Dissociation Constants of Some N-(Alkyl/Cyclohexyl)-2-mercaptopoacetamides & the Formation Constants of Their Complexes with Dialkyltin(IV)

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Stoichiometric and thermodynamic dissociation constants of eleven N-(aryl/cyclohexyl)-2-mercaptopoacetamides have been determined. Their thermodynamic stepwise and overall formation constants with \( R_2SnCl_2 \) (\( R = CH_3, C_2H_5 \) and \( n-C_4H_9 \)) have been determined. The complexation equilibria have been investigated in dioxane-water mixture (75% v/v) at 30 \( \pm \) 0.1°C and ionic strength \( I = 0.1 \) M.

The ionic nature of dialkyl tin dichloride was first established by Seyferth et al. Later Tobias and co-workers carried out a more accurate e.m.f. study of dimethyl tindichloride in an aqueous medium and laid down the sequence for acidic behaviour of trialkyltin(IV) and dialkyltin(IV) cations.

In the present note we report the results of our studies of complex formation equilibria involving eleven N-(aryl/cyclohexyl)-2-mercaptopoacetamides and dialkyltin(IV) cations (alkyl = CH\(_3\), C\(_2\)H\(_5\) and \( n-C_4H_9 \)).

The ligands, R'NHCOCH\(_2\)SH, were synthesised by the method of Guha-Sircar. The purity of ligand was established on the basis of their elemental and spectroscopic analyses. Peroxide-free dioxane was obtained by the standard procedure. Dimethyltin dichloride, diethyltin dichloride and \( n \)-dibutyltin dichloride (Alfa Inorganics) were distilled before use.

The solutions containing ligand (0.01 M) and ligand (0.0025 M) were separately titrated potentiometrically at \( \mu = 0.1 \) M (NaCl) against 0.5 M and 0.1 M carbonate-free NaOH solutions at 30 \( \pm \) 0.1°C. The changes in pH were recorded as a function of [OH\(^-\)] and suitable pH corrections applied pertaining to the dioxane-water mixture (75% v/v). The correction factor was found to be 0.13 which was added to pH meter readings prior to the calculation of equilibration data.

**Evaluation of stoichiometric and thermodynamic dissociation constants of the ligands**

N-(Ar/yl/cyclohexyl)-2-mercaptopoacetamides have as weak acids. Their thermodynamic dissociation constants may be calculated from the expression:

\[
pK_d = pQ_d + 2 \log \left( \frac{1}{y^2} \right)
\]

where \( pK_d \) and \( pQ_d \) are thermodynamic and stoichiometric dissociation constants.

For the evaluation of \( pQ_d \), the ratios of \([HA]/[A^-]\) were calculated at different pH intervals, while \( pK_d \) was obtained by adding 1.84 [2 \( \log (1/y^2) \)] to \( pQ_d \). The value of \( pQ_d \) and \( pK_d \) have been listed in Table 1.

**Formation constant of metal complexes**

The values of stoichiometric formation constants \( \log Q_1 \) and \( \log Q_2 \) were calculated by least-squares method using Irving-Rossotti equation along with the following expressions:

\[
\log [L^-] = pH - pQ_d + \log ([L_o] - [\text{NaOH}])
\]

\[
\bar{n} = \frac{[L_o] - [L^-]}{[M_o]} \left( \frac{[L^-]}{Q_d + 1} \right)
\]

and

\[
\frac{[n]}{[n-1][L]} = \frac{[2 - \bar{n}][L^-]}{[\bar{n} - 1]} Q_1 Q_2 - Q_1
\]

where \([M_o]\) and \([L_o]\) are the total metal and ligand concentrations, \([L^-]\) is the free ligand concentration and \( n \) is the number of ligand molecules bound per atom of the metal, calculated from \( pH \) titration data obtained prior to the precipitation of metal complex during the titration of the metal-ligand mixture with NaOH. The values have been listed in Table 1.

The values of \( \log Q_1 \) and \( \log Q_2 \) have also been calculated by the correction term method. The stoichiometric formation constants were converted into their thermodynamic values by adding 3.68 to \( \log Q_1 \) and 1.84 to \( \log Q_2 \) as given by Eqs (5) and (6):

\[
\log K_1 = \log Q_1 + 4 \log (1/y^2)
\]

\[
\log K_2 = \log Q_2 + 2 \log (1/y^2)
\]

The value of \( \log (1/y^2) \) was calculated from the polynomial Eq. (7) given by Irving and Mehnout:

\[
\log (1/y^2) 30^\circ C = 0.0933 + 1.0933 + 1.035n_2
\]

\[
+ 0.3142n_2^2 + 6.635n_2^3
\]
Table 1 — Stoichiometric and Thermodynamic Dissociation Constants of N-(Aryl/Cyclohexyl)-2-mercaptoacetamides and Their Complexes with Dialkyltin Dichloride by the Least Squares Method

<table>
<thead>
<tr>
<th>Metal ion*</th>
<th>( \log Q_1 )</th>
<th>( \log Q_2 )</th>
<th>( \log Q_1 Q_2 )</th>
<th>( \log K_1 )</th>
<th>( \log K_2 )</th>
<th>( \log \beta_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9.28(9.31)</td>
<td>6.64(6.61)</td>
<td>15.92(15.92)</td>
<td>12.96(13.04)</td>
<td>8.48(8.46)</td>
<td>21.44(21.50)</td>
</tr>
<tr>
<td>B</td>
<td>9.16(9.20)</td>
<td>6.25(6.23)</td>
<td>15.41(15.43)</td>
<td>12.86(12.88)</td>
<td>8.09(8.08)</td>
<td>20.95(20.96)</td>
</tr>
<tr>
<td>C</td>
<td>9.16(9.19)</td>
<td>5.99(5.98)</td>
<td>15.15(15.17)</td>
<td>12.84(12.92)</td>
<td>7.83(7.84)</td>
<td>20.67(20.76)</td>
</tr>
<tr>
<td>Ligand = p-ClC_6H_4NHCOCH_2SH, ( pQ_0 = 9.15, pK_0 = 11.99 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>9.24(9.29)</td>
<td>6.53(6.52)</td>
<td>15.77(15.81)</td>
<td>12.92(13.03)</td>
<td>8.37(8.34)</td>
<td>21.29(21.37)</td>
</tr>
</tbody>
</table>

Values in the parenthesis are those obtained by correction term method.

where \( n_2 \) refers to the mol fraction of dioxane recalculated with the atomic weights \( (c = 12.01 \) and \( H = 1.008 \). The value of \( \log (1/\gamma^2) \) was found to be 0.92.

It can be seen from Table 1 that the introduction of an electron donating substituent in the phenyl ring results in a decrease in the dissociation constant leading to a higher \( pQ_0 \) while an electron withdraw-
ing group increases the dissociation constant leading to a lower $pQ_D$ value. If the phenyl ring is replaced by the cyclohexyl group then $pQ_D$ decreases by 0.5 log unit. This is probably due to the fact that the cyclohexyl moiety is saturated and non-planar with respect to the other part of the ring.

It has been observed that smaller the dissociation constant of the ligand, the greater is the magnitude of formation constant. However, N-(cyclohexyl)-2-mercaptoacetamide, which has a relatively higher dissociation constant, forms much weaker complexes with $\pi$-bonded dialkyltin(IV) cations because of the steric effect of N-(cyclohexyl) moiety which retards the formation of both 1:1 and 1:2 complexes.

The magnitudes of thermodynamic formation constants for title metal-ligand system indicated the Leden-Chatt $\beta$ character for dialkyltin(IV) cations and $d\tau - d\pi$ bonding between tin and sulphur.

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References