The influence of aryl ligands on the chemical hardness of triarylitin cations [1]

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Abstract

The ^{19}F NMR investigation of exchange equilibria in the systems $Ar_3SnSC_6H_4F\text{-}4 + Ph_3SnCl$ has shown that the chemical hardness of Ar_3Sn^+ cations decreases with increase in electron-accepting ability of aryl ligands. It has been found that the influence of aryl ligands on the chemical hardness of Ar_3Sn^+ cations is well described by σ° constants of substituted phenyl groups. The correlation of $\log K_e$ with the electronegativities of Ar_3Sn groups strongly suggests the contribution of electronegativity factors. © 1997 Elsevier Science S.A.

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1. Introduction

Recently there has been considerable interest in the problems of chemical hardness [1]. Thus, studies have been carried out devoted to quantum chemical calculations of chemical hardness for simple organic groups and organoelement groups containing key atoms of light elements [2]. At the same time, there are no systematic calculated or experimental data on quantitative or qualitative regularities concerning the influence of the nature of organometallic groups or cations on their chemical hardness. In particular, there is no information on quantitative regularities of ligand influence on the chemical hardness of organometallic groups or cations. On the basis of qualitative evidence, it has been established that soft ligands can both decrease [3] and increase [4] the chemical hardness of metal-containing groups.

At the same time, in connection with the problems of application of the HSAB principle [5] in organometallic chemistry, it seems desirable to perform quantitative studies of ligand influence on the chemical hardness of organometallic groups or cations. Thus, for example, in the preceding communication [6], the influence of aryl ligands on the chemical hardness of $ArHg^+$ cations was

investigated. As a result, it has been established that an increase in the electron-withdrawing ability of aryl ligands decreases the chemical hardness of such cations. Furthermore, it has been found that the influence of aryl ligands is best described by σ° constants of substituted phenyl groups. In this connection it was considered interesting to find out to what extent the above regularities apply to other organometallic cations of Ar_nM^+ type.

A suitable approach to the study of these problems involves investigation of exchange reactions of the general type

$$QX + Q^*Y \rightleftharpoons Q^*X + QY$$
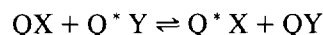
where Q and Q^* represent cation-like fragments of molecules, whereas X and Y represent anion-like fragments. According to the HSAB principle [7], such reactions should proceed with the formation of compounds containing combinations of molecular fragments of 'hard–hard' and 'soft–soft' type. In the case of organometallic compounds of main group metals containing metal–heteroatom bonds, such studies can easily be performed, since the exchange reactions proceed readily on the preparative and even on the NMR timescale [8].

Recently, on the basis of investigation of exchange equilibria involving derivatives of triphenyltin and

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[1] Dedicated to the memory of Professor Yu.T. Struchkov.

triphenyllead, it has been shown [9] that for the exchange reactions of the above type controlled by chemical hardness of Q^+ and Q^{+*} cations, as well as of X^- and Y^- anions, the equilibrium constant can be described by the following expression:

$$\log K_e = B(\eta_{Q^-} - \eta_{Q^{+*}})(\eta_{Y^-} - \eta_{X^-})$$

where η corresponds to the chemical hardness of cations and anions. If the variation of equilibrium constant is connected with the changes in only one cation, then the following expression is obtained:

$$\log K_e = a\eta_{Q^+} + c$$

if Q^+ represents an organometallic cation L_nM^+, the influence of the ligand L on $\log K_e$ will reflect its influence on the chemical hardness of the L_nM^+ cation.

2. Results and discussion

According to the above considerations, and with the aim of determining the nature of the aryl ligand influence on the chemical hardness of Ar_3Sn^+ cations, ^{19}F NMR has been applied in the present work to study equilibrium constants for the exchange reactions

$$Ar_3SnSC_6H_4F\text{-}4 + Ph_3SnCl \rightleftharpoons Ph_3SnSC_6H_4F\text{-}4$$
$$+ Ar_3SnCl \qquad (1)$$
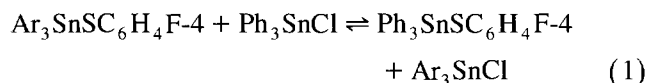
where $Ar = 4\text{-}CH_3C_6H_4$, $4\text{-}FC_6H_4$, $4\text{-}ClC_6H_4$, $3,4\text{-}Cl_2C_6H_3$, $3,4,5\text{-}Cl_3C_6H_2$.

The use of these model reactions was determined for the following reasons. It has been shown previously [10] that compounds of type R_3SnX containing Sn–Cl and Sn–S bonds readily undergo exchange reactions. From Table 1 it may be seen that the fluorine chemical shifts in the compounds $Ar_3SnSC_6H_4F\text{-}4$ are sensitive to the nature of the aryl ligands, and differ sufficiently. For the anionic ligands Cl^- and PhS^-, the parameters of chemical hardness are known [7], and are equal to 19 and 14 kcal/mol^{-1} respectively. According to these data, the Cl^- anion is harder and the PhS^- is softer. It could be expected that the chemical hardness of the 4-$FC_6H_4S^-$ anion will not be very different from that of the PhS^- anion. In addition, inspection of Stuart–Brig-

Table 1
[19]F chemical shifts for the 4-FC_6H_4S group in the compounds $Ar_3SnSC_6H_4F\text{-}4$ in benzene solution

Ar	FCS (ppm)
4-$CH_3C_6H_4$	3.34
Ph	3.08
4-FC_6H_4	2.14
4-ClC_6H_4	1.85
3,4-$Cl_2C_6H_3$	0.74
3,4,5-$Cl_3C_6H_2$	−0.25

Table 2
Equilibrium constants in benzene at 25 °C for the reactions of $Ar_3SnSC_6H_4F\text{-}4$ with Ph_3SnCl

Ar	K
4-$CH_3C_6H_4$	1.1
Ph	1
4-FC_6H_4	0.65
4-ClC_6H_4	0.57
3,4-$Cl_2C_6H_3$	0.24
3,4,5-$Cl_3C_6H_2$	0.15

leb molecular models has shown that Cl and $SC_6H_4F\text{-}4$ groups have similar steric requirements with respect to Ar_3Sn.

Finally, it has been established that the exchange reactions of the above type are slow at room temperature on the ^{19}F NMR timescale. Thus, it has been found that, for a benzene solution of the mixture of (4-$CH_3C_6H_4)_3SnSC_6H_4F\text{-}4$ and $Ph_3SnSC_6H_4F\text{-}4$ compounds at 0.02 M concentration, two ^{19}F NMR signals are observed at 3.33 and 3.07 ppm relative to PhF. The situation does not change after addition to the solution of Ph_3SnCl at the same concentration. These data indicate that the possible exchange reactions are slow on the ^{19}F NMR timescale.

Further, it has been found that, after mixing benzene solutions of (4-$CH_3C_6H_4)_3SnSC_6H_4F\text{-}4$ and Ph_3SnCl at 0.04 M concentration, the second signal, which belongs to $Ph_3SnSC_6H_4F\text{-}4$, appears in the ^{19}F NMR spectrum. After some time the ratio of signal integral intensities becomes constant. These data indicate that in solution the exchange equilibrium is established according to Eq. (1). The attainment of equilibrium usually requires several minutes. The determination of integral intensities of ^{19}F NMR signals belonging to one of the reactants and one of the products bearing the 4-fluorophenyl tag allowed us to determine the equilibrium constants for the reactions studied, which are presented in Table 2.

According to the HSAB principle, it should be expected that the distribution of Ar_3Sn^+ and Ph_3Sn^+ cations between the harder Cl^- and softer $^-SC_6H_4F\text{-}4$ anions will be determined by the relative chemical hardness of these cations. Inspection of Table 2 shows that the nature of aryl ligands affects considerably the equilibrium constant, which decreases with increase in electron-withdrawing ability of the aryl ligands. This corresponds to the fact that the increase in electron-accepting ability of aryl ligands leads to an increase in ability of the Ar_3Sn^+ cations to form a bond with the softer $^-SC_6H_4F\text{-}4$ anions. In accordance with the HSAB principle, this should mean that the chemical hardness of the Ar_3Sn^+ cations decreases with increase in electron-withdrawing ability of the aryl ligands.

Thus, for Ar_3Sn^+ cations the same regularities are

observed as for $ArHg^+$ cations [6]. For the latter it had been found that the influence of the aryl ligands on $\log K_e$ and consequently on chemical hardness [9] is well described by σ° constants of substituted phenyl groups. In this connection the values of $\log K_e$ for the exchange reactions studied have been correlated with σ° constants of substituted phenyl groups [11]. The σ° values for polysubstituted phenyl groups have been calculated as the sum of σ° values for the corresponding monosubstituted phenyl groups.

As a result, a good correlation has been found, which is expressed by the following equation:

$$\log K_e = -0.79 \sigma^\circ - 0.05 \quad r = 0.994 \quad s = 0.04$$

In accord with the previously obtained data [9], these results indicate that the influence of aryl ligands on the chemical hardness of Ar_3Sn^+ cations is well described by σ° constants of substituted phenyl groups.

At the same time it should be taken into account that the Cl and SC_6H_4F-4 ligands may possess different electronegativities. In fact, it has been found that for the compounds $(4\text{-}FC_6H_4)_3SnSC_6H_4F$-4 and $(4\text{-}FC_6H_4)_3SnCl$ the fluorine chemical shifts for the $(4\text{-}FC_6H_4)_3Sn$ group in benzene solution are equal to -3.61 and -4.41 ppm respectively. This indicates the lower electronegativity of the SC_6H_4F-4 ligand as compared with that of the Cl ligand.

In this connection it should be indicated that it has previously been concluded [7] that the necessity exists to take into account electronegativity factors in applying the HSAB principle. In addition, it has recently been shown [12] that the HSAB principle is probably strictly obeyed only for the cases where the electronegativities of competing partners are equal. This is consistent with the earlier conclusion [13] that for the exchange reactions involving different organometallic derivatives of HX-acids

$$R_nMX + R_mM^*Y \rightleftharpoons R_nMY + R_mM^*X$$
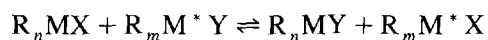
the position of the equilibrium depends not only on the nature of the central metal atom and the R groups, but also on the difference in polarities of M–X and M*–X, as well as of M–Y and M*–Y bonds.

Recently, the electronegativities of Ar_3Sn groups have been calculated [14]. In addition, it has been shown that they correlate closely with σ° constants of substituted phenyl groups. In this connection the data obtained in the present investigation suggest the existence of a correlation between $\log K_e$ values for the exchange reactions studied and the electronegativity values κ for the Ar_3Sn groups. Indeed, a good correlation between these values has been found, which is expressed by the following equation:

$$\log K_e = -0.46\kappa + 1.58 \quad r = 0.993 \quad s = 0.04$$

This result affords strong evidence that the influence of aryl ligands on the observed chemical hardness of Ar_3Sn^+ cations, which decreases with increase in electron-accepting ability of aryl ligands, is a consequence of the electronegativity variation for Ar_3Sn groups, which favours bond formation between the more electronegative Ar_3Sn group and the less electronegative $4\text{-}FC_6H_4S$ ligand. At present, further studies concerning the problem of electronegativity contributions to chemical hardness are in progress.

3. Experimental

$^{19}F\{^1H\}$ NMR spectra were recorded on a Bruker WP-200 SY spectrometer operating at 188.31 MHz for fluorine. The values of fluorine chemical shifts were determined at 25 °C for 0.02 M solutions of compounds in benzene by the replacement method with respect to a solution of PhF in the same solvent and at the same concentration. Resonance conditions were stabilized by the deuterium signal from D_2O placed between the walls of a 5 mm tube and a 4 mm enclosure containing the solution of the sample or of the standard. The determination error of fluorine chemical shifts was not greater than ± 0.02 ppm.

The exchange equilibria have been studied in benzene at 25 °C. The starting concentrations of reactants were equal to 0.04 M. For the preparation of reaction mixtures, equimolar quantities of reactants were weighed into the same stoppered weighing bottle and dissolved in the necessary volume of solvent.

After the attainment of equilibrium the integral intensities of the ^{19}F NMR signals were determined for one of the reactants $Ar_3SnSC_6H_4F$-4 (I_R) and one of the products $Ph_3SnSC_6H_4F$-4 (I_P). According to the equation of the exchange reactions and to the equal starting concentrations of the reactants, the equilibrium constants were determined by using the formula $K_e = (I_P/I_R)^2$. The equilibrium was attained by using both pairs of reactants, and consistent data were obtained. The relative error in equilibrium constant did not exceed $\pm 10\%$.

The compounds used in the present investigation include triaryltin 4-fluorothiophenoxides $Ar_3SnSC_6H_4F$-4, Ar = Ph [15], $4\text{-}CH_3C_6H_4$ [16], $4\text{-}FC_6H_4$ [17], $4\text{-}ClC_6H_4$ [16], $3,4\text{-}Cl_2C_6H_3$ [18], $3,4,5\text{-}Cl_3C_6H_2$ [18] and triaryltin chlorides Ar_3SnCl, Ar = Ph [19], $4\text{-}CH_3C_6H_4$ [19], $4\text{-}FC_6H_4$ [20], $4\text{-}ClC_6H_4$ [21], $3,4\text{-}Cl_2C_6H_3$ [22], $3,4,5\text{-}Cl_3C_6H_4$ [22]. They were prepared by the reported procedures and identified by melting points. Benzene was dried over $CaCl_2$ and distilled before use.

Acknowledgements

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