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Preliminary Communication

On the relationship of the equilibrium constants of exchange reactions involving HX-acids and their organometallic derivatives L_nMX with the absolute and chemical hardness of corresponding anions and cations

Alexander S. Peregudov, Elena M. Rokhlina
and Dmitrii N. Kravtsov

A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of Russia, Vavilov St. 28, 117813 Moscow, (Russian Federation)

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Abstract

The exchange equilibria: $Ph_3Sn{-}X + Ph_3Pb{-}SC_6H_4F{-}4 \rightleftarrows Ph_3Pb{-}X + Ph_3Sn{-}SC_6H_4F{-}4$ (X = OH, Cl, Br, I) have been studied in $CHCl_3$ by ^{19}F NMR. Good correlations of equilibrium constant logarithm with the Pearson parameters of absolute and chemical hardness have been found. On the basis of these relationships and general consideration of exchange equilibria it has been shown that the study of exchange reactions involving hard and soft HX-acids and their L_nM-derivatives permits study of quantitative regularities in ligand influence on the hardness of organometallic cations.

Key words: Tin; Lead; Hardness; Equilibria; Fluorine; Nuclear magnetic resonance

Quantitative prediction of the relative reactivities of metal-element σ-bonds in organometallic compounds L_nMX and their comparison with that of hydrogen–element bonds in related HX-acids is an important problem in chemistry. Most fruitful in this respect from the thermodynamic point of view has been the HSAB principle proposed by Pearson [1]. New perspectives were recently opened by the data on absolute hardness η [$\eta = 1/2(I - A)$] of atoms and cations [2,3]. At the same time experimental data for L_nM-groups are lacking, except for $(CO)_5Mn$. The thermodynamic parameters of equilibrium (1):

$$A^1{-}B + A{-}B^1 \rightleftarrows A^1{-}B^1 + A{-}B \qquad (1)$$

were used by Pearson for quantitative determination of chemical hardnesses $\tilde{\eta}$ of cations and anions [4]. In the above equation A and A^1 are cations, and B and B^1 are anions of different hardness. The $\tilde{\eta}$ values were calculated from available bond energy data for gas phase, in particular, for monovalent metal cations (Li, Na, Tl, Cs, Cu, Ag) and proton. In contrast, corresponding data on organometallic cations are rather limited [5] due to the fact that determination of formation enthalpies for these compounds is difficult [6].

The relative hardnesses of different L_nM-groups and hydrogen may be determined in organic solvents by studying the exchange reactions of metal–hydrogen (2) and metal–metal (3) type:

$$L_nM{-}X + H{-}Y \rightleftarrows L_nM{-}Y + HX \qquad (2)$$

$$L_nM{-}X + L_nM^*{-}Y \rightleftarrows L_nM^*{-}X + L_nM{-}M{-}Y \qquad (3)$$

involving hard and soft acids and their L_nM-derivatives. In a previous study [7] we investigated the reactions (2) and (3) in different solvents in systems involving hard acetate (X = OAc) and soft 2,6-dimethylthiophenoxide ($Y = SC_6H_4Me_2$-2,6) anions. It was found that in $CHCl_3$ the hardness of cations increases in the order:

$$PhHg^+ < Ph_3Pb^+ < Ph_3Sn^+ < H^+$$

This sequence is in the completely opposite direction to increasing η values for metals: Sn (3.05 Ev) < Pb (3.53) < Hg (5.54). This probably indicates inversion of the hardness of Ph_nM-groups with respect to that of the central metal atom due to ligand influence or, less likely, an effect of solvent in going from the gas phase to relatively inert $CHCl_3$. It should be also noted that our results may have been influenced not only by the hardness of key atoms in HX-acids but also by the differences in steric requirements of L_nM-groups and hydrogen atom with respect to OAc and $SC_6H_4Me_2$-2,6 moieties as well as by possible chelating in L_nMOAc.

In order to answer the question whether the quantitative connection between the hardnesses of anions and the relative stabilities of two metal–element bonds exists, the equilibrium constants K_e have been determined in $CHCl_3$ for the exchange reactions of the tin–lead type:

$$Ph_3Sn{-}X + Ph_3Pb{-}Y \rightleftarrows Ph_3Sn{-}Y + Ph_3Pb{-}X \qquad (4)$$

Correspondence to: Dr. A.S. Peregudov.

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TABLE 1. Equilibrium constants for the exchange reactions (4): $Ph_3Sn{-}X + Ph_3Pb{-}Y \rightleftarrows Ph_3Sn{-}Y + Ph_3Pb{-}X$ (4) in $CHCl_3$ and parameters of absolute (η) [3] and chemical ($\tilde{\eta}$) [4] hardness of X and Y

System	X	Y	$K_e(4)$	η_X (Ev)	$\tilde{\eta}_X$ (Kcal)	η_Y (Ev)	$\tilde{\eta}_Y$ (Kcal)
4a	OH	Sc_6H_4F-4	$1.4 \cdot 10^{-3}$	5.67	27	3.08	14
4b	Cl	SC_6H_4F-4	0.51	4.7	19	3.08	14
4c	Br	SC_6H_4F-4	3.5	4.2	18	3.08	14
4d	I	SC_6H_4F-4	45.0	3.7	15	3.08	14
4e	Cl	Br	0.10	4.7	19	4.2	18

in systems involving the softer Ph_3Pb and the harder Ph_3Sn groups. X and Y are anions with known hardnesses—OH, Cl, Br, I and SPh. We suppose that SPh and SC_6H_4F-4 have the same hardness because $K_e(4)$ for X = SPh and Y = SC_6H_4F-4 equals 1.

From Table 1 it follows that for systems (4a–d) with the same Y, K_e increases with decreasing hardness of X in the order:

OH < Cl < Br < I

A more detailed analysis reveals that good correlations of log K_e with η or $\tilde{\eta}$ are observed:

$$\log K_e(4) = -2.27\eta + 10.14 \quad (r = 0.996) \qquad (5)$$

$$\log K_e(4) = -0.37\tilde{\eta} + 7.10 \quad (r = 0.993) \qquad (6)$$

On the basis of the above data and symmetry considerations and by taking into account that for the exchange reactions of the general type:

$$Q{-}X + Q^{\star}{-}Y \rightleftarrows Q^{\star}{-}X + Q{-}Y$$

$K_e = 1$ and $\log K_e = 0$, if $\eta_Q = \eta_{Q^{\star}}$ or $\eta_X = \eta_Y$, it may be concluded that the dependence of equilibrium constant on the hardness of cations and anions will be given by the equation:

$$\log K_e = B(\eta_Q - \eta_{Q^{\star}})(\eta_Y - \eta_X).$$

If $Q^{\star}$, X and Y are constant, we obtain again:

$$\log K_e = a\eta + c.$$

Thus for $Q = L_nM$ the ligand influence on log K_e will reflect the influence of ligands on the hardness of organometallic cations.

This is the basis for the study of quantitative regularities in the influence of the ligand on the hardness of organometallic cations. Previously the influence of ligand on the hardness of the metal has been discussed only in qualitative terms [8,9].

Thus it may be supposed that the study in inert solvents of exchange reactions (2) and (3), involving soft and hard HX-acids and their organometallic derivatives as well as of reaction (7):

$$L_nM{-}X + M^{\star}{-}Y \rightleftarrows L_nM{-}Y + M^{\star}{-}X \qquad (7)$$

where $M^{\star}$ represents monovalent cations with known hardness as mentioned previously [4], will allow determination of the hardness of organometallic cations. Such investigations are in progress.

1. Experimental details

The compounds studied have been synthesized by conventional methods and their preparation has been described elsewhere [10,11]. The investigation of exchange equilibria was performed with a Bruker WP-200 SY NMR spectrometer operating at 188.31 (^{19}F) and 74.63 MHz (^{119}Sn). Values of K_e for systems 4a–d (Table 1) were determined by integrating the fluorine signals separately observed in the ^{19}F NMR spectrum from two 4-fluorophenyl groups. The ^{19}F chemical shifts relative to fluorobenzene are 3.09 ppm for $Ph_3SnSC_6H_4F$-4 [$^6J(^{19}F,^{119}Sn) = 13.5$ Hz] and 3.87 ppm for $Ph_3PbSC_6H_4F$-4 [$^6J(^{19}F,^{207}Pb) = 24.4$ Hz]. K_e for system 4e was determine by integrating two ^{119}Sn signals in the ^{119}Sn NMR spectrum from Ph_3SnCl and Ph_3SnBr (rather broad owing to halogen exchange). The ^{119}Sn chemical shifts relative to Me_4Sn are −45.8 ppm for Ph_3SnCl and −61.1 ppm for Ph_3SnBr. It should be noted that the experimental value K_e(4e) (0.10) is in very good agreement with the value 0.15 calculated from K_e(4b) and K_e(4c). This confirms the reliability of the results obtained.

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