Electrochemical Investigations of Several Transition Metal Tris(acetylacetonate) Complexes

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Abstract

The voltammetry of a number of $M(acac)_3$ complexes (M = Fe, Ru, Co, Rh or Ir: $acac^-$ = acetylacetonate) have been studied. A variety of electrochemical behavior has been found. When M = Fe or Ru, a reversible reduction was found, $E_{1/2}$ = –0.61 and –0.70 V respectively. M = Co showed a highly irreversible reduction at $E_{1/2}$ = –1.10 V. All complexes undergo oxidation, the potential and character depending on the metal centre. With M = Fe, Co or Rh, the oxidation is irreversible (Ep_a = +1.70, +1.70, +1.74 V respectively). When M = Ru or Ir, both show a reversible oxidation ($E_{1/2}$ = +1.05 and +1.29 V respectively) which, although showing no tendency to undergo any following reactions on the voltammetric time-scale, proved not to be sufficiently stable over the longer time period required for electrosynthesis. Both oxidized species show a reaction with DMF. Preliminary kinetic studies showed the reaction not to be a simple second order process. The general trend in redox potentials and the varying chemical stability of the electrochemically produced cations were in keeping with the higher oxidation state becoming more favorable down the triad.

Introduction

Transition metal acetylacetonate complexes have been well known for many years and have been subjected to study by a wide range of techniques [1, 2]. Research in this area is still progressing rapidly, for example, $Ru(acac)_3$ ($acac^-$ = acetylacetonate) is currently undergoing extensive investigation regarding its catalytic properties [3–6].

$Ru(acac)_3$ has been studied electrochemically in both aqueous [7] and non-aqueous [8, 9], N,N′-dimethylformamide and acetonitrile, solvents, principally by polarography, where a reversible reduction has been observed. This metal-based Ru(III)/Ru(II) couple has been investigated as a function of supporting electrolyte where the addition of $NaClO_4$ or $LiClO_4$ to acetonitrile resulted in a positive shift in the reduction step, interpreted as a two step association between the reduced product $[Ru(acac)_3]^{1-}$ and alkali-metal ions [7, 8]. Substituent groups on the ligand also affect reduction potentials, where a linear relationship has been found between half-wave potential and the Taft inductive parameter [8, 9].

During the course of an electrochemical study of $Ru(acac)_3$ with stationary electrodes, we have found that the reduction shows behavior analogous to that previously reported from polarographic studies but unexpectedly, we also found a reversible $[Ru(acac)_3]^0/[Ru(acac)_3]^+$ couple, of which the chemical stability of the oxidized species proved to be dependent on solvent. The possibility of being able to prepare transition metals in uncommon oxidation states, stabilized by acetylacetonate ligands, prompted us to extend our study to a number of other $M(acac)_3$ complexes (M = Fe, Ir, Rh and Co). The electrochemistry of these complexes will also be discussed and compared with $Ru(acac)_3$.

Experimental

Materials

$Ru(acac)_3$ [10] and $Rh(acac)_3$ [11] were prepared by literature methods. $Ir(acac)_3$ and $Co(acac)_3$ were purchased from Johnson Matthey Inc., $Fe(acac)_3$ from Mackenzie Chemical Works, Inc., and were used without further purification.

Standard solutions for electrochemical experiments were prepared in acetonitrile, methylene chloride, tetrahydrafuran and N,N′-dimethylformamide, all employing $n\text{-}Bu_4NBF_4$ (0.1 M) as supporting electrolyte. All solvents were purified under nitrogen by standard techniques.

Instrumentation

Voltammetric studies employed a BAS 100 Electrochemical analyzer, interfaced with a Houston

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Instrument HIPLOT DMP-40 plotter and a BAS CIA Programmable Cell Stand, and a three-electrode configuration with full positive feed back resistance compensation. Gold, platinum and glassy carbon microdisks were used as working electrodes. Platinum wire counter electrodes and a Ag/AgCl reference electrode (against which ferrocene was oxidized at +0.53 Volts) were employed in conjunction with the working electrodes in all voltammetric experiments. Routine scan rates were 100 mV s^{-1} in cyclic voltammetry and 10 mV s^{-1} in other modes.

