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Relative Affinities of Ligands for Alkyl-Mercury Cations

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The formation constants for RHgX complexes with R=Me, Et, Pr, and Bu and X=OH, Cl, Br, and I have been determined in water, KNO_3 0.1 M *at 25°C, by means of a potentiometric technique. Two different stability scales have been found, (1) MeHgX > EtHgX > PrHgX > BuHgX, for X=Cl, Br, OH and (2) MeHgI < EtHgI < PrHgI. Such different behaviour suggests that the softness of RHg^+ acids increases on increasing the R chain length.*

Introduction

At this time a great deal of information has appeared about the formation constants of several organo-mercury[1] and perfluoroalkyl-mercury cations with a great variety of anionic ligands. J. J. Lagowsky *et al.* have been interested in a general investigation of the formation constants of fluoroalkyl-[2] and perfluoroalkyl-mercury[3] compounds of the formula R_FHgX ($R_F=(CF_3)_2CF-$, CF_3CHF-, CF_3CH_2-, CF_3-, C_2F_5-, C_3F_7-, X=OH, Cl, Br, I). By varying the degree of fluorination of the alkyl group they estimated, for a given ligand X, how the complex stability is affected by the electronegativity of the fluoro-alkyl- or perfluoroalkyl groups. Such data, togheter with those for RHgSCN compounds[4] (R=Me, Et, Pr, Bu, i–Pr, and i–Bu) represent the only examples of a systematic investigation of the relative affinities of organomercury cations for ligand ions when the organic group around the metal is changed.

Schwarzenbach[5] has pointed out that the methylmercuric ion can be regarded as a simple soft acid. It seems likely that the soft character of homologous series of organometallic cations RHg^+ must change on changing the organic group attached to the metal. We have determined therefore the formation constants of the complexes RHgX (R=Me, Et, Pr, and Bu; X=Cl, Br, I, and OH) in order to elucidate the effect of the organic group on the softness of the RHg^+ acids.

Experimental Section

Materials. Aqueous solution of alkyl-mercuric hydroxides were prepared by the action of an excess of moist silver oxide on weighed amounts of alkylmercury bromides. After the solid was filtered off the solution molarity was checked by acid-base potentiometric titration in the presence of an excess of halide ions[6] in order to determine the OH^- concentration. In addition the RHg^+ cation total concentration was determined polarographically.[7] The molarities found by the two different analytical methods agree to within 1-1.5%.

The alkyl-mercury bromides commercially available from K&K Labs (USA) were furtherly purified by crystallization from ethanol. The propyl- and butylmercury bromides were synthetised by the Slotta and Jacobi method.[8] All other starting materials were reagent grade of high purity from C. Erba, Milan, Italy.

Apparatus and Procedure. A mV-pH meter «Knick» mod. pH 35 equipped with a glass electrode Ingold 201, saturated calomel electrode system was used to follow the titration with nitric acid (10^{-2}-10^{-3} *M*) of solutions of alkyl-mercuric hydroxides and the same solutions in the presence of known amounts of ligands (Cl^-, Br^-, and I^-). The glass electrode was calibrated with buffer solutions (C. Erba, Milan) in the pH range 5-10. The total salt concentration (0.1 *M*) was kept constant by adding KNO_3 salt. All titrations were carried out under a nitrogen atmosphere in a cell thermostatted at 25°±0.1.

The RHgX formation constants (K, M^{-1}) were calculated from the obtained potentiometric titration data by the method of Schwarzenbach.[5] The value $K_w=10^{-13.78}$ for the water ionic product[9] at 25° has been used.

Results and Discussion

The log K-values (25°, I=0.1 KNO_3) are given in Table I. Values of log K, as obtained at 20° and I=0.1 (KNO_3) are listed in comparison with those previously reported[5] under the same experimental conditions. The listed values represent the data obtained from at least six potentiometric titrations for each complex.

