

Electrochemical studies on cobalt tris (acetylacetonate)

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Abstract. The electrochemical reduction of cobalt acetylacetonate ($\text{Co}(\text{acac})_3$) at the mercury electrode in propylene carbonate and DMSO has been carried out using dc polarography, controlled potential coulometry, chronoamperometry and cyclic voltammetry. In propylene carbonate, polarograms showed two well defined waves, one wave being an adsorption pre-wave, the other an irreversible, diffusion-controlled electron transfer process. From chronoamperometry the diffusion coefficient was determined. Cyclic voltammetry confirmed the polarographic results, although additional adsorption waves were found. In DMSO, results were similar to those in propylenecarbonate. However, polarograms showed no adsorption pre-wave and additional adsorption waves found in propylene carbonate in the cyclic voltammograms were absent. The mechanism of the reduction process in both solvents is discussed.

Keywords. Cobalt tris (acetylacetonate) ; electrochemical studies ; dimethyl sulphoxide ; propylene carbonate.

1. Introduction

During electrochemical studies on mixed ligand complexes of transition metals, where the mixed ligands were β -diketonates and monothiocarbamates, it was necessary to check the literature for reported work on the transition metal β -diketonates complexes in order that the complex electrochemistry of the mixed-ligand complexes might be elucidated. Surprisingly, there was found to be a lack of information on this type of complex. Patterson and Holm (1972) found that Ru(III) β -diketonates showed uncomplicated polarographic behaviour in DMF or acetonitrile at the platinum electrode with current-voltage curves indicative of reversible or quasi reversible, one electron transfer reactions. $E_{1/2}$ values were very strongly influenced by the nature of the chelate ring substituents.

The case of reduction increased as the number and type of electron-releasing substituents were decreased. It was concluded that, for the Ru(III) complexes,

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the molecular orbitals accommodating electrons in the reduction process must possess appreciable ligand character. However, no work has been reported on the behaviour of metal complexes of acetylacetonate at the mercury electrode. In the present work, the electrochemical behaviour of cobalt (acac)₃ in propylene carbonate and DMSO at the mercury electrode was investigated.

2. Experimental section

2.1 Preparation of cobalt tris (acetylacetonate)

The complex was prepared in a manner similar to that by Bryant and Fernelius (1957). A mixture of 5g CoCo₃ and 40 cm³ of acetylacetonate in a 250 cm³ conical flask was heated to 90–95° C. The mixture was stirred rapidly with a magnetic stirrer, while 60 cm³ of 10% H₂O₂ was added dropwise: the addition required about 45 min, the temperature being maintained at 90–95° C. At the end of the reaction, the liquid layer was an intense green colour and a quantity of green solid deposited. The mixture was chilled to –10° C in an ice/salt bath to precipitate any further product, followed by filtering on a Buchner funnel. The crystals were dried at 110° C for 20 min and boiling benzene added until the crystals just dissolved. 300 cm³ of petroleum ether was added slowly (over a period of 3min) to the warm benzene solution and the mixture cooled in an ice/salt bath. The resulting product was filtered and air-dried.

2.2 Analytical data

Tris (acetylacetonato) Co(III) :	m.p. 210° C (lit. value 213° C).
Calcd (for C ₁₅ H ₂₁ O ₆ Co) :	C, 50.7 ; H, 5.94
Found :	C, 50.49 ; H, 5.98.

Propylene carbonate was purified by reduced pressure distillation at 120–130° C. Distillation was carried out twice, with collection of the middle 60% fraction. It was stored in a dark bottle over type 5A molecular sieve. DMSO was purified by vacuum distillation of the bulk material, the middle fraction being collected. It was stored over molecular sieves.

A Princeton Applied Research (PAR) model electrochemistry system was employed for the polarographic (dme), the cyclic voltammetric (hmde) and the chronoamperometric (hmde) studies. All potentials were measured against Ag/AgClO₄ (0.02 M)/NaClO₄ (0.2 M) reference electrode in propylene carbonate or DMSO. Supporting electrolyte used was 0.2M NaClO₄. The reference electrode potentials were checked daily against an aqueous Ag/AgCl(s)/KCl(satd) electrode. The auxiliary electrode was platinum. For constant potential coulometry with a mercury-pool electrode (diameter 4.6 cm), a Beckman Electroscan 30 instrument was employed. All electrochemical measurements were carried out at 25 ± 0.2° C, the solution being degassed with pre-dried, oxygen-free nitrogen,

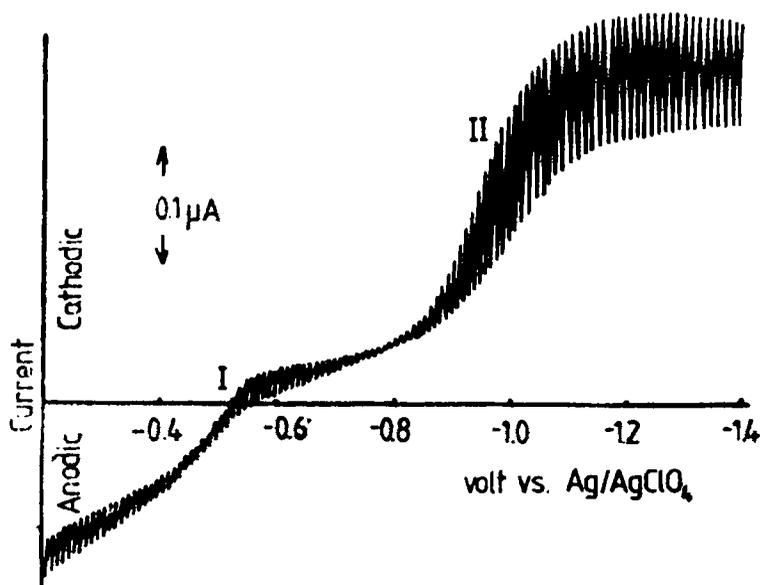


Figure 1. Polarogram of $\text{Co}(\text{acac})_3$ (1.00 mM) in propylene carbonate with 0.1 M NaClO_4 and 0.008% TRX-100 ($T = 25^\circ \text{C}$; Hg height = 67.5 cm).

3. Results and Discussion

3.1 D. C. polarography and controlled-potential coulometry

In propylene carbonate, polarograms showed two well-defined waves (figure 1) with $E_{1/2}$ values of $-0.497 \pm 0.006 \text{ V}$ (wave I) and $-0.980 \pm 0.006 \text{ V}$ (wave II) against the Ag/AgClO_4 (0.02 M), NaClO_4 (0.2 M) reference electrode.

The limiting current, i_d , of wave I was found to be independent of concentration, whereas that of wave II was essentially proportional to concentration. The effect of varying the height of the mercury showed a linear increase of limiting current with increase in mercury height for wave I, while $i_d \cdot h_{\text{corr}}^{-1/2}$ was essentially constant for wave II. The observations appear to imply that wave I is an adsorption wave and wave II is a diffusion-controlled electron transfer process. Further, the temperature coefficient of $1.4 \pm 0.3\%$ per degree for wave II over the temperature range $25\text{--}48^\circ \text{C}$ is consistent with a diffusion controlled process (Meites 1965).

The log-plot analysis of wave II showed marked curvature with initial slope of 0.095 and a final slope of 0.149, indicating departure from reversible behaviour for the electron-transfer process. Cathodic controlled potential coulometry was carried out at -0.7 V , i.e., on the plateau of wave I and gave a zero value for 'n', confirming the absence of a reduction process. On the other hand, cathodic coulometry on the plateau of wave II (-1.2 V) gave the following results for 3 separate determinations.

No. of moles (N°)	Current (coulombs) (Q)	No. of electrons (n)
1.078×10^{-5}	0.9545	0.92
4.968×10^{-6}	0.4698	0.98
6.933×10^{-6}	0.6370	0.95

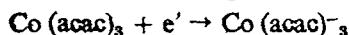
Wave II, therefore, represents a reduction process involving one electron.

The effect of water on the reduction process was examined. It was found that the limiting current for wave II was independent of water concentration up to 10M. However, above 1M concentration of water, there was a slight shift of $E_{1/2}$ towards more positive potentials.

The effect of free ligand was investigated by the addition of sodium acetylacetonate to a solution of $\text{Co}(\text{acac})_3$ containing 0.008% TRX-100. Polarograms showed a very marked increase in the height of wave I, with little or no effect on wave II. This indicates that wave I has associated with it an anodic reaction depending on the concentration of free ligand (Meites 1965). The likely reaction is the oxidation of mercury in the presence of acetylacetonate anions.

Anodic coulometry was carried out on a solution of sodium acetylacetonate at -0.2 V with supporting electrolyte present. UV spectra were also recorded at various intervals over several hours. The latter showed steady depletion of the ligand in solution. At the same time, a whitish precipitate confirmed as $\text{Hg}(\text{acac})_2$ was produced. For the anodic coulometry, the number of electrons involved in the anodic process was one, indicating an anodic reaction produced by the oxidation of mercury in the presence of acetylacetonate ligand.

During controlled-potential coulometry of a 0.25 mM $\text{Co}(\text{acac})_3$ solution at -1.2 V, in the presence of supporting electrolyte, UV spectra were recorded at hourly intervals. Initially, the spectrum was that of $\text{Co}(\text{acac})_3$. However, as electrolysis proceeded, a new spectrum continued to develop which was found to be identical to that for $\text{Co}(\text{acac})_2$. At the same time, the solution began to develop a pink tinge. From the polarographic and coulometric data, it is concluded that the reduction process represented by wave II is, as follows



This reaction is irreversible and the reduction product dissociates in the following way,



The free acetylacetonate anion takes part in the anodic reaction associated with wave I.

3.2. Chronoamperometry

Chronoamperograms for different solutions of $\text{Co}(\text{acac})_3$ were recorded over the whole potential range of wave II, i.e., -0.86 to 1.1 V.

Current (i_t) versus (time) $^{-1/2}$ plots were straight lines: the resulting data are shown in table 1.

The linear plots of i_t against $t^{-1/2}$ provide further evidence that the electrode reaction responsible for wave II is diffusion-controlled.

Table 1. Diffusion coefficient of $\text{Co}(\text{acac})_3$ in propylene carbonate (0.1 M NaClO_4 ; 0.008% TRX-100, $T = 25^\circ\text{C}$).

Concentration (mM)	Slope of i_p vs $t^{-1/2}$ (amp sec^{-1}) $\times 10^{-7}$	Diffusion Coefficient (D) ($\text{cm}^2 \text{sec}^{-1}$) $\times 10^{-7}$
1. 0.22	4.89	5.14
2. 0.20	4.42	5.08
3. 0.21	4.72	5.05
	Average 5.09 ± 0.05	

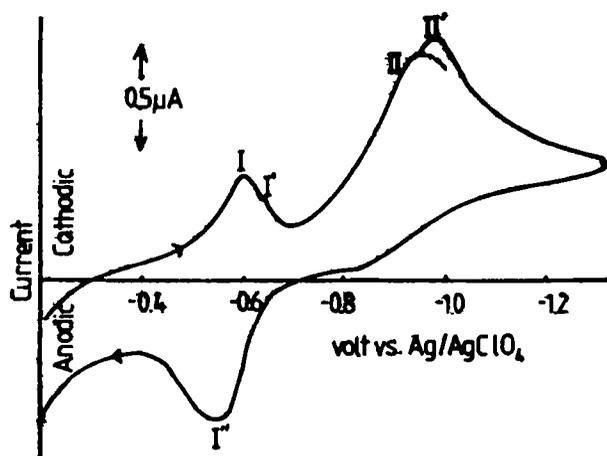


Figure 2. Cyclic voltammogram of $\text{Co}(\text{acac})_3$ (0.50 mM) in propylene carbonate with 0.1 M NaClO_4 and 0.008% TRX-100 ($V = 0.02 \text{ V/s}$; $T = 25^\circ\text{C}$).

3.3. Cyclic voltammetry

A typical cyclic voltammogram for $\text{Co}(\text{acac})_3$ is shown in figure 2. Peaks I' and II' were found to show the characteristics of adsorption waves. At low concentrations ($< 0.2 \text{ mM}$) and low scan rates, they appear as sharp, separate peaks. At higher concentrations, I' appears as a shoulder which merges with an enlarged peak I in subsequent cycles. Peak II', however, merges with peak II in the first scan and separates as a shoulder in subsequent scans. At high scan rates, it again merges with peak II. Peak II is diffusion-controlled and corresponds to the diffusion-controlled wave found in polarography. The peak height is usually distorted by the presence of peak II', which is presumably due to the adsorption of reactant molecules (Wopschall and Shain 1967).

On the anodic sweep, there is no peak corresponding to peak II indicating the irreversibility of the electrode reaction in agreement with the polarographic results.

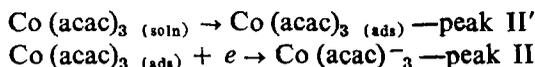
The anodic peak I'' was found to increase on addition of the ligand as sodium acetyl acetonate. As the original solution contained no free acetylacetonate ions, peak I'' must be associated with the ions released by the reaction product.

Current flow ceases when a limiting thickness is attained and, at slow scan rates, the limiting thickness appears to be attained at all concentrations studied. At high scan rates, (e.g., 0.5 V/sec), concentrations above 0.6 mM produce limiting thickness.

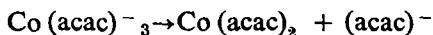
The cathodic peak I appears to be symmetrical with a slight shoulder, I', which is smoothed out at high scan rates and concentrations. The peak current, very small on the initial scan becomes larger with subsequent scans with the peak potential shifting towards a more negative potential and engulfing peak I'. Peak I is therefore, attributed to the stripping of the deposition product from the electrode.

Detailed investigation of the diffusion controlled peak II was not possible due to the distortion caused by the proximity of peak II'.

In summary, the mechanism on the basis of cyclic voltammetry which is in agreement with the polarographic results, appears to be as follows :



The reverse process is negligible as the reaction is irreversible. Co (acac)_3^- is released into solution and dissociates in the following way



In the presence of (acac) ions, mercury is oxidized ultimately producing Hg (acac)_2 . Peak I'' is due to the deposition of Hg (acac)_2 until a limiting thickness is obtained. Peak I is caused by the stripping of the deposit. Peak I' which was shown to be an absorption wave may be due to re-absorption of some of the stripped Hg (acac)_2 .

4. Electrochemical investigations in DMSO

Polarograms of Co (acac)_3 in DMSO under the same conditions as for propylene carbonate showed reduction wave at $E_{\frac{1}{2}} = -0.650$ V. The pre-wave found in propylene carbonate, however, was absent (figure 3). It is interesting to consider the apparent solvent dependency of this pre-wave. It will be recalled that the pre-wave in propylene carbonate occurred at $E_{\frac{1}{2}} = -0.497$ V which is on the descending position of the first electrocapillary maximum as shown on the electrocapillary curve (figure 4a). It was proposed that this pre-wave is due to the adsorption of a first layer of the product Hg (acac)_2 on the electrode. Now the descending parts of an electrocapillary maximum refers to a negatively-charged mercury drop (Kolthoff and Lingane 1952). It would appear, therefore, that adsorption is reasonable in this region due to the electropositive nature of the mercuric complex. For an adsorption pre-wave to occur in DMSO, it would have to be at a potential less negative than -0.65 V, the half-wave potential. However, as shown in the electrocapillary curve for Co (acac)_3 in DMSO (figure 4b) this would be on the ascending part of the curve, where the mercury drop has a positive charge (Kolthoff and Lingane 1952). Conditions would not, therefore, be favourable for the adsorption of the mercuric complex onto the electrode.

Cyclic voltammograms of Co (acac)_3 in DMSO under the same conditions as in propylene carbonate were, apart from the absence of additional adsorption waves found in the latter solvent, almost identical (figure 5). Peak II represents the reduction process

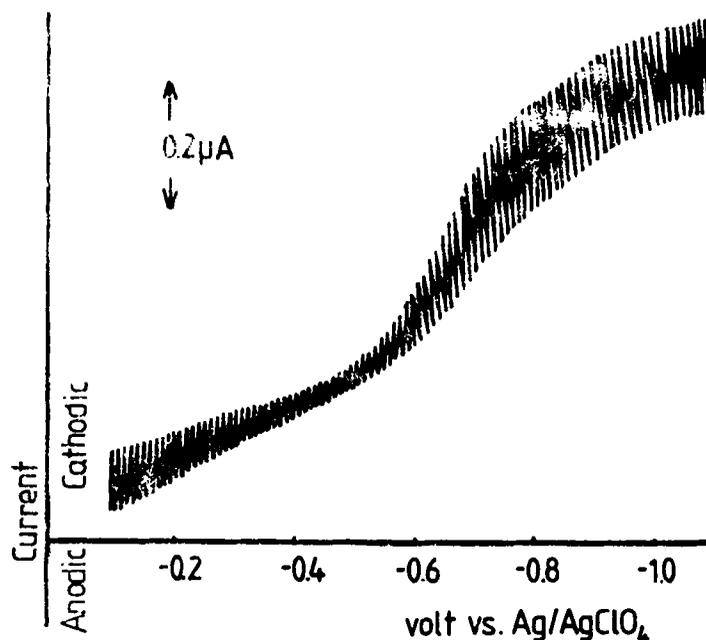


Figure 3. Polarogram of $\text{Co}(\text{acac})_3$ (0.53 mM) in DMSO with 0.1 M NaClO_4 and 0.008% TRX-100 ($T = 25^\circ\text{C}$; Hg height = 67.5 cm).

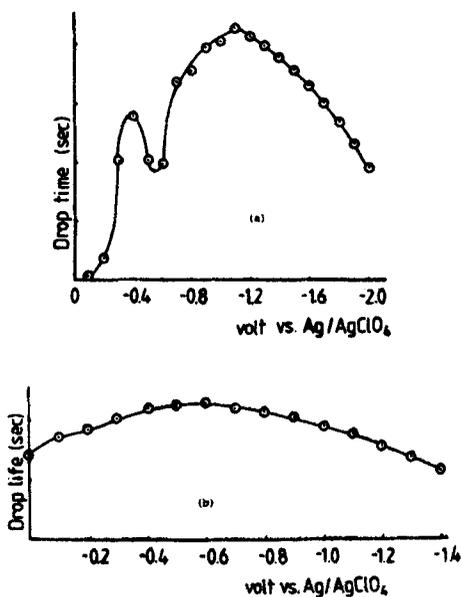
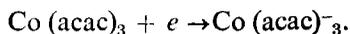


Figure 4. Electrocapillary curves of $\text{Co}(\text{acac})_3$ (1.00 mM) (a) in propylene carbonate, (b) in DMSO with 0.1 M NaClO_4 and 0.008% TRX-100.



$E_{p,c}$ shifted cathodically as scan rate increased. At a scan rate of 0.5 V/sec $E_{p,c} = -0.720\text{ V}$. This represents a 60 mV shift for a 10-fold increase in scan

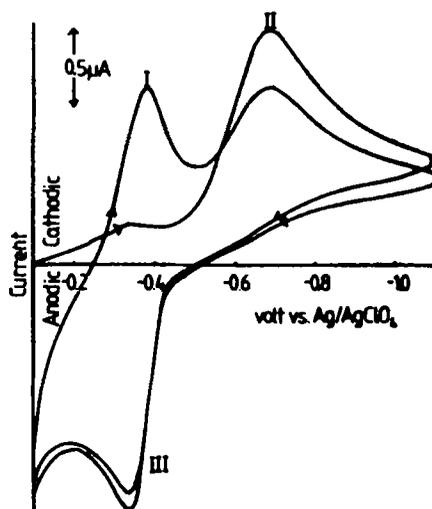


Figure 5. Cyclic voltammogram of $\text{Co}(\text{acac})_3$ (0.53 mM) in DMSO with 0.1 M NaClO_4 and 0.008% TRX-100 ($V = 0.1 \text{ V/s}$; $T = 25^\circ \text{C}$).

rate which is in accord with diagnostic criteria for an irreversible charge transfer (Brown and Lange 1971). As expected for an irreversible process, there is no corresponding peak to peak II on the anodic sweep.

Anodic peak III represents deposition of $\text{Hg}(\text{acac})_2$ onto the electrode, until a limiting thickness is achieved. The presence of $\text{Hg}(\text{acac})_2$ was confirmed by exhaustive electrolysis, which resulted in the formation of a greyish precipitate and a pink coloration in the solution. Microanalysis and IR spectroscopy confirmed the grey precipitate as $\text{Hg}(\text{acac})_2$.

Peak I is due to the stripping of the deposition from the cathode. It was found that on the initial scan, when no deposit is present, no stripping current is present (figure 5).

In other respects, the mechanism of reduction in DMSO is identical to that in propylene carbonate.

References

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