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Preliminary communication

THE RELATIVE SOFTNESS OF UNIVALENT ORGANOMETALLIC CATIONS ($PhHg^+$, Ph_3Pb^+, Ph_3Sn^+) AND THE PROTON UPON FORMATION OF M—O, M—S, H—O AND H—S BONDS

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Summary

The exchange equilibria in systems involving organomercury-, lead- and tin-acetates and 2,6-dimethylthiophenoxides have been studied. According to the data obtained in aprotic solvents the relative softness of the proton and corresponding univalent organometallic cations increases in the order: $H^+ < Ph_3Sn^+ < Ph_3Pb^+ < PhHg^+$, the differences in softness increasing considerably in going from chloroform to pyridine.

At present there appear to be no data in the literature on the relative softness (as in Pearson's classification [1]) of different univalent organometallic cations such as R_nM^+ (with the central atom of a non-transition heavy metal) and the proton in aprotic solvents, nor any on the influence of the nature of the solvent on the relative softness of these cations. In order to study this problem in the case where the anions are $2,6\text{-}Me_2C_6H_3S^-$ (a soft Lewis base) and AcO^- (a hard Lewis base), we determined the equilibrium constants for the exchange reactions (1) in different solvents by NMR [2]:

$$XOAc + YSC_6H_3Me_2\text{-}2,6 \rightleftarrows YOAc + XSC_6H_3Me_2\text{-}2,6 \qquad (1)$$

($X \neq Y$ = PhHg, Ph_3Pb, Ph_3Sn, H; solvents are $CHCl_3$, Py, $PhNO_2$).

From Table 1 it may be seen that in $CHCl_3$ the softest Lewis acid is the PhHg-cation, and the hardest one is the proton. The Ph_3Pb- and Ph_3Sn-cations occupy the intermediate positions; the increasing relative softness is in the order $H^+ < Ph_3Sn^+ < Ph_3Pb^+ < PhHg^+$.

In going from the solutions of the corresponding systems in $CHCl_3$ to those in strongly polar, but weakly solvating $PhNO_2$, the difference in relative softness between the Ph_3Sn-cation and proton practically does not change, whereas that between the PhHg- and Ph_3Pb-cations increases although insignificantly. At the same time, in the systems studied the transfer from chloroform to solvating

TABLE 1

EQUILIBRIUM CONSTANTS FOR THE EXCHANGE REACTIONS (1)[a]

X	Y	Solvent	Equilibrium constant
PhHg	Ph_3Pb	$CHCl_3$	5.3 ± 0.5[b]
		$C_6H_5NO_2$	9.3 ± 1.0[c]
		C_5H_5N	> 100
PhHg	Ph_3Sn	$CHCl_3$	> 100
PhHg	H	$CHCl_3$	> 100
Ph_3Sn	H	$CHCl_3$	9.0 ± 3.6
		$C_6H_5NO_2$	12.0 ± 2.0
		C_5H_5N	> 100

[a] Concentration of reactants 0.1—0.2 *M*; for the system with X = PhHg and Y = Ph_3Pb it has been shown that a five-fold decrease in reagent concentration does not influence the value of the equilibrium constant. [b] For this system it has been shown that the change in reactant ratio (concentration of XOAc = 0.1 *M*, that of $YSC_6H_3Me_2$-2,6 0.3 *M*) does not affect the equilibrium constant. [c] The concentrations of the reactants are 0.05 *M*.

pyridine increases the differences in relative softness for the above indicated pairs of cations by more than a factor of 20.

On the basis of these data it can be supposed that the relative softness of univalent organometallic cations and the proton in an aqueous medium may be significantly different from their relative softness in sufficiently inert solvents or in vacuum.

The study of the relative softness of the proton and univalent organometallic cations with the central atom of a heavy non-transition metal is being carried out for other pairs of cations and anions.

References

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2 D.N. Kravtsov, A.S. Peregudov, E.M. Rokhlina and L.A. Fedorov, J. Organometal. Chem., 77 (1974) 199.