Chelating Tendencies of some $N$-(2-Acyl-1,3-Indandione) Tri Alkyl Ammonium Iodides


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(Z. Naturforsch. 26 b, 865—869 [1971]; received May 17, 1971)

The L-T.M.A.I. and L-T.E.A.I. have been synthesised and their dissociation constants are $7.943 \times 10^{-10}$ and $1.413 \times 10^{-10}$ respectively. The potentiometric studies show that these reagents form 1 : 1 complex with copper (II) and iron (II). The stability constants of copper complex and iron complex with L-T.M.A.I. are 5.75 and 6.05 respectively and for L-T.E.A.I., 5.97 and 6.215 respectively. The free energy of complex formation at 25 °C are 7841 cal/mole and 8150 cal/mole for Cu(II)-L-T.M.A.I. and Fe(II)-L-T.M.A.I. respectively, whereas the free energy of the Cu(II)-L-T.E.A.I. and Fe(II)-L-T.E.A.I. are 8141 cal/mole and 8375 cal/mole respectively.

Recent survey of the literature reveals that there is a growing tendency to prepare reagents which are stable and more soluble so that they can be more useful for analytical methods viz. conductometry, potentiometry and polarography. Most commonly used solubilising groups are —OH, —COOH, —SO$_2$OH, and the quaternary ammonium group. YOE 1, KLOOSTER 2, and EPFRAIM 3 have studied the effect of introducing such solubilising groups and have shown that the introduction of such groups does not appreciably effect the properties of the complex-forming groups but yields water soluble inner complex anions rather than the usual insoluble innercomplex precipitate with metal ions. COOK and MARTIN 4 have studied the chelating tendency of some substituted 2-(Pyridyl) and 2-(quinolyl)-1,3-indandiones with bivalent metals and have also reported the formation constants of these metal complexes. The present work was therefore undertaken to prepare such reagents and to study their detailed properties.

The present paper communicates the synthesis of reagents possessing a trialkyl ammonium group. This group possesses greater solubilising action than the corresponding acid groups. Accordingly $N$-(2-acetyl-1,3-indandione) trimethyl ammonium iodide (L-T.M.A.I.) and $N$-(2-acetyl-1,3-indandione) triethyl ammonium iodide (L-T.E.A.I.) have been synthesised. The chelating properties of these reagents with transition metal ions such as copper (II) and iron (II) have been studied by potentiometric and gravimetric methods. The $\beta$-ketolkylation reaction of heterocyclic tertiary bases as reported by KING 5, 6 has been extended to aliphatic tertiary amines viz. trimethyl amine and triethyl amine, using 2-acetyl-1,3-indandione giving corresponding trimethyl, triethyl quaternary compounds.

Preparation of 2-acetyl-1,3-indandione

The 2-acetyl-1,3-indandione was obtained by the reaction of dimethyl phthalate and acetone in the presence of sodium methoxide according to the method of KILGORE 7.

Preparation of $N$-(2-acetyl-1,3-indandione trimethyl ammonium iodide (L-T.M.A.I.)

2-acetyl-1,3-indandione (5.0 gm) was added to a solution of iodine (6.5 gm) in methanol (10 ml) and triethyl amine (10 ml) was then added gradually with constant shaking. A vigorous reaction started immediately with the evolution of heat. The reaction mixture was allowed to cool and left overnight. The dark coloured solid separated was filtered and washed with transition metal ions such as copper (II) and iron (II) have been studied by potentiometric and gravimetric methods. The $\beta$-ketolkylation reaction of heterocyclic tertiary bases as reported by KING 5, 6 has been extended to aliphatic tertiary amines viz. trimethyl amine and triethyl amine, using 2-acetyl-1,3-indandione giving corresponding trimethyl, triethyl quaternary compounds.

Experimental

Preparation of 2-acetyl-1,3-indandione

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4 J. R. COOK and D. F. MARTIN, J. inorg. nuclear Chem. 26, 5717 [1964].

5 L. C. KING, J. Amer. chem. Soc. 66, 894 [1944].

6 L. C. KING and McWHIRTER, J. Amer. chem. Soc. 68, 717 [1946].

with little methanol to separate it from trimethyl ammonium hydro iodide. The latter being more soluble in methanol. The compound is dark green crystalline solid (m.p. 221 °C — 223 °C) highly soluble in water but insoluble in ether (3.5 g yield 70%).

\[ C_{14}H_{16}NO_3I \]

Calc. N 3.75 I 34.04.

Found N 3.65 I 37.0.

Preparation of N-(2-acyl-1,3-indandione) triethyl ammonium iodide (L-T.E.A.I.)

This was prepared by method similar to L-T.M.A.I. using trimethylamine (13 ml). It is a brown crystalline solid m.p. 131 °C — 132 °C. It is highly soluble in water but insoluble in ether. It was recrystallised from absolute ethanol (3.7 gm, yield 74%).

\[ C_{17}H_{22}NO_3I \]

Calc. N 3.37 I 30.6,

Found N 4.0 I 33.2.

Acid dissociation constant

The acid dissociation constants have been determined potentiometrically. The pH titrations are carried out using a Cambridge pH-meter (±0.02). The solution m/50 of the ligands were prepared in distilled water by accurate weighing and a known amount was titrated with alkali (NaOH) m/5 free from CO\textsubscript{3}\textsuperscript{2-}. The test solution was maintained at 25 ± 0.1 °C in a double-walled vessel, by circulating water from a thermostat and stirred by a small glass paddle. A micro-burette was used whose nozzle was dipped in the covered vessel containing the solution and the glass and calomel electrodes dipped in it.

Similar procedure was used to determine the formation constant. A m/50 copper sulphate (A.R.) solution and m/50 Mohr’s salt (AR) solution were prepared in distilled water by accurate weighing. All other reagents used were of analytical grade.

Gravimetric method for establishing the composition of the complex

The complex was precipitated in the pH range 5.6 — 6.0. Precipitate was filtered through a Whatmann filter paper No. 42. The precipitate was washed several times with distilled water and then dried at 70 °C in the oven. Weigh 0.1 gm of the complex accurately in a beaker (Pyrex). The organic matter was oxidised with conc. nitric acid and evaporated to dryness. The residue was then treated with conc. sulphuric acid and evaporated to dryness. The residue was dissolved in dil. sulphuric acid and copper was determined in the solution iodometrically. The ratio of copper(II) to ligands i.e. L-T.M.A.I. and L-T.E.A.I. was 1 : 1. For results see Table I.

The organic matter was oxidised with conc. nitric acid. The residue was then ignited at 800 °C and weighed as Fe\textsubscript{2}O\textsubscript{3}. The metal: ligand ratio was thus found to be 1 : 1. For results see Table I.

<table>
<thead>
<tr>
<th>Name of the complex</th>
<th>Percentage of Cu in the complex</th>
<th>Percentage of Fe(II) in the complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>Found</td>
<td>Theoretical</td>
</tr>
<tr>
<td>1. Cu(II)-L-T.M.A.I.</td>
<td>14.4</td>
<td>13.65</td>
</tr>
<tr>
<td>2. Cu(II)-L-T.E.A.I.</td>
<td>13.18</td>
<td>13.05</td>
</tr>
<tr>
<td>3. Fe(II)-L-T.M.A.I.</td>
<td>—</td>
<td>13.02</td>
</tr>
<tr>
<td>4. Fe(II)-L-T.E.A.I.</td>
<td>—</td>
<td>11.22</td>
</tr>
</tbody>
</table>

Table I. Metal/ligand ratio.

Calculations

Dissociation constant

BJERRUM defined the degree of formation of the proton complexes $\tilde{\eta}_H$ as the average no. of protons attached to the ligand. The acid, dissociation constants (pK's) were calculated by BJERRUM’s method:\footnote{B. J. BJERRUM, Metal Ammine formation in aqueous solution, P. Hasse & Sons, Copenhagen 1957.}

$$\tilde{\eta}_H = \frac{C_A - (Na^+ + H^+ - OH^-)}{C_A}$$

Where $C_A$ is the analytical concentration of the acid. A plot of $\tilde{\eta}_H$ against pH gave the formation curve for the protonation of the ligand. The pH at $\tilde{\eta}_H = 0.5$ gave the value of pK\textsubscript{i}, see Table II.

The values were corrected by Least Square Method.

<table>
<thead>
<tr>
<th>Name of the Reagent</th>
<th>Dissociation constant $K_i$</th>
<th>Formation constant of copper complex</th>
<th>Formation constant of Ferrous complex</th>
<th>Free Energy Copper complex [Cals/mole]</th>
<th>Free Energy Ferrous complex [Cals/mole]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. N-(2-acyl-1,3-indandione)-trimethyl-ammonium-iodide</td>
<td>$7.943 \times 10^{-10}$</td>
<td>5.75</td>
<td>6.05</td>
<td>7841</td>
<td>8150</td>
</tr>
</tbody>
</table>

Table II. Dissociation and formation constants.
Formation Constants of some Bivalent Metal Ion Chelates of \(N(2\text{-hydroxy-1-naphthalidene})\) Anthranilic Acid (Schiff Base)


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(Z. Naturforsch. 26 b, 867—869 [1971]; received May 25, 1971)

Protonation constants \((\log K_1^H \text{ and } \log K_2^H)\) of the Schiff base derived from 2-hydroxy-1-naphthaldehyde and anthranilic acid and, the formation constants of certain bivalent metal ion chelates have been determined potentiometrically in 50 per cent (vol./vol.) dioxan solutions \((\mu = 0.1 \text{ M NaClO}_4)\). The stabilities of these metal chelates are in the order, \(\text{UO}_2 > \text{Cu} > \text{Ni} > \text{Co} > \text{Zn} > \text{Cd}\), in which the sequence of those of first transitional metal ion chelates are in agreement with Irving and Williams order.

No systematic study of the formation constants of bivalent metal ion chelates of \(N\)-(2-hydroxy-1-naphthalidene) anthranilic acid (abbr. \(H_2\text{NA}\)) has been carried out. It is, therefore, of interest to investigate the protonation constants of \(H_2\text{NA}\) and formation constants of its metal chelates. The measurements were carried out in 50 per cent dioxan at \(30 \pm 0.1 \text{ °C}\) as the ligand and its metal chelates are insoluble in water.