,6	+ HSC_6H_4Br-2	1.0

polar effects of substituents have no appreciable influence on the position of the equilibrium.

The introduction of *ortho*-substituents containing lone electron pairs leads to a pronounced displacement of the equilibrium in favour of the *ortho*-substituted phenylmercury thiophenoxides. The equilibrium constant increases in the order: $F \approx Cl < Br < OCH_3 < NO_2$. This can be explained by the greater strength of intramolecular coordinate bonds with the C_6H_5Hg group [1] than with the $(C_6H_5)_2Sb$ group [2] in the organometallic derivatives of *o*-substituted thiophenols.

Equilibrium constants for the exchange of (III) with substituted thiophenols (eqn. 2) which is also slow on the PMR time scale, indicate that the equilibrium is only slightly influenced by the polar effects of the 4-$(CH_3)_2N$ and 3,5-Cl_2 substituents. The non-randomness of the equilibrium for the exchange of (III) and $(C_6H_5)_2SbSC_6H_4CH_3$-2 (IV) with C_6H_5SH arises from the increased steric requirments of the $(C_6H_5)_2Sb$ group compared with those of hydrogen. *ortho*-Halogen substituents decrease the equilibrium constant by a factor of approximately 4, whereas according to the Van der Waals' radii for the halogen and methyl substituents [3] and the data for (III) and (IV), it should have been reduced only two-fold in the case of non-bonded interactions with the *ortho*-substituents. This may be a consequence of the greater strength of the internal hydrogen bond in *ortho*-halothiophenols [4] relative to that of the intramolecular coordinate bond involving the $(C_6H_5)_2Sb$ group. A further decrease in equilibrium constant with an *o*-NO_2 group demonstrates the increasing difference in the strengths of the chelate rings involving hydrogen and the $(C_6H_5)_2Sb$ group on passing from the five-membered to six-membered ring, whereas in the case of the *o*-CH_3O group the strengths of the chelate rings appear to be comparable.

$$(C_6H_5)_2SbSC_6H_3(CH_3)_2\text{-}2,6 + HSAr \rightleftharpoons HSC_6H_3(CH_3)_2\text{-}2,6 + (C_6H_5)_2SbSAr \qquad (2)$$

Experimental

PMR spectra were recorded on a Hitachi—Perkin—Elmer R-12 spectrometer at 34°. 0.1 *M* solutions of reactants were used, the error in equilibrium constants being not greater than ± 10%. The diphenyl(arylthio)stibines and phenylmercury thiophenoxides studied in the present communication were prepared by the action of $[(C_6H_5)_2Sb]_2O$ and C_6H_5HgOH on the corresponding thiophenols and were characterized by their melting points, R_F's and analytical data.

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