Coulometry and electrosynthetic experiments employed a platinum gauze working electrode, a platinum counter electrode, separated by a frit and salt-bridge from the electrolyte solutions, and a Ag/AgCl reference electrode.

Cell solutions, normally 1.0×10^{-3} M in complex were degassed with solvent-saturated argon prior to measurements, and a flow of argon over the surface of the solution maintained at all times.

Results and Discussion

Electrochemical Reduction and Oxidation of Ru(acac)$_3$

Electrochemical data from cyclic voltammetric experiments at a Pt working electrode are summarized in Table I. Virtually identical results were obtained using Au or glassy carbon. In all solvents the reductive couple analyzed as a one electron reversible diffusion controlled process the potential being invariant with changing working electrode or solvent. The cyclic voltammetry results were confirmed by differential pulse voltammetry, where, using a pulse amplitude of 50 mV we see a peak whose current was the same irrespective of direction of scan, and a peak potential difference $|\Delta Ep| = 50$ mV [12].

TABLE I. Cyclic Voltammetric Data for Oxidation and Reduction of Ru(acac)$_3$ in Various Solvents [a].

Solvent	Oxidation		Reduction	
	E_p^{ox}	E_p^{red}	E_p^{red}	E_p^{ox}
CH_2Cl_2	+1.16	+1.1	−0.74	−0.68
CH_3CN	+1.07	+1.01	−0.73	−0.67
THF	+1.235	+1.145	−0.69	−0.63
DMF	+1.05	[b]	−0.785	−0.705

[a] Conditions: scan rate = 100 mV s^{-1}, 0.1 M n-Bu_4NBF_4 supporting electrolyte, E_p^{ox} = oxidation peak potential, E_p^{red} = reduction peak potential. [b] No current response on reverse scan.

As noted by Endo [7, 8], the addition of sodium or lithium perchlorate to acetonitrile solutions, resulted in a shift to positive potentials, in the latter case accompanied by a loss of chemical reversibility due to the product precipitating from solution. Coulometry in acetonitrile (n-Bu_4NBF_4/0.1 M) at −0.725 volts confirmed the process to be a one electron step, to yield a product which was fairly stable in the absence of oxygen. When potential changed to −0.60 volts, the material was reduced in 95% yield to the original species. Attempts to electrosynthesize the reduced species as its lithium salt from acetonitrile ($LiClO_4$/0.1 M) at −0.65 volts resulted only in the brown precipitated material effectively coating the platinum gauze working electrode surface which could not be removed by vigorous stirring of the solution.

On turning our attention to the oxidation process, the cyclic voltammetric data in acetonitrile, methylene chloride and tetrahydrofuran analyzed as a reversible one electron couple, with no tendency for the oxidized species to undergo further reaction on the electrochemical time-scale. The differential pulse voltammetry confirmed these observations, with peak current independent of direction of scan and $Ep_a - Ep_c = |\Delta E|$ (the pulse amplitude). Comparing the oxidation and reduction processes (Fig. 1) we can see the similar current responses obtained for both couples in cyclic voltammetric and differential pulse voltammetric modes, illustrating that the same number of electrons were involved in both steps. This was also confirmed by stirred voltam-

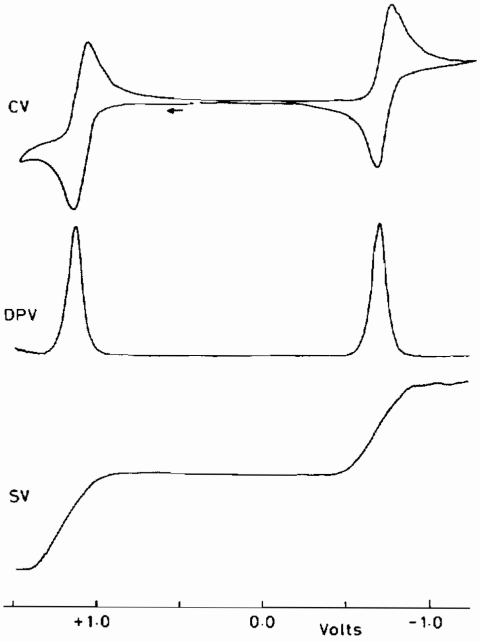

Fig. 1. Comparison of voltammetric techniques for Ru(acac)$_3$ in 0.1 M n-Bu_4NBF_4/acetonitrile.

metry, where current of oxidation and reduction are identical.

On examining N,N′-dimethylformamide solutions, however, the reversibility of the $[Ru(acac)_3]^0$/$[Ru(acac)_3]^+$ couple was lost with no return wave character being in evidence. By using a mixed CH_3-CN–DMF solvent system we observed that as the DMF concentration was increased, the return-to-forward peak current ratio (ip_r/ip_f) decreased, and as the scan rate was increased the ipr/ipf ratio increased towards unity. Thus, we can assign the lack of reversibility to an irreversible chemical reaction which follows the charge transfer step. This explains the previous assignment of the oxidation as quasi-reversible as it was only studied in dimethylformamide by polarography [9].

The product of the chemical following reaction was itself redox active, as could be seen by the development of a new quasi-reversible reduction at $E_{1/2} = -0.30$ volts, which grew in importance as the DMF concentration, and consequently the following reaction, increased.

Attempts to prepare the DMF reaction product by electrolysis resulted in failure due to the close proximity of the solvent front.

The highly reversible nature of the oxidation in acetonitrile etc, which would formally give an uncommon Ru(IV) species, warranted further attention. Ru(IV) complexes of the type $[Ru(trpy)(bpy)_2O]^{2+}$ (trpy is 2,2′,2″-terpyridine; bpy is 2,2′-bipyridine) and $[Ru(bpy)_2(py)O]^{2+}$ (py is pyridine) are currently undergoing investigation concerning their kinetic and mechanistic properties to oxidize various organic moieties [13, 14] (*e.g.* 2-propanol to acetone, and aromatic carboxylates to alcohols) and possible catalytic oxidation of water [15]. The ability of these complexes to participate in a number of reversible redox couples, giving metal oxidation states ranging from Ru(IV) to Ru(II) was an essential feature in their oxidizing capabilities. Our findings that $Ru(acac)_3$ could be both oxidized and reduced to yield stable species presented possibilities of similar behavior. The long term stability of the Ru(IV) complex was, therefore, of primary importance. Electrosynthesis on $Ru(acac)_3$ in acetonitrile was carried out at +1.1 V. During the course of electrolysis the solution color changed from bright orange to very dark purple. Cyclic voltammograms were recorded both before and after exhaustive oxidation. The oxidation and reduction responses observed prior to electrolysis disappeared and were replaced by an ill-resolved oxidation, its close proximity to the solvent front preventing analysis.

Coulometry of $[Ru(acac)_3]^0$/$[Ru(acac)_3]^+$ gave an n value of 3 ± 1 electrons/mol, indicative of multi-electron processes involving oxidation of unknown species formed after the initial formation of $[Ru(acac)_3]^+$. At the positive potentials required for oxidation, these species were apparently also oxidized. Indeed, voltammetry at an intermediate stage of electrolysis showed a reversible oxidation at +0.2 V, and a highly irreversible oxidation at approximately +1.4 V. Development of the latter process as electrolysis continued resulted in the ill-resolved wave seen close to solvent front after electrolysis completed. Both were completely absent in the initial voltammograms.

Although these following reactions were sufficiently slow so that over the normal voltammetric time-scale no indications of their presence were observed they become significant over the longer time-scale of electrolysis.

Chemical oxidation using perchloric acid gave the same dark purple solution, which gave the same voltammetric response as solutions produced electrochemically.

Comparisons with Similar Systems

Due to the somewhat unexpected oxidative behavior of $Ru(acac)_3$, we were prompted to examine a number of similar $M(acac)_3$ complexes, where M = Fe, Ir, Rh or Co. The electrochemical details from cyclic voltammetry are listed in Table II.

TABLE II. Cyclic Voltammetric Data for Oxidation and Reduction of $M(acac)_3$; (M = Fe, Co, Rh and Ir) [2].[a]

Metal	Oxidation		Reduction	
	E_p^{ox}	E_p^{red}	E_p^{red}	E_p^{ox}
Fe	+1.70	[b]	−0.70	−0.52
Co	+1.80	[b]	−1.10	[b]
Rh	+1.74	[b]	[c]	
Ir	+1.24	+1.18	[c]	

[a] Conditions: acetonitrile solvent, 0.1 M $n\text{-}Bu_4NBF_4$ as supporting electrolyte, scan rate = 100 mV s^{-1}, E_p^{ox} = oxidation peak potential, E_p^{red} = reduction peak potential. [b] No current response on reverse scan. [c] No redox activity within available solvent limit.

$Fe(acac)_3$ has been previously examined in a number of studies [16–18]. As reported, we also found a reversible reduction, assigned to a metal-based Fe(III)/Fe(II) couple. We found however that it was essential to use a freshly polished electrode for each voltammogram, otherwise, coating on the electrode surface resulted in increased peak-to-peak separations and a more limited positive range. This occurred on all electrode surfaces available. An irreversible oxidation was also present, which has not been previously reported, being at sufficiently positive potentials to be unobservable by polarography, and only clearly defined using a newly polished electrode. Cooling the solution to −50 °C gave no improvement on reversibility.

On comparison, we found that Ru(acac)$_3$ was more difficult to reduce than Fe(acac)$_3$ (by 0.1 V). We also found that not only was Ru(acac)$_3$ easier to oxidize than Fe(acac)$_3$ (by 0.65 V) but that the oxidized species was stable on the electrochemical time-scale. These trends were in keeping with the higher oxidation being more favorable down the triad. This results in the formally Fe(IV) species being produced at more positive potentials than the analogous Ru(acac)$_3$ and the lack of any chemical reversibility.

The acetylacetonates of the Co, Rh, Ir triad were also examined. As expected, only Co(acac)$_3$ showed any reduction behavior within the available solvent limits. The highly irreversible nature of the reduction, which presumably results in Co(II), can be interpreted as yielding $[Co(acac)_3]^-$ which rapidly loses acac$^-$ to give $[Co(acac)_2]^o$, which then oligomerizes. All three complexes were susceptible to oxidation. Only Ir(acac$_3$), however, is chemically reversible (Fig. 2 compares cyclic voltammetry of Rh(acac)$_3$ and Ir(acac)$_3$). We again observe the expected trend that the higher oxidation state becomes more stable down the triad with corresponding shift to less positive potentials.

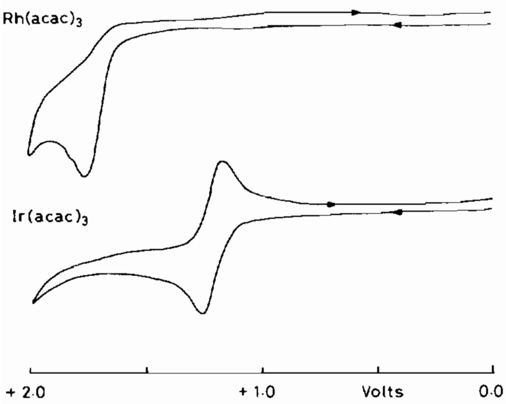

Fig. 2. Cyclic voltammetry of Rn(acac)$_3$ and Ir(acac)$_3$ in 0.1 M–0.1 M Bu_4NBF_4/acetonitrile, scan He = 100 mV s^{-1}.

The oxidation of Ir(acac)$_3$ would lead to a formally Ir(IV) centre. Crystalline hexafluoro- [19], hexabromo- [20], and hexachloroiridates [21, 22] and a variety of aquated complex ions [23] such as $[IrCl_3(H_2O)_3]^+$, $[IrCl_5(H_2O)]^-$ and $[IrCl_4(H_2O)_2]$ have been characterized, where Ir is in the (IV) oxidation state.

Attempts, however, to prepare the $[Ir(acac)_3]^+$ species electrochemically, showed that, although there was no apparent tendency for $[Ir(acac)_3]^+$ to undergo further reaction on the voltammetric time-scale, over a longer time period the oxidized species was not stable. Coulometry gave a N value of 3 ± 1 electrons/mol, indicative of multi-electron processes involving oxidation of unknown species formed after initial formation of $[Ir(acac)_3]^+$. This closely similar behavior to Ru(acac)$_3$ was also mirrored in its reaction with dimethylformamide. Using a mixed CH_3CN/DMF solvent, and observing ip_r/ip_f, as the concentration of DMF was increased, the ip_r/ip_f decreased; likewise, as the scan rate was increased, the ip_r/ip_f also increased, confirming an EC mechanism.

To obtain further information regarding the $[M(acac)_3]^+$/DMF reaction (M = Ru or Ir), a kinetic study was attempted. The simplest reaction scheme envisaged was an overall second order reaction which was first order with respect to both $[M(acac)_3]^+$ and DMF. This situation could be further simplified by running the reaction under a mixed CH_3CN–DMF solvent, but holding the DMF concentration in large excess and therefore, effectively constant (2.5 M), and varying the M(acac)$_3$ concentration, typically in the range 2×10^{-4} to 5×10^{-3} molar. The method of Nicholson and Shain [24] was used to determine rate constants for a first order following reaction by measuring ip_r/ip_f from CV. A plot of the individual rate constants obtained *versus* the M(acac)$_3$ concentration should produce a linear relationship, the gradient giving the overall second order rate constant.

We have found, however, that at a given concentration the rate constant consistently varied with scan rate. Further, a plot of rate constant at a given scan rate *vs.* concentration of M(acac)$_3$ gave a parabolic relationship. This signified that the overall second order reaction scheme put forward was too simple to represent the actual mechanism, leaving the nature of the $[M(acac)_3]^+$ DMF reaction still open to speculation.

Conclusions

The reversibility of the one-electron oxidation of Ru(acac)$_3$ and Ir(acac)$_3$ indicated the possibility that both $[Ru(acac)_3]^+$ and $[Ir(acac)_3]^+$ might be synthetically accessible. Unfortunately, however, this proved not to be the case. The ability of tris(dithio-carbamates) to stabilize the IV oxidation state has been cited to be of general occurence [9, 25]. A mixed-diketone-dithiocarbamate ligand system may result in further stability and enable isolation and characterization, not only for Ru(acac)$_3$ and Ir(acac)$_3$, but the effect on the electrochemistry on related iron systems would also be of interest (*e.g.* $[Fe(Et_2(dtc))_3]^+$ has been prepared [25]).

During the course of our study, we have assumed that both oxidation and reduction behavior has been largely metal-based, giving M(IV) and M(II) species respectively.

Studies have shown that the $[Ru(acac)_3]^0/[Ru(acac)_3]^-$ couple is strongly influenced by substituent groups on the ligand [8, 9], yielding a linear plot of $E_{1/2}$ *vs. meta*-Hammett parameter. This was interpreted as the redox active orbital possessing appreciable ligand character. The assignment of a redox-process as being substantially metal- or ligand-based in character from electrochemical studies alone must be treated with extreme caution. However, it should be noted that changing the metal centre does result in a substantial shift in half-wave potential, arguing favorably for metal-based processes.

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