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# The Electrochemical Reduction of the Bis(acetylacetonato)nickel(II) Complex in Acetonitrile

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## Abstract

The cathodic behaviour of the bis(acetylacetonato)nickel(II) complex was investigated in acetonitrile solution by cyclic voltammetry and controlled potential electrolysis. Irrespective of the electrode material employed, this species undergoes a complicated reduction process involving chemical reactions preceding and following the charge transfer step and leading to the formation of metallic nickel as the ultimate product. For this reduction, a mechanistic scheme is proposed which is consistent with the data. Evidence for the formation in the solution of mono(acetylacetonato)nickel(II) and tris(acetylacetonato)nickel(II) complexes were also obtained.

## Introduction

Bis(acetylacetonato)nickel(II) in the presence of reducing agents is a well recognized catalyst for very important organic reactions such as, for instance, oligomerization, polymerization, hydrogenation and isomerization of olefins, hydrosilylation of alkynes and coupling of organic halides [1]. As a general rule, the synthesis of organic compounds promoted in the homogeneous phase by metal complexes occurs through at least one redox step involving the metal, in which one of the organic reagents is activated. Therefore, it appears convenient to study the reduction of the mentioned complex by employing an electroanalytical procedure which is, in principle, the best approach for investigating the redox properties of an electroactive metal complex [2].

Quite discordant findings are apparent in the previously reported electroanalytical investigations on the reduction of bis(acetylacetonato)nickel(II) complex. The voltammetric behaviour of this species in 1,2-dimethoxyethane gives evidence for only one cathodic process which requires an $n_e$ value equal to unity [3]. Conversely, in dimethylsulphoxide three reduction steps are observed in which an overall number of electrons equal to two is involved [4].

In particular, conflicting evidence has been obtained in acetonitrile. Either one [5] or two [6, 7] cathodic processes have been observed in fact at a mercury electrode. In the former case [5], 0.6 mol of electrons per mol of nickel complex appears to be required in the reduction process which leads to metallic nickel; in the latter case [7], two mol of electrons are spent in the overall reduction and a soluble nickel complex is obtained. No reduction is observed on platinum electrodes [7], while a single two-electron cathodic process is detected when a glassy-carbon electrode is employed [8].

Since acetonitrile is one of the most generally employed solvents for carrying out organic reactions catalyzed by the combination of bis(acetylacetonato)nickel(II) and reducing agents, we have performed the present electroanalytical investigation on this complex just in this medium by employing three different electrodes (Pt, Hg and glassy-carbon).

## Experimental

### *Chemicals*

All the chemicals employed were of reagent grade quality. Acetonitrile was further purified by distilling repeatedly from phosphorous pentoxide and stored on molecular sieves (0.4 nm) under nitrogen atmosphere. The supporting electrolyte tetrabutylammonium perchlorate (TBAP) was prepared from perchloric acid and tetrabutylammonium hydroxide, recrystallized from methanol and dried in a vacuum oven at 50 °C.

Stock solutions of anhydrous nickel(II) perchlorate were prepared by anodic oxidation in TBAP-acetonitrile solutions of metallic nickel [9]. Tetrabutylammonium acetylacetonato (TBA-acac) and bis(acetylacetonato)nickel(II) (Niacac$_2$) were synthesized as reported in the literature [10, 11]. Fully deoxygenated nitrogen, previously equilibrated to the vapour pressure of acetonitrile, was used in the removal of dissolved oxygen.

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*Apparatus and Procedure*

Voltammetric experiments were carried out in a three-electrode cell. A glassy-carbon or a platinum disk, as well as a gold sphere freshly covered with mercury, were used as the working electrode, surrounded by a Pt-spiral counter-electrode. The potential of the working electrode was probed by a Luggin capillary-reference electrode compartment whose position was made adjustable by mounting it on a syringe barrel.

Coulometric and preparative tests were carried out in an H-shaped cell with cathodic and anodic compartments separated by a sintered glass disk. The working electrode was a glassy-carbon sheet or a platinum gauze as well as a mercury pool, and a nickel spiral was used as counter-electrode. In all cases an aqueous SCE was used as reference electrode.

The employed voltammetric unit was a three-electrode system assembled with the MP-System 1000 equipment in conjunction with a digital logic function generator made up locally [12]. The recording device was either a Hewlett-Packard 7040 A X–Y recorder or a Tracor Northern NS 570 A Digital Storage Oscilloscope/Waveform Digitizer with analogic output for X–Y recorders, depending upon the scan rate employed.

In the controlled potential electrolyses an Amel Model 552 potentiostat was used and the associated coulometer was an Amel integrator Model 731. Spectrophotometric measurements were made on a Zeiss PMQ II or a Perkin-Elmer 575 spectrophotometer. Unless otherwise stated, all the electroanalytical measurements were made at 25 °C.

For the detection of metallic nickel, suitable amounts of the electrolyzed solutions were filtered through a sintered glass crucible under nitrogen. The precipitate thus obtained was washed with degassed $CH_2Cl_2$ to remove traces of nickel complexes and then dissolved in the minimum volume of hot concentrated nitric acid. The resulting solution was assayed with the standard dimethylglyoxine test.

## Results and Discussion

Figure 1 reports the cyclic voltammetric profile recorded at a mercury electrode on acetonitrile solutions of the investigated complex. In the forward scan only one cathodic process is observed, with which one anodic peak is associated. The typical shape of surface redox processes [13] exhibited by this anodic peak allows its attribution to the reoxidation of finely divided metallic nickel evidently formed on the electrode surface during the cathodic process (as it could be visually observed). The same picture is also observed when platinum or glassy-carbon are employed as electrode materials, except for the location of the associated anodic peak which is displayed at slightly more positive potential values.

The analysis of the cathodic peak indicates that it involves a CE process, *i.e.* an electrochemical reaction

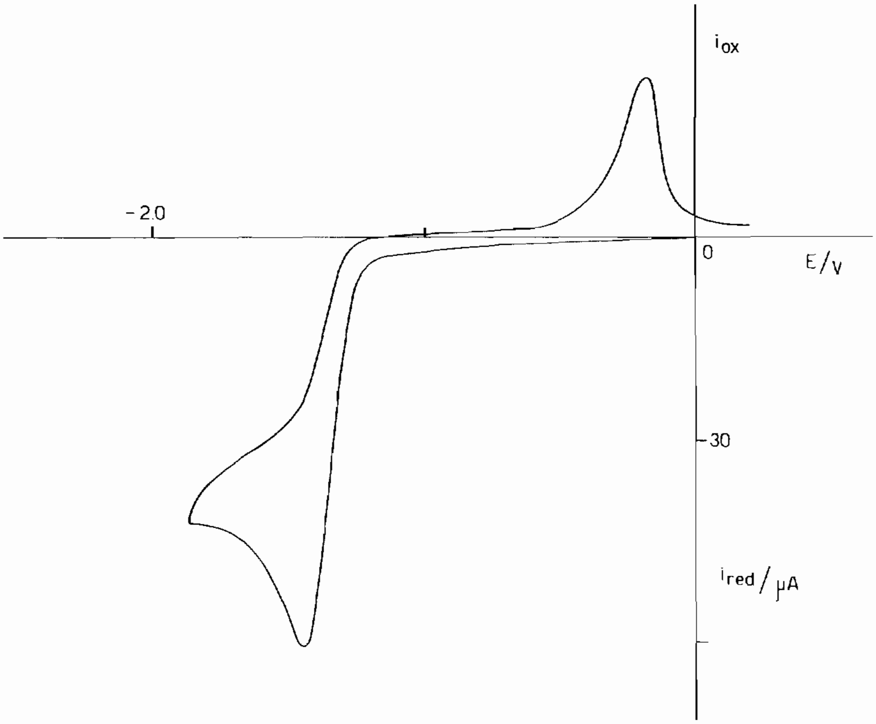

Fig. 1. Cyclic voltammetric curve recorded with a mercury covered gold microelectrode on a $CH_3CN$ solution containing $[Ni(acac)_2]$ ($5 \times 10^{-3}$ M) and TBAP (0.1 M). Scan rate 0.1 V $s^{-1}$.

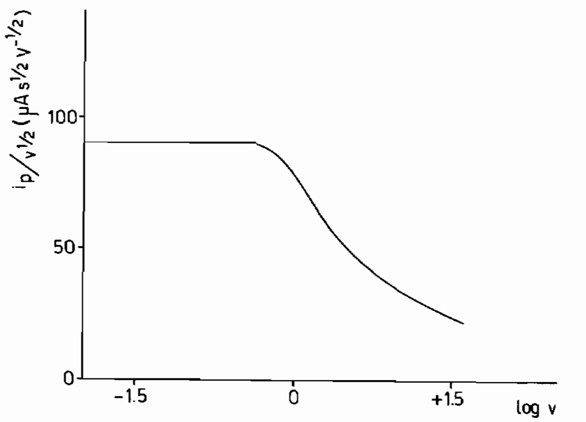

Fig. 2. Behaviour of the ratio $i_p/v^{1/2}$ as a function of the scan rate in voltammetric experiments. Experimental conditions: $[Ni(acac)_2]$ ($2.5 \times 10^{-3}$ M) and TBAP (0.1 M) in $CH_3CN$; temperature 25 °C.

in which the electrode step is preceded by a relatively slow chemical reaction providing the electroactive species. An increase of the scan rate causes in fact both the peak to take on progressively a sigmoidal shape and, at the same time, the relevant ratio $i_p/v^{1/2}$ to decrease as shown in Fig. 2 [14].

In connection with the occurrence of such an electrochemical process, it is worthwhile to note that the visible UV spectra recorded on the green acetonitrile solutions of bis(acetylacetonato)nickel(II) are coincident with those obtained (using KBr pellets) on the same complex in the solid state which is known to display a hexacoordinate octahedral structure owing to the formation of trimers [15]. Since the existence of these trimers is also well recognized in several solvents [4, 16], it is conceivable to attribute the chemical kinetic control of the cathodic process to the relatively slow occurrence of the following chemical equilibrium affording the monomeric species as the real electroactive species:

$$[Ni(acac)_2]_3 + 6\,S \overset{k}{\rightleftarrows} 3[Ni(acac)_2S_2]^* \qquad (1)$$

$(S = CH_3CN)$

Two other interesting features are presented by the cathodic process. By comparing the height of the relevant peak recorded at sufficiently low scan rates ($\leqslant 0.1$ V $s^{-1}$, *i.e.* when the preceding chemical reaction does not affect apparently the process, see Fig. 2) with that displayed by the species $[Ni(dppe)_2]^{2+}$ for which the occurrence of a one-electron reduction has been shown unambiguously [17, 18], the mol of electrons involved per mol of nickel complex result to be about 0.6. Moreover, the increase of the scan rate over 1 V $s^{-1}$ causes in the reverse scan the appearance and progressive increase of an anodic peak giving rise to an appreciably reversible cathodic–anodic system with the reduction peak.

Both these findings can be accounted for by admitting that the charge transfer is coupled not only with the mentioned preceding chemical step, but also with a following chemical reaction involving the decay of the primary reduction product and which is able to subtract a part of the electroactive species.

Controlled potential coulometric experiments substantiate these expectations in that both 0.66 mol of electrons per mol of nickel(II) initially present result to be spent in the reduction process, and finely divided metallic nickel can be detected in the electrolyzed solutions. At the end of these electrolyses the solutions remain fairly green in colour, but the relevant voltammetric profile does not give evidence of any electrochemical process. However, the cathodic peak due to the bis(acetylacetonato)nickel(II) reduction is completely restored in the voltammetric profile recorded on these electrolyzed solutions when nickel perchlorate is added in a molar ratio equal to 1 : 3 with respect to the initial nickel content. Further addition of $Ni(ClO_4)_2$ causes only the appearance and increase of a second cathodic peak located at more positive potentials (−0.9 V, see later).

The whole of these results suggests that the mentioned subtraction of the electroactive nickel complex in the following chemical reaction is caused by the $acac^-$ ions released in the decay of the primary reduction product (yielding also metallic nickel) which leads to the formation of an higher-order complex no longer reducible in the accessible potential range, according to the following reaction sequence:

$$[Ni(acac)_2S_2] + 2\,e^- \longrightarrow [Ni(acac)_2]^{2-} + 2\,S \qquad (2)$$

$$[Ni(acac)_2]^{2-} \longrightarrow Ni_{(s)} + 2\,acac^- \qquad (3)$$

$$2\,acac^- + 2[Ni(acac)_2S_2] \longrightarrow 2[Ni(acac)_3]^- + 4\,S \qquad (4)$$

$$3[Ni(acac)_2S_2] + 2\,e^- \longrightarrow 2[Ni(acac)_3]^- + Ni_{(s)} + 6\,S \qquad (5)$$

The occurrence of the preceding chemical reaction (1) prevents the study of the following reactions (3) and (4) by evaluating the change of the voltammetric response caused by a change in the potential scan rate. A definitive check for the formation of the higher-order complex $[Ni(acac)_3]^-$ has been however obtained by monitoring voltammetrically the solution during some titrations. In these titrations, TBA–acac was added stepwise to solutions containing known amounts of nickel perchlorate and the complete voltammetric picture recorded after each addition. The nickel(II) reduction peak at −1.1 V [9]

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*Here and in the following, the octahedral structure has been preferred also for the monomeric species since the corresponding square-planar monomer is expected to exhibit an intense red colour [16] which is not at all observed in the solutions.

initially present decreases progressively, while the appearance and concomitant increase of a new cathodic peak located at less negative potential values (−0.9 V, see Fig. 3, full line) is observed. This 'peak conversion' is complete for a ligand to nickel molar ratio equal to 1 : 1 and the height of the peak obtained under these conditions is equal to half of that relative to $Ni(ClO_4)_2$.

When the ligand to nickel(II) concentration ratio is greater than 1 : 1, the emerged peak lowers progressively in favour of the peak relative to the bis(acetylacetonato)nickel(II) complex which reaches its maximum height (1/3 of that relative to $Ni(ClO_4)_2$) for a molar ratio equal to 2 : 1, as shown in Fig. 3, dashed line. Further increase of the mentioned ratio up to 3 : 1 causes the complete disappearance of this last peak also (see Fig. 3).

These results leave no doubt that different nickel(II) complexes can be obtained in suitable experimental conditions. They can be easily explained by admitting that one, two or three $acac^-$ ions may enter the coordination sphere of the metal leading to the complexes $[Ni(acac)S_4]^+$, $[Ni(acac)_2S_2]$ and $[Ni(acac)_3]^-$ respectively, the last being non-electroactive. The lower height exhibited by the peak due to $[Ni(acac)_2S_2]$ if compared with that relative to $Ni(ClO_4)_2$ (which is known to involve a two-electron process) is accounted for by reaction (5), while for the reduction of the $[Ni(acac)S_4]^+$ species the following sequence has to be considered:

$$[Ni(acac)S_4]^+ + 2\,e^- \longrightarrow Ni_{(s)} + acac^- + 4\,S \qquad (6)$$

$$acac^- + [Ni(acac)S_4]^+ \longrightarrow [Ni(acac)_2S_2] + 2\,S \qquad (7)$$

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$$2\,[Ni(acac)S_4]^+ + 2\,e^- \longrightarrow [Ni(acac)_2S_2] + 6\,S + Ni_{(s)} \qquad (8)$$

It must be remarked that this last reaction also accounts for the second cathodic peak shown in the profile referring to the reduction of the monoacetylacetonato complex (see Fig. 3, full line); this peak can be attributed in fact to the bis(acetylacetonato) species formed at the electrode surface during the cathodic scan.

Further evidence for the association reactions (4) and (7) have been obtained by adding $Ni(ClO_4)_2$ to the solutions obtained at the end of the above described titration experiments and exhibiting the profile reported with a dotted line in Fig. 3. When a molar ratio 0.5 : 1 is attained between the added nickel(II) and the initial nickel(II) content, the peak due to the bis(acetylacetonato) complex (dashed line in Fig. 3) is regenerated as it occurs also after addition of $Ni(ClO_4)_2$ to the exhaustively electrolyzed solutions (see above). Its height is in full agreement

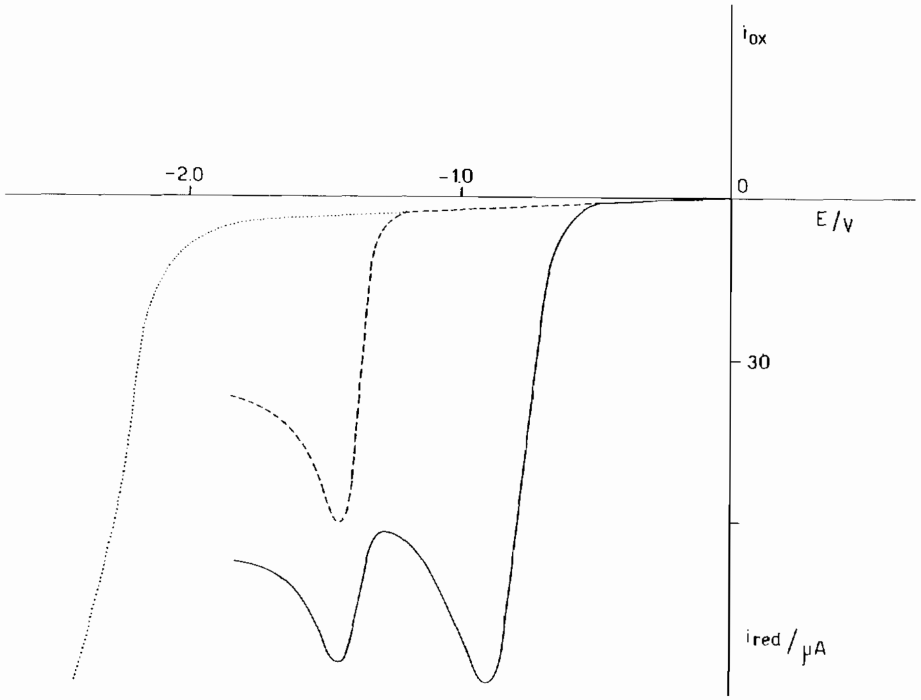

Fