

Electrochemistry of Homogeneous Catalysts: Correlation of the Electrochemistry and the Ziegler—Natta Catalytic Activity of Metal Acetylacetonate Complexes

By: C. W. Anderson, K. R. Lung, and [Terence A. Nile](#)

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Abstract:

A series of metal acetylacetonates $[M(acac)_n]$ was characterized electrochemically using cyclic voltammetry and Differential Pulse Voltammetry. The Nicholson and Shain criteria [1, 2] was used to determine the electrochemical reduction mechanisms of these complexes. It was found that the reversibility of the electrochemical reduction is inversely proportional to the Ziegler—Natta catalytic activity of the metal acetylacetonate complex.

Article:

Introduction

In the 1964 classic theoretical electrochemistry paper by Nicholson and Shain [1], the fundamental theory for the investigation of the homogeneous chemical reactions succeeding heterogeneous charge transfer was developed. Using the Nicholson and Shain criteria, the nature of the dissociation reaction following the electrochemical reduction of the metal acetylacetonates can be investigated [2, 3]. The use of this technique in the study of an inorganic complex was recently demonstrated [4].

It is known that metal acetylacetonate complexes are active Ziegler—Natta homogeneous catalysts for hydrogenation and hydrosilylation [5-7]. In a typical catalytic reaction, an active catalyst is generated by the combination of the metal acetylacetonate and a reducing agent. The resulting catalytic system is often quite complicated. Although the structure of the active catalytic intermediate has been speculated [8], the isolation or identification of the actual active catalyst has not been reported. In reality, the isolation of the active catalyst is expected to be difficult. In order for the intermediate generated by reduction of the metal complex to be an active catalyst, this intermediate must be kinetically labile. Otherwise, the active catalyst will be too stable to ensure an active turnover of the substrate and the product.

The general approach to the study of Ziegler-Natta catalyst systems is to monitor the rate of reactant uptake or the rate of product formation [5-8] by UV, IR and NMR spectroscopy. This study represents one of the first attempts to characterize Ziegler—Natta catalyst system using electrochemical methods.

TABLE I. Oxidation and Reduction Peak Potentials of Transition Metal Acetylacetonate Complexes.

	E (oxidation)*	E (reduction)*	E (differential** pulse)	No. of electrons (reduction)
Ni(II)	0.20 V	-1.45 V	-1.37 V	2
Co(III)	0.31	-0.86	-0.86	1
Fe(III)	0.55	-0.68	-0.67	1
Cr(III)	-1.75	-1.89, -2.11	-1.78	2 (stepwise)
Cu(II)	0.05, -0.55	-1.01, -1.48	-1.00	2 (stepwise)

*Cyclic voltammogram peak potentials vs. Ag/AgCl at 100 mV/sec.
vs. Ag/AgCl. Pulse height = 50 mV, scan rate = 5 mV/sec.

**Differential pulse voltammetry reduction peak potential

One of the Nicholson and Shain criteria, the ratio of anodic to cathodic peak (i_{pa}/i_{pc}), is used. The results obtained were correlated with known Ziegler-Natta catalytic activities of the metal acetylacetonate complexes.

Results

The number of electrons transferred in the electrochemical reduction and the peak potentials are summarized in Table I.

Copper(II) acetylacetonate showed two reduction peaks at -1.01 V and -1.48 V *versus* Ag/AgCl reference. The first peak at -1.01 V corresponds to a Cu(II) to Cu(I) reduction. At -1.48 V, the complex was reduced to Cu(0) and metallic copper was plated onto the surface of the electrode. During the reverse scan, Cu(0) on the electrode surface was reoxidized. The sharp symmetrical anodic stripping peak at 0.05 V is typical of surface redox processes [9] (see Fig. 1).

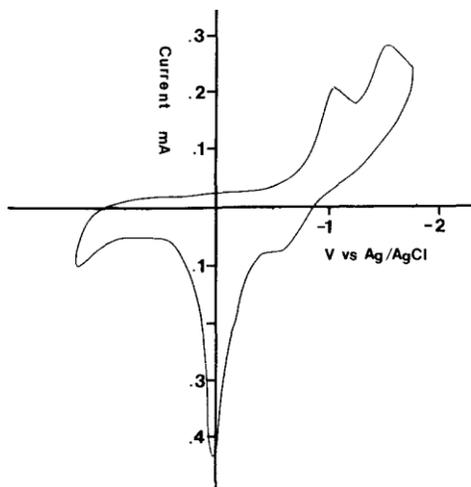


Fig. 1. Cyclic voltammogram of 3.5 millimolar $\text{Cu}(\text{acac})_2$ in $\text{CH}_3\text{CN}/0.1$ M tetrabutylammonium perchlorate. Scan rate = 100 mV/sec.

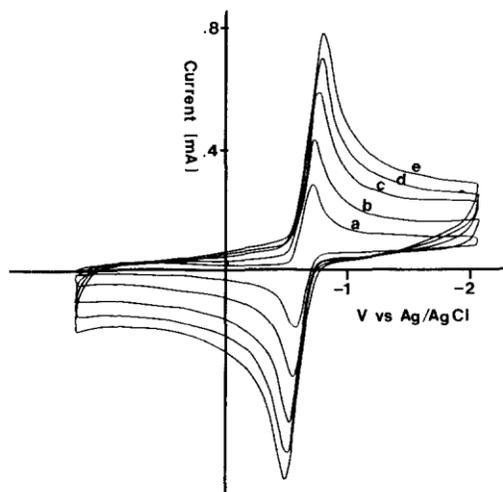


Fig. 2. Cyclic voltammograms of 3.5 millimolar $\text{Fe}(\text{acac})_3$. An example of a reversible redox couple. Scan rate in mV/sec: a = 100 , b = 200 , c = 300 , d = 400 , e = 500 .

Chromium(III) acetylacetonate also showed a two step reduction process corresponding to a stepwise Cr(III) to Cr(II) and a Cr(II) to Cr(I) reduction. Iron(III) acetylacetonate and cobalt(III) acetylacetonate showed a quasi-reversible redox process with significant differences in reversibility (see Fig. 2 and 3). Nickel(II) acetylacetonate showed an irreversible two electron reduction peak.

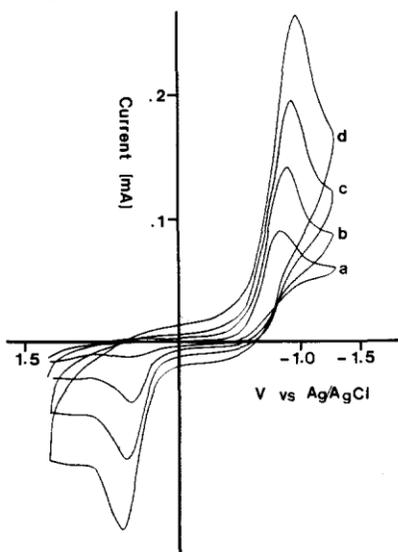


Fig. 3. Cyclic voltammograms of 3.8 millimolar $\text{Co}(\text{acac})_3$. An example of a semi-reversible redox couple showing a lower i_{pa}/i_{pc} ratio at lower scan rate. Scan rate in mV/sec: a = 100 , b = 200 , c = 300 , d = 400 .

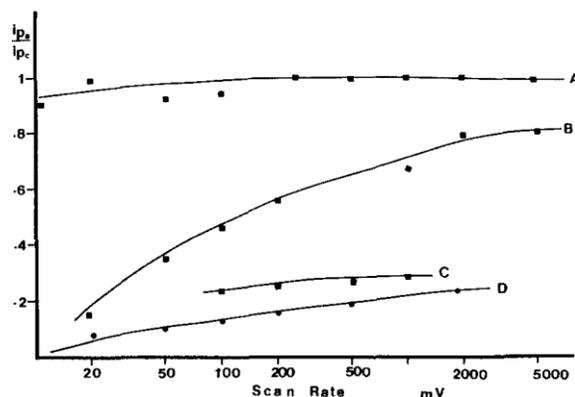


Fig. 4. Anodic-cathodic peak current ratio plots. i_{pa}/i_{pc} vs. $\log(\text{scan rate})$. A = $\text{Fe}(\text{acac})_3$, B = $\text{Co}(\text{acac})_3$, C = $\text{Cr}(\text{acac})_3$, D = $\text{Ni}(\text{acac})_2$.

Nicholson and Shain plots of anodic and cathodic current ratios (i_{pa}/i_{pc}) are shown in Fig. 4. The shape of the i_{pa}/i_{pc} plot clearly indicated that Ni(II), Co(III), Cu(II) and Cr(III) acetylacetonates underwent a heterogeneous electron transfer followed by a homogeneous chemical reaction during which the reduced metal acetylacetonate dissociated to a neutral $M(\text{acac})_{n-1}$ species and an acac^- free ligand (an EC mechanism according to the Nicholson and Shain criteria). For $\text{Co}(\text{acac})_3$ this interpretation is further supported by results obtained from cyclic voltammetry performed in a thin layer cell (Fig. 5). In this experiment, the thickness of the cell is less than the diffusion layer of most substances during a typical experiment [17]. Therefore, the acac^- generated from the dissociation of the metal acetylacetonate could not diffuse significantly away from the electrode surface. Under these diffusion limiting experimental conditions, the i_{pa}/i_{pc} ratio of Ni(II) and Co(III) acetylacetonates approached 1.0.

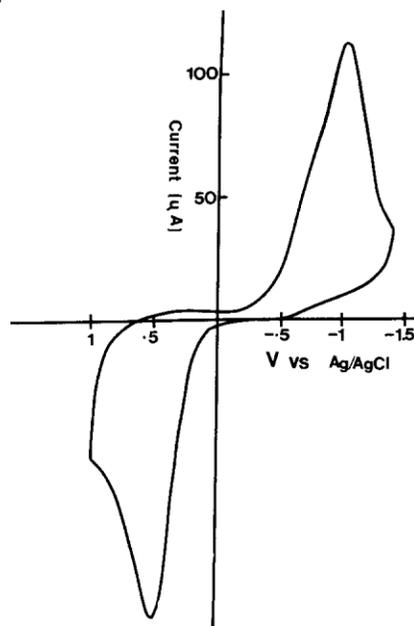
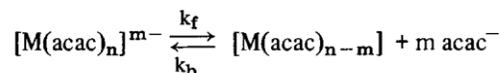
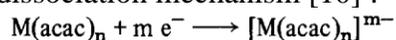


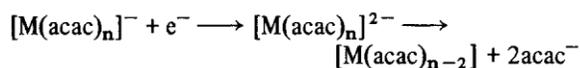
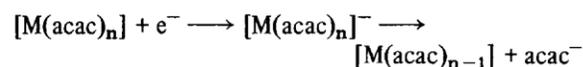
Fig. 5. Thin layer cyclic voltammogram of 3.5 millimolar $\text{Co}(\text{acac})_3$. Scan rate = 2 mV/sec.

Cyclic voltammograms of $\text{Co}(\text{acac})_3$ and $\text{Fe}(\text{acac})_3$ at variable scan rates are shown in Figs. 2 and 3. The reduction—dissociation processes of the metal acetylacetonates are summarized by eqns. 1 and 2. Spectroelectrochemical studies by Murray and Heineman showed that $\text{Fe}(\text{acac})_3$ undergoes an EC reduction—dissociation mechanism [10]:



$M = \text{Co(II)}, \text{Fe(III)}, \text{Ni(II)}$

(1)



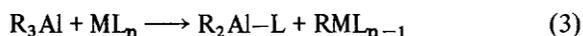
$M = \text{Cu(II)}, \text{Cr(III)}; n = 2 \text{ for Cu(II)}, n = 3 \text{ for Cr(III)}$

(2)

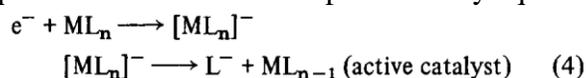
Discussion

Several different mechanisms have been speculated for metal acetylacetonate Ziegler—Natta catalysis. These proposed mechanisms have several features in common. It is generally known that during the activation of the metal acetylacetonate catalyst, the metal atom is chemically reduced and one or more of the acac^- ligands is lost after the reducing agent is added.

For catalytic systems involving alkylating reducing agents, it is generally believed that the metal complex is alkylated while one of the ligands is lost (eqn. 3):



In the case of a non alkylating method such as electrochemical generation of active catalyst from metal acetylacetonates [11, 12], the sequence of events can be represented by eqn. 4:



This reduction—dissociation mechanism is a common feature of Ziegler—Natta catalyst systems involving metal acetylacetonates. In general, the reducing agents used in Ziegler—Natta catalytic systems are thermodynamically energetic enough to reduce the acetylacetonate complexes. Therefore, the rate of catalytic reaction is not likely to be determined by the chemical reduction. Rather, it is more likely that the overall activity of the catalytic system is controlled by subsequent steps in the catalytic cycle.

It is proposed that the chemical reduction step can be simulated by a heterogeneous electrochemical reduction at an inert carbon electrode. Electrochemical generation of an active catalyst form $[M(\text{acac})_n]$ has been demonstrated by Lemkuhl and coworkers [11, 12]. In this study, we focus on the step immediately following the reduction of the metal acetylacetonate complex: the dissociation of the reduced activated complex leading to the availability of a coordination site.

$\text{Cu}(\text{acac})_2$ was easily reduced electrochemically to copper metal catalytically inactive species. This is consistent with the results obtained by Sloan [6] which showed that $\text{Cu}(0)$ metal was precipitated when Bu^i_3Al was added to $\text{Cu}(\text{acac})_2$. Other acetylacetonates showed the following reversibility order: $\text{Fe} > \text{Co} > \text{Cr} = \text{Ni}$. The Ziegler—Natta catalytic activities for the hydrogenation of cyclohexene of these complexes follow the reverse order as follows: $\text{Ni} > \text{Co} > \text{Fe} > \text{Cr} \gg \text{Cu}$ [5]. In other words, the Ziegler—Natta activity is inversely proportional to the electrochemical reversibility except for $\text{Cr}(\text{acac})_3$. This can be rationalized because $\text{Cr}(\text{acac})_3$ has the most negative reduction potential, *i.e.* it is the most difficult to reduce. So, in this case the reduction may be the rate determining step in Ziegler—Natta catalysis, not the dissociation of the acac ligand. Further experiments are underway to confirm this hypothesis.

Through the use of the Nicholson and Shain criteria, it was demonstrated that the irreversibility was caused by the relative rates of dissociation (k_f) and recombination (k_b) of the homogeneous chemical dissociation of the reduced metal complex taking place away from the electrode (an EC mechanism). It was also observed that the more reversible the electrochemical redox couple, the less active the catalyst tends to be. Therefore, in the more active catalyst, one of the acac⁻ ligands is lost irreversibly after the reduction. This means that the acac⁻ is effectively removed from the coordination sphere after the reduction. In a chemical reduction by lithium aluminum hydride or aluminum hydride [12-14], a similar dissociation of the metal acetylacetonates takes place. The irreversible dissociation of one of the acac⁻ ligand may also be an important rate determining step in Ziegler—Natta catalysis, as effective removal of acac⁻ frees a vacant coordination site, allowing a molecule of the substrate to bind to the metal. This in turn permits coordination of the substrates to take place.

Experimental

Reagents

Tetrabutylammonium perchlorate, the electrolyte, was purchased from Alfa Chemicals (Danvers, Massachusetts) and was used without further purification. Acetonitrile, the electrochemical solvent, was Eastman spectroscopic grade and was distilled over calcium hydride under nitrogen before use. Metal acetylacetonates were obtained commercially or synthesised by literature methods. $\text{Cu}(\text{acac})_2$ and $\text{Cr}(\text{acac})_3$ were purified by vacuum sublimation before use. All acetylacetonate complexes were heated to 110°C at 1 torr for eight hours to remove any water of hydration before use. All other chemicals were reagent grade or better and were used as received.

Apparatus and Procedure

Cyclic voltammograms were obtained with a Princeton Applied Research (P.A.R.) Model-173 potentiostat, a P.A.R. Model-179 digital coulometer and a P.A.R. Model-175 programmer. Voltammograms slower than 500 mV/sec were recorded with an I.B.M.-Instrument Company Model-7424M X-Y recorder. A Tecmar Model-

DT5712 (Tecmar Inc., Cleveland, Ohio) high resolution analog to digital converter [15] interfaced to a microcomputer and a Tektronix Model-564 storage oscilloscope were used to record voltammograms faster than 500 mV/sec. Differential Pulse Voltammograms were obtained with a P.A.R. Model-174 Polarographic Analyzer and a P.A.R. Model-315 Controller.

An I.B.M. Instrument Company single compartment cell, a double junction Ag/AgCl reference electrode, a glassy carbon disk electrode [16] (Tokai Electrode Mfg. Co., Tokyo, Japan) and a platinum auxiliary electrode were used. The solvent was purged with nitrogen for 5 minutes before the metal acetylacetonate was added. Nitrogen was presaturated with CH₃CN by bubbling through a CaH₂/CH₃CN wash tower before it was admitted into the electrochemical cell. The construction and properties of the thin-layer electrochemical cell have been described elsewhere [17].

Conclusion

Electrochemistry, capable of monitoring the generation and disappearance of transient intermediates, is obviously a powerful tool in the study of homogeneous catalysis. The use of other electrochemical techniques such as spectroelectrochemistry and chronoamperometry to measure k_f and k_b and investigation of the effect of the very negative reduction potential of Cr(acac)₃ on the catalytic activity are under progress.

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