THE COBALT (II)-TRIPHENYLPHOSPHINE OXIDE SYSTEM IN ACETONE SOLUTION:
A CLEAR MANIFESTATION OF THE SYMBIOTIC EFFECT

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Received on 13/11/86

ABSTRACT

The successive and overall stability constants associated with the Co(ClO4)2 – triphenylphosphine oxide (tppo) system, at 25°C, in acetone solution, have been determined. The body of experimental evidence indicates that mononuclear Co(II)-tppo complexes with stoichiometries ranging from 1:1 to 1:5 are formed. The species comprising up to two tppo exist in both tetrahedral and octahedral configurations. The remaining species are tetrahedral. The presently obtained results, in connection with those previously found for the CoCl2-tppo system (acetone medium, 25°C) clearly indicate that tppo forms markedly more stable complexes with CoCl2 that with Co(II); this is not readily understood in the light of simple theoretical considerations. The reported results are tentatively rationalized by taking into account the “symbiotic effect”.

INTRODUCTION

A set of earlier papers from this laboratory dealt with the determination of the composition and thermodynamic stability of complex species formed in binary systems comprising Cobalt(II) halides and some unidentate organic ligands, e.g., phosphate oxides, pyridines, pyrazoles and sulfoxides at 25°C, in acetone medium 1–3. In an endeavour to extend the previous work, the behaviour of the Cobalt (II) perchlorate-triphenylphosphine oxide (tppo) system, in the referred solvent and temperature has been investigated. The primary aim of the present study is to compare the mentioned system with a previously investigated one at very close experimental conditions—namely, the Cobalt(II) Chloride-tppo system 1.

LIST OF MAIN SYMBOLS AND ABBREVIATIONS

A absorbance
ac acetone
c particular value of n
Ct total ligand concentration
CM total Co(II) concentration
F0 Frumencus’ function defined as indicated in equation (3')
I ionic strength

Kn stoichiometric step stability constant defined as indicated in equation (1)
[L] molar concentration of free ligand
m,n numbers of ligands in complexes of general formula CoClm(tppo)n
pL =−log[L]
tpco triphephenylphosine oxide
α C formation degree of Co(tppo)C2 species
βn stoichiometric overall stability constant defined as indicated in equation (2).
βn octahedral Co(tppo)C2 species
βn tetrahedral Co(tppo)C2 species
ε mean molar absorptivity of the solution, at λ = 636 nm
ε0 n octahedral Co(tppo)C2 species
ε1 n tetrahedral Co(tppo)C2 species
ε mn molar absorptivity of complexes of general formula CoClm(tppo)n at λ = 636 nm.
λ wavelength, in nm
Λm molar conductance (S. cm². mol⁻¹)
n average number of ligands bound to the central group

EXPERIMENTAL

Materials and Solutions

Cobalt(II) perchlorate hexahydrate was prepared from 70% perchloric acid and Cobalt(II) carbonate, a slight excess of the latter being employed. The salt was recrystallized from water, conveniently dried and dissolved in anhydrous acetone. The dehydration of cobalt perchlorate solutions, as well as the purification and dehydration of acetone, were carried out as previously reported 1,3. Stock solutions of the metal salt were standardised by complexometric titration with EDTA. Triphenylphosphine oxide (Koch-Light), recrystallized from anhydrous acetone solution, was dried at 90°C for 36 hours.

Other chemicals used were of analytical purity.
Apparatus

Grade "A" glassware and "Metrohm" mod. 655 Dosimat automatic burettes were employed for all volumetric work. A "Cary" mod. 219 UV-Vis spectrophotometer, with a water-jacketed cell holder thermostatically controlled at 25.0±0.05°C (equipped with 1 cm optical path quartz cells) and a precision of ±0.0001 in absorbance measurements, was used. Conductances were measured with a "Metrohm" mod. E527 instrument. All the experiments were performed in a low-moisture room maintained at 25±1°C. A "Prológica" mod. CP-500 microcomputer was used for the calculations.

CONDUCTOMETRIC STUDY

From Table I it can be seen that solutions with different \( \frac{C_L}{C_M} \) proportions show molar conductances compatible with 1:2 electrolytes in acetone\(^4\) allowing to suppose a lower association degree between perchlorate and cationic complex species. The slight rise of conductance with increasing ligand concentration could be due to a smaller tendency of the cationic complex species to bind perchlorate in comparison with Co(acac)\(\text{H}^2\), at least up to \( \frac{C_L}{C_M} = 8.00 \). Thus, the equilibria in the system can be represented (without taking into account solvation effects), generally, by the equation:

\[
\text{Co}^{2+} + n(\text{tppo}) \rightleftharpoons \text{Co}(\text{tppo})_{n}^{2+}
\]

and the step and overall stability constants, respectively, defined by:

\[
K_n = \frac{[\text{Co}(\text{tppo})_{n}^{2+}]}{[\text{Co}(\text{tppo})_{n-1}^{2+}][\text{tppo}]}
\]

and

\[
\beta_n = \frac{[\text{Co}(\text{tppo})_{n}^{2+}]}{[\text{Co}^{2+}]^{n}([\text{tppo}]^{n}}
\]

### Table I

Molar conductance of acetonitrile solutions with different \( \text{tppo/Co(ClO}_4)_2 \) proportions. \( C_M = 1.500 \text{ mM} \).

<table>
<thead>
<tr>
<th>( \frac{C_L}{C_M} )</th>
<th>0</th>
<th>1.00</th>
<th>2.67</th>
<th>4.00</th>
<th>5.67</th>
<th>7.17</th>
<th>8.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Lambda_M )</td>
<td>158</td>
<td>163</td>
<td>169</td>
<td>173</td>
<td>173</td>
<td>185</td>
<td>188</td>
</tr>
</tbody>
</table>

SPECTROPHOTOMETRIC STUDY

Figure 1 reveals that, at least for \( \frac{C_L}{C_M} \geq 4.5 \) relations, the absorption spectra seem to be characteristic of four-coordinated cobalt(II) in a tetrahedral environment (exhibiting four overlapping bands with maxima at 561, 585, 604 and 636 nm); the spectrophotometric method can be applied to study the system.

The stability constants were determined from absorbance measurements made at \( \lambda = 636 \text{ nm} \) (Figure 2) by combining the method of corresponding solutions with the Fronaeus' computation technique\(^5\). The ionic strength could not be adjusted with \( \text{LiClO}_4 \) because of the interaction between lithium ions and tppo molecules\(^6\); a similar behaviour is shown by the tetaethylammonium cation. So, the ionic strength changed from 4.5 to 13.5 mM. The obtained results are given in Table II. There is a reasonable compatibility between the computed values for these constants and the experimental formation curve, as can be seen in Figure 3.
TABLE II

Stability constants obtained for the Co²⁺ - tppe system.

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>βₙ</td>
<td>570±50</td>
<td>(2.07±0.55)×10⁶</td>
<td>(1.3±1.0)×10⁷</td>
<td>(1.4±1.1)×10⁹</td>
<td>(2.0±1.5)×10¹¹</td>
</tr>
<tr>
<td>log βₙ</td>
<td>2.76±0.04</td>
<td>5.32±0.11</td>
<td>7.11±0.31</td>
<td>9.15±0.37</td>
<td>11.30±0.42</td>
</tr>
<tr>
<td>Kₙ</td>
<td>570±50</td>
<td>363±60</td>
<td>63±30</td>
<td>108±15</td>
<td>143±20</td>
</tr>
<tr>
<td>log Kₙ</td>
<td>2.76±0.04</td>
<td>2.56±0.07</td>
<td>1.8±0.2</td>
<td>2.03±0.06</td>
<td>2.16±0.06</td>
</tr>
</tbody>
</table>

although the uncertainty limits are wide, mainly for the three last species. This fact may be understood considering the distribution curves of the system (Figure 4) and taking into account the above mentioned experimental conditions.

The stability constants of the CoCl₂-tppe system are given in Table III. By comparison between data from Tables II and III it can be verified that the CoCl₂ (tppe)₆ complexes are more stable than the Co(tppe)₂Cl₂ ones, specially concerning the first species. This fact can be explained in terms of the "Symbiotic effect"⁷,⁸ afforded by the hard base Cl⁻ on the borderline acid Co²⁺, allowing the CoCl₂ acid to be harder and its interaction with tppe stronger.

Concerning the fifth tppe molecule in the last complex of the Co²⁺ - tppe system, we can say that several Co(II) systems in acetone medium form tetrahedral species with 1: 5¹,³ and 1: 6⁹ stoichiometries; this is only understandable by admitting ion-pairing (CoCl₂⁺; Cl⁻; Co₆Cl₂⁻, 2Cl⁻) and/or outer sphere complex formation (CoCl₂ L₂; CoCl₃ L₂ 2L). In the case of the Co²⁺ - tppe system there is only the latter possibility, enhanced by the fact that the fifth tppe molecule may interact with Co(tppe)Cl⁵⁻ whose hardness should be high because of the symbiotic effect.

![Figure 2. Co²⁺-tppe system. Dependence of the mean molar absorptivity on total ligand concentration. (A: C₇M = 1.5 mM; B: C₇M = 3.0 mM; C: C₇M = 4.5 mM).](image)

![Figure 3. Co²⁺-tppe system. Experimental (◯) and calculated (full curve) formation curves.](image)

TABLE III

Stability constants of the CoCl₂-tppe system¹, in acetone medium, at 25°C (all species are tetrahedral and almost undissociated).

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>βₙ</td>
<td>(1.40±0.10)×10⁴</td>
<td>(6.77±0.95)×10⁶</td>
<td>(1.77±0.40)×10⁹</td>
</tr>
<tr>
<td>log βₙ</td>
<td>4.15±0.03</td>
<td>6.83±0.06</td>
<td>9.25±0.10</td>
</tr>
<tr>
<td>Kₙ</td>
<td>(1.40±0.10)×10⁴</td>
<td>483±33</td>
<td>261±24</td>
</tr>
<tr>
<td>log Kₙ</td>
<td>4.15±0.03</td>
<td>2.68±0.03</td>
<td>2.42±0.04</td>
</tr>
</tbody>
</table>
of the four hard tppos. Otherwise, we must admit some kind of interaction between inner and outer sphere tppos molecules\[10,11\]. The calculation of the molar absorbivities, \(\varepsilon_n\), associated with the complex species formed in the system was performed by using the equation:

\[ y = \frac{\varepsilon F_0}{[L]} = \varepsilon_1 \beta_1 + \varepsilon_2 \beta_2 [L] + \ldots + \varepsilon_5 \beta_5 [L]^4 \]  

(3)

where

\[ F_0 = 1 + \beta_1 [L] + \beta_2 [L]^2 + \ldots + \beta_5 [L]^5 \]  

(3')

From Figure 4 it can be verified that at the beginning of the useful range (pL = 3.6 - 3.0 or [L] = 0.25-1.00 mM) there are only the two first species in solution. For this reason, a linear relationship holds in this region:

\[ y = 1.120 \times 10^4 + 9.572 \times 10^4 [L] \]  

(4)

Combining equation (4) with the \(\beta_1\) and \(\beta_2\) values (Table II) we obtained \(\varepsilon_1 = 19.6\) and \(\varepsilon_2 = 46.2\). The \(\varepsilon_n\) values for \(n > 2\) could not be computed from equation (3) probably due to inaccuracy of the corresponding stability constants, as above mentioned. It was only possible to calculate the \(\varepsilon_n\) value corresponding to the last species (\(\varepsilon_5 = 372\)) by graphical extrapolation of \(\varepsilon\) vs. 1/[L] plot, to 1/[L] = 0.

The abnormal sigmoid shape of the \(\varepsilon\) vs. \(C_L\) curves (Figure 2), together with the obtained values for \(\varepsilon_1\) and \(\varepsilon_2\) (too small for tetrahedral Co(II) configuration), suggests the existence of octahedral (o) and/or pentacoordinated species in addition to the tetrahedral (t) ones, in configurational equilibria that have precedents in other Co(II) systems in nonaqueous media\[12-16\]. In our case, such equilibrium seems to exist only within the two first species as the mentioned deformation of the \(\varepsilon\) vs. \(C_L\) curves occurs almost only in the region in which [L] = 0–3 mM.

The existence of pentacoordinate Co(II) species may be practically neglected because it seems that these complexes are closely related with steric demands of polidentate ligands\[15\]. On the other hand, we could not find any evidence about their presence in solution.

Among the different logical combinations of configurations (Table IV), that considering \(o \cong t\) equilibria in both Co(tppo)\(^{+2}\) and Co(tppo)\(^{4+}\) species was found to be the most probable. Assuming \(\varepsilon_1^t = \varepsilon_2^t = 0\) (at \(\lambda = 636\) nm), the stability constants of the complex species in configurational equilibria were estimated from approximate values for the molar absorbivities of the tetrahedral species calculated by means of the empirical equation:

\[ \varepsilon_n^t \approx \varepsilon_m^t + 6.6 \text{ (mVn)} \]  

(5)

by using \(\varepsilon_m^t\) values calculated from previously reported data:\[1: \varepsilon_{10}^t = 130; \varepsilon_{20}^t = 215; \varepsilon_{21}^t = 267; \varepsilon_{22}^t = 307\) and \(\varepsilon_{33}^t = 339\). Thus, the \(\varepsilon_n^t\) values associated with the Co(tppo)\(^{+2}\) species should be: \(\varepsilon_1^t = 137; \varepsilon_2^t = 228; \varepsilon_3^t = 287; \varepsilon_4^t = 333\) and \(\varepsilon_5^t = 372\).

### TABLE IV.

#### Logical combinations of configurations for the two first species present in the Co\(^{2+}\)-tppo system.

<table>
<thead>
<tr>
<th>combination number</th>
<th>Co(tppo)(^{+2})</th>
<th>Co(tppo)(^{4+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>t</td>
</tr>
<tr>
<td>3</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td>4</td>
<td>0 (\approx t)</td>
<td>0 (\approx t)</td>
</tr>
<tr>
<td>5</td>
<td>0 (\approx t)</td>
<td>0 (\approx t)</td>
</tr>
</tbody>
</table>

By combining of \(\varepsilon_1^t\) and \(\varepsilon_2^t\) values with equation (4), and considering \(\beta_1 = \beta_0^t + \beta_1^t\) and \(\beta_2 = \beta_2^t + \beta_3^t\), the stability data given in Table V were found. As we can see, the octahedral configuration is more favoured than tetrahedral one in the Co(tppo)\(^{+2}\) complex; the opposite occurs for Co(tppo)\(^{4+}\), which seems logical.

![Figure 5. Co\(^{2+}\)-tppo system. Dependence of the mean molar absorptivity on total ligand concentration. \(\Theta\) experimental curve in the 0.9 mM \(C_L\) range. Full curve: calculated from Table V data (\(C_M = 1.5\) mM; \(C_M^\prime = 4.5\) mM).](image)
TABLE V

Co\textsuperscript{2+}-tppo system: estimated values for the stability constants of the species in configurational equilibrium

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta^0_n$</td>
<td>488</td>
<td>1.65 \times 10^6</td>
</tr>
<tr>
<td>$\beta^i_n$</td>
<td>82</td>
<td>4.20 \times 10^4</td>
</tr>
<tr>
<td>$K^0_n$</td>
<td>488</td>
<td>338</td>
</tr>
<tr>
<td>$K^i_n$</td>
<td>82</td>
<td>512</td>
</tr>
</tbody>
</table>

Finally, calculated $\epsilon$ vs. $C_L$ curves in the whole useful $C_L$ range (Figure 6) show a sigmoid format similar to that of experimental curves (Figure 2); this is not observed using any other combination from Table IV.

ACKNOWLEDGEMENTS

The sponsorship from FAPESP and CNPq through grants and fellow ships is gratefully acknowledged.

REFERENCES


Figure 6. Co\textsuperscript{2+}-tppo system. Calculated curves from the data contained Tables II and V. ($C^i_M = 1.5$ mM; $C^0_M = 4.5$ mM).