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

M.H.M Pacciullio, M. Molina and C.B. Melios

Instituto de Química – UNESP, Caixa Postal 174 – Araraquara (SP)

ABSTRACT

The successive and overall stability constants associated with the $Co(ClO_4)_2$ – 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 stoicheiometries 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 $CoCl_2$-tppo system (acetone medium, 25°C) clearly indicate that tppo forms markedly more stable complexes with $CoCl_2$ 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.*, phosphine 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 Colbalt (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
C_L total ligand concentration
C_M total Co(II) concentration
F_o Fronaeus' function defined as indicated in equation (3')
I   ionic strength

K_n stoicheiometric 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 $CoCl_m(tppo)_n^{(2-m)+}$
pL $-log[L]$
tppo triphenylphosphine oxide
α_c formation degree of $Co(tppo)_c^{2+}$ species
β_n stoicheiometric overall stability constant defined as indicated in equation (2).
β_n^o stoicheiometric overall stability constant of octahedral $Co(tppo)_n^{2+}$ species
β_n^t stoicheiometric overall stability constant of tetrahedral $Co(tppo)_n^{2+}$ species
ϵ mean molar absorptivity of the solution, at $\lambda = 636$ nm
ϵ_n^o molar absorptivity of octahedral $Co(tppo)_n^{2+}$ species
ϵ_n^t molar absorptivity of tetrahedral $Co(tppo)_n^{2+}$ species
ϵ_{mn} molar absorptivity of complexes of general formula $CoCl_m(tppo)_n^{(2-m)+}$, at $\lambda = 636$ nm.
λ wavelength, in nm
Λ_M molar conductance (S. cm² .mol⁻¹)
ñ 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 authomatic burettes were employed for all volumetric work. A "Cary" mod. 219 UV-Vis. spectrophotometer, with a water-jacketed cell holder thermostatically controlled at $25.00\pm0.05^{\circ}C$ (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 $25\pm1^{\circ}C$. A "Prológica" mod. CP-500 microcomputer was used for the calculations.

CONDUCTOMETRIC STUDY

From Table I it can be seen that solutions with different C_L/C_M proportions show molar conductances compatible with $1:2$ electrolytes in acetone[4] allowing to suppose a low 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 $Co(ac)_6^{+2}$, at least up to $C_L/C_M = 8.00$. Thus, the equilibria in the system can be represented (without taking into account solvation effects), generally, by the equation:

$$Co^{+2} + n(tppo) \rightleftharpoons Co(tppo)_n^{+2}$$
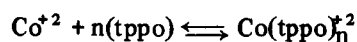
and the step and overall stability constants, respectively, defined by:

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

and

$$\beta_n = \frac{[Co(tppo)_n^{+2}]}{[Co^{+2}][tppo]^n} \qquad (2)$$

TABLE I

Molar conductance of acetonic solutions with different tppo/Co(ClO₄)₂ proportions. $C_M = 1.500$ mM.

C_L/C_M	0	1.00	2.67	4.00	5.67	7.17	8.00
Λ_M	158	163	169	173	179	185	188

SPECTROPHOTOMETRIC STUDY

Figure 1 reveals that, at least for $C_L/C_M \geqslant 4.5$ 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 stibility constants were determined from absorbance measurements made at $\lambda = 636$ nm (Figure 2) by combining the method of corresponding solutions with the Fronaeus' computation technique[1,3]. The ionic strength could not be adjusted with LiClO₄ because of the interaction between lithium ions and tppo molecules[5,6]; 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,
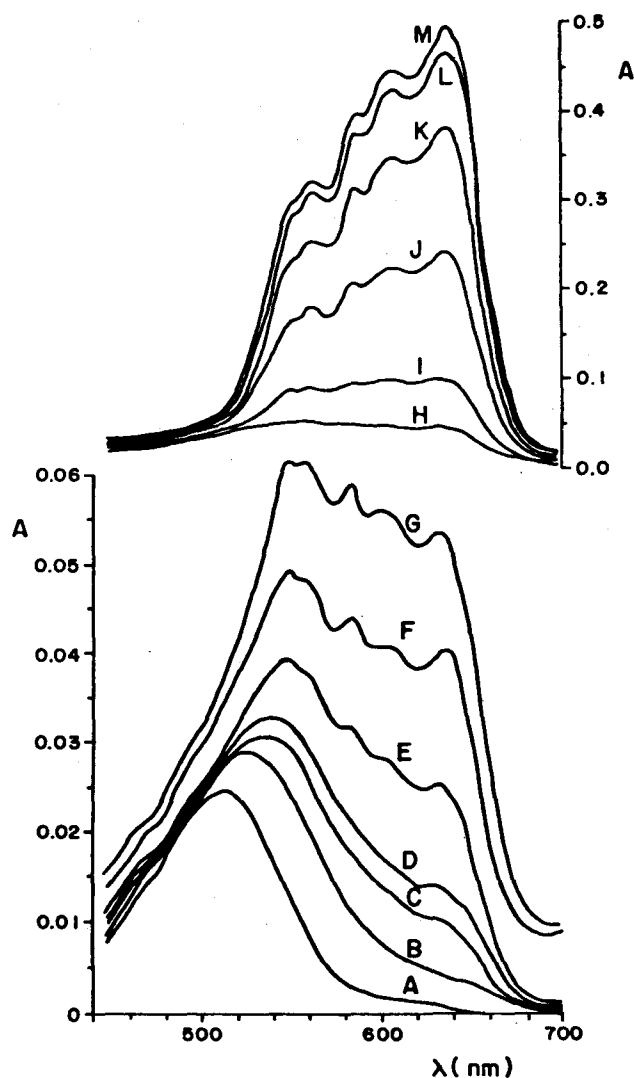

Figure 1. Absorption spectra of tppo: Co(ClO₄)₂ mixtures in different proportions. $C_M = 1.50$ mM. (A = 0:1; B = 2.7:1; C = 4.0:1; D = 4.5:1; E = 5.7:1; F = 6.3:1; G = 8.0:1; H = 7.2:1; I = 10:1; J = 17:1; K = 30:1; L = 43:1; M = 57:1).

TABLE II

Stability constants obtained for the Co^{+2} — tppo system.

n	1	2	3	4	5
β_n	570±50	$(2.07±0.55)·10^5$	$(1.3±1.0)·10^7$	$(1.4±1.1)·10^9$	$(2.0±1.5)·10^{11}$
$\log \beta_n$	2.76±0.04	5.32±0.11	7.11±0.31	9.15±0.37	11.30±0.42
K_n	570±50	363±60	63±30	108±15	143±20
$\log K_n$	2.76±0.04	2.56±0.07	1.8±0.2	2.03±0.06	2.16±0.06

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 $CoCl_2$-tppo system are given in Table III. By comparision between data from

Figure 2. Co^{+2}-tppo system. Dependence of the mean molar absorpitivity on total ligand concentration. (A: C_M^I = 1.5 mM; B: C_M^{II} = 3.0 mM; C: C_M^{III} = 4.5 mM).

Tables II and III it can be verified that the $CoCl_2$ (tppo)$_n$ complexes are more stable than the $Co(ttpo)_n^{+2}$ 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 Co^{+2}, allowing the $CoCl_2$ acid to be harder and its interaction with tppo stronger.

Concerning the fifth tppo molecule in the last complex of the Co^{+2} — tppo system we can say that several Co(II) systems in acetone medium form teetrahedral species with 1: 5[1,3] and 1: 6[9] stoicheiometries; this is only understandable by admiting ion-pairing ($CoClL_3^+$. Cl^-; $CoL_4^{+2}.2Cl^-$) and/or outer sphere complex formation ($CoCl_2 L_2.L$; $CoCl_2 L_2.2L$). In the case of the Co^{+2} — tppo system there is only the latter possibility, enhanced by the fact that the fifth tppo molecule may interact with $Co(tppo)_4^{+2}$ whose hardness should be high because of the symbiotic effect

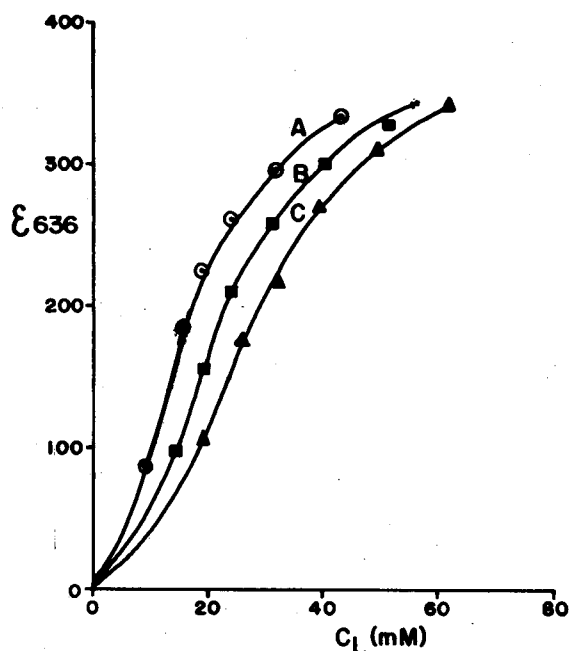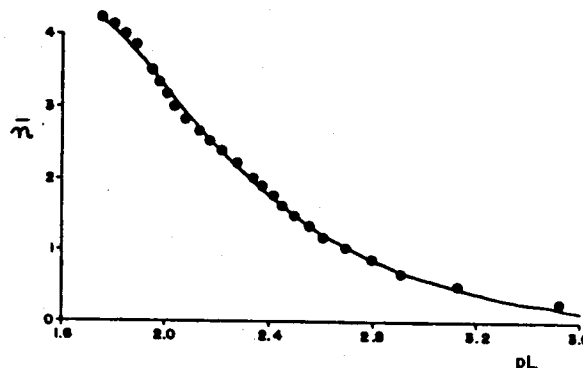Figure 3. Co^{+2}-tppo system. Experimental (●) and calculated (full curve) formation curves.

TABLE III.

Stability constants of the $CoCl_2$-tppo system[1], in acetone medium, at 25ºC (all species are tetrahedral and almost undissociated).

n	1	2	3
β_n	$(1.40±0.10).14^4$	$(6.77±0.95).10^6$	$(1.77±0.40).10^9$
$\log \beta_n$	4.15±0.03	6.83±0.06	9.25±0.10
K_n	$(1.40±0.10).10^4$	483±33	261±24
$\log K_n$	4.15±0.03	2.68±0.03	2.42±0.04
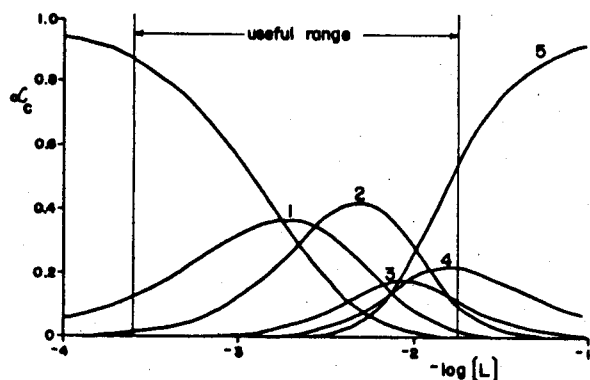
Figure 4. Co^{+2}-tppo system. Distribution curves.

Among the different logical combinations of configurations (Table IV), that considering $o \rightleftarrows t$ equilibria in both $Co(tppo)^{+2}$ and $Co(tppo)_2^{+2}$ species was found to be the most probable. Assuming $\epsilon_1^0 = \epsilon_2^0 = 0$ (at $\lambda = 636$ nm), the stability constants of the complex species in configurational equilibrium were estimated from approximate values for the molar absorptivities of the tetrahedral species calculated by means of the empirical equation:

$$\epsilon_n^t \simeq \epsilon_{mn}^t + 6.6 \ (m+n) \tag{5}$$

by using ϵ_{mn}^t values calculated from previously reported data[1]: $\epsilon_{10}^t = 130$; $\epsilon_{20}^t = 215$; $\epsilon_{21}^t = 267$; $\epsilon_{22}^t = 307$ and $\epsilon_{23}^t = 339$. Thus, the ϵ_n^t values associated with the $Co(ttpo)_n^{+2}$ species should be: $\epsilon_1^t = 137$; $\epsilon_2^t = 228$; $\epsilon_3^t = 287$; $\epsilon_4^t = 333$ and $\epsilon_5^t = 372$.

TABLE IV.

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

combination number	$Co(tppo)^{+2}$	$Co(tppo)_2^{+2}$
1	0	0
2	0	t
3	t	t
4	0	$0 \rightleftharpoons t$
5	$0 \rightleftharpoons t$	$0 \rightleftharpoons t$

of the four hard tppo. Otherwise, we must admit some kind of interaction between inner and outer sphere tppo molecules[10,11]. The calculation of the molar absorptivities, ϵ_n, associated with the complex species formed in the system was performed by using the equation:

$$y = \frac{\epsilon F_O}{[L]} = \epsilon_1 \beta_1 + \epsilon_2 \beta_2 [L] + \ldots + \epsilon_5 \beta_5 [L]^4 \tag{3}$$

where

$$F_O = 1 + \beta_1 [L] + \beta_2 [L]^2 + \ldots + \beta_5 [L]^5 \tag{3'}$$

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:

$$y = 1.120 \times 10^4 + 9.572 \times 10^6 [L] \tag{4}$$

Combining equation (4) with the β_1 and β_2 values (Table II) we obtained $\epsilon_1 = 19.6$ and $\epsilon_2 = 46.2$. The ϵ_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 ϵ_n value corresponding to the last species ($\epsilon_5 = 372$) by graphical extrapolation of ϵ vs. $1/[L]$ plot, to $1/[L] = 0$.

The abnormal sigmoid shape of the ϵ vs. C_L curves (Figure 2), together with the obtained values for ϵ_1 and ϵ_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[12-14]. In our case, such equilibrium seems to exist only within the two first species as the mentioned deformation of the ϵ vs. C_L curves occurs almost only in the region in which $[L] \sim 0-3$ 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.

By combining de ϵ_1^t and ϵ_2^t values with equation (4), and considering $\beta_1 = \beta_1^0 + \beta_1^t$ and $\beta_2 = \beta_2^0 + \beta_2^t$, 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 $Co(tppo)_2^{+2}$, which seems logical.
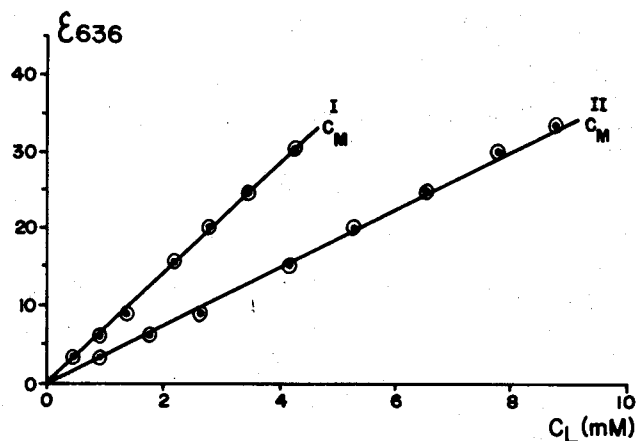

Figure 5. Co^{+2}-tppo system. Dependence of the mean molar absorptivity on total ligand concentration. $\bullet$: experimental curve in the 0-9 mM C_L range. Full curve: calculated from Table V data ($C_M^I = 1.5$ mM; $C_M^{II} = 4.5$ mM).

TABLE V

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

n	1	2
β_n^o	488	$1.65 \cdot 10^5$
β_n^t	82	$4.20 \cdot 10^4$
K_n^o	488	338
K_n^t	82	512

Finally, calculated ϵ 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.
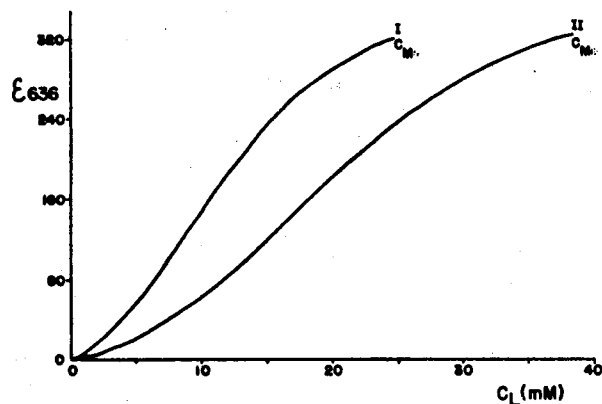

Figure 6. Co^{+2}-tppo system. Calculated curves from the data contained Tables II and V. (C_M^I = 1.5 mM; C_M^{II} = 4.5 mM).

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