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Table I. Log K-values of the RHgX complexes at 25°, I=0.1 KNO_3

Cation RHg^+	Ligand X^- OH^-	Cl^-	Br^-	I^-
	9.32 ± 0.03 [a]			8.70 ± 0.03 [a]
	9.37 [b]			8.60 [b]
$MeHg^+$	9.00 ± 0.03	4.90 ± 0.03	5.98 ± 0.04	7.70 ± 0.03
$EtHg^+$	8.80 ± 0.03	4.78 ± 0.04	5.90 ± 0.03	7.85 ± 0.02
n—$PrHg^+$	8.66 ± 0.02	4.65 ± 0.04	5.80 ± 0.04	8.20 ± 0.03
n—$BuHg^+$	8.61 ± 0.02	4.55 ± 0.03	5.74 ± 0.03	—

[a] Our data at 20°, I=0.1 KNO_3. [b] Log K-values at 20°, I=0.1 KNO_3 (see reference 5).

Table II. $Log(K_I/K_{Cl})$-values between RHgI (or R_FHgI) and RHgCl (or R_FHgCl) complexes

R group	$\log(K_I/K_{Cl})$	R_F group	$\log K_{I_F}$ [a] (R_FHgI)	$\log K_{Cl_F}$ [a] (R_FHgCl)	$\log(K_{I_F}/K_{Cl_F})$
CH_3	2.80	CF_3	9.63	5.78	3.85
C_2H_5	3.07	C_2F_5	9.66	5.64	4.02
n-C_3H_7	3.55	C_3F_7	9.96	5.56	4.40

[a] From reference 3.

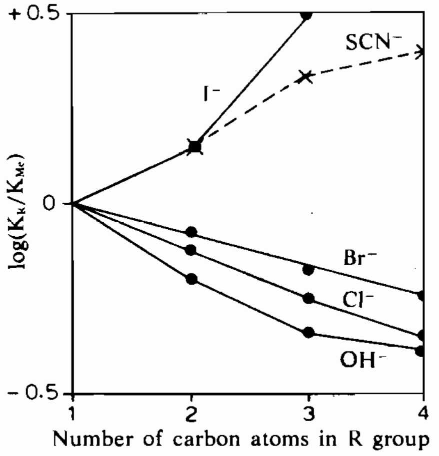

Figure 1. Plot of $\log(K_R/K_{Me})$ *versus* the number of carbon atoms in the R group of RHgX complexes (X=OH, Cl, Br, I, and SCN). See reference 4.

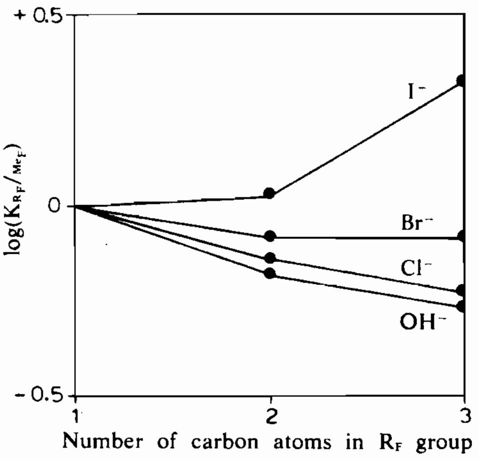

Figure 2. Plot of the $\log(K_{R_F}/K_{Me_F})$ *versus* the number of carbon atoms in the R_F groups of R_FHgX complexes (from Powell and Lagowski, see reference 3).

In an attempt to represent the trend of the stability order on varying either the R group or the ligand X, in Figure 1 log (K_R/K_{Me}) is plotted against the number of carbon atoms in the alkyl group. The figures K_R and K_{Me} represent the logarithms of the formation constants of the RHgX and MeHgX complexes respectively with the same ligand X. In Figure 2, log (K_{R_F}/K_{Me_F}) has been plotted against the number of carbon atoms in R_F groups of R_FHgX. The data are from Powell and Lagowski.[3]

On comparing the two Figures, it may be seen that in both the RHgX and R_FHgX complexes stability decreases on increasing the chain length of the R group for X=OH, Cl, and Br, but that it increases for X=I. In addition, it may be seen (cf. Table II) that an increase is observed in the value log (K_I/K_{Cl}), that is, in the difference between log K's of the RHgI (or R_FHgI) and RHgCl (or R_FHgCl) complexes respectively. It may be concluded that such a behaviour indicated an increasing softness of the RHg^+ and R_FHg^+ acids in the orders $Me < Et < n$—$Pr < n$—Bu and $CF_3 < C_2F_5 < C_3F_7$ respectively. Even though the softness of the RHg^+ and R_FHg^+ acids varies on changing the R groups, it is to be noted that the same order of stability, $Cl^- < Br^- < I^- < OH^-$, is observed for a particular RHg^+ as has been reported for the methylmercuric cation.[5,10]

It seems likely that these changes in stabilities can be correlated with the occurrence of two effects: (1) the change in softness on increasing the R chain length togheter (2) with the increasing hardness[5] of the bases $I^- < Br^- < Cl^- < OH^-$.

In order to explain the influence of these effects we will take into consideration the following factors;[10] (a) electronegativity of the R groups, (b) solvation effects on the RHg^+ and RHgX species, (c) covalent character of the RHg---X bonding, and (d) π-bonding from the mercury d-orbitals to suitable ligands.

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(10) R. G. Pearson, *J. Am. Chem. Soc.*, *85*, 3533 (1963) and references therein.

Considering electronegativity effects alone, one can explain the stability sequence,

$$\mathrm{MeHgX} > \mathrm{EtHgX} > \mathrm{PrHgX} > \mathrm{BuHgX} \quad (1)$$
$$(\mathrm{X} = \mathrm{OH},\ \mathrm{Cl},\ \mathrm{Br})$$

but not the following one;

$$\mathrm{MeHgI} < \mathrm{EtHgI} < \mathrm{PrHgI} \quad (2)$$

We have noted also for $R_{4-n}SnCl^{-}_{n+1}$ complexes[11,12] (n = 1,2,3) that stability increases on increasing the electronegativity or the carbanion stability of the R groups[13,14] in the order Bu < Pr < Et < Me.

Regarding solvation effects, it has been reported[5] that the methylmercuric ion has a characteristic coordination number of 1. It follows that the complexed ion is relatively free of strong interactions with water molecules or the other ligands.[15] Nevertheless, the relatively small solvation around the RHg^{+} and RHgX moieties must decrease on increasing the R chain length as it has been suggestd[16,17] for R_2Tl^{+} organocations. In our case, if only this effect is operating the RHgX stability would increase on increasing the chain length of R. This happens for the ligand I^{-} but not for the others, and solvation effects explain only scale (2).

The covalent character of the RHg---X bond depends on both R and X. It seems likely that, at constant X, the covalent bond character RHg---X increases by replacement of more electronegative R group,[18] that is, in the sequence Bu < Pr < Et < Me. In addition, the observed RHg---X bond lengths[19] for the MeHgCl and MeHgBr, 2.282 Å and 2.406 Å respectively (compare the difference 0.124 Å of the two values with that of 0.156 Å and 0.158 Å for the difference between the bond lengths between Br–Br, Cl–Cl, and C–Cl, C–Br respectively), suggests that the covalent character of the bond increases in the X order Cl < Br < I.

Sequence (1) thus seems to be determined by the electronegativity of the R groups; as the chain length increases, so the covalent character of the RHg–X bond decreases and the complex becomes relatively less stable.

As can be seen from Table II, the iodide complexes are more stable than the chloride ones. This may be explained by considering that in RHg---I bonding there exists a partial π-contribution, probably due to the back-donation of the mercury 5d-orbitals to the empty 5d-orbitals of iodide. The +I effect of the R groups, increasing with the decreasing in the R electronegativity, helps the π-bonding formation and these two associated factors explain the sequence (2).

With regard to the greater stabilities of the R_FHgX in comparison with those of RHgX complexes (cf. Table II), in our opinion, an important role is played by solvation effects, which are more important in the stabilization of R_FHgX than of RHgX complexes. This is supported by the fact that the solubility of the trifluoromethylmercuric iodide in water is 0.16 *M* in comparison to that of methylmercuric iodide,[6] 1×10^{-3} *M*. The greater solvation around the mercury centre in R_FHgX depends upon the increased electronegativity[20] of the perfluoroalkyl group with respect to that of alkyl.

In the case of RHgSCN complexes,[4] stability increases in the order Me < Et < Pr < Bu (see Figure 1). This order is the same as that for the iodide complexes and may be explained similarly. In fact basic ligands such as SCN^{-} and I^{-} have been considered[10] to have available empty d-orbitals to accept electronic charge via π-bonds.

It seems reasonable to us to conclude that in the absence of steric requirements one coul expect different stability or reactivity sequences[21,22] for given organometallic species with the metal σ-bonded to the carbon, by varying solvents, ligands or the reacting electrophilic or nucleophilic species.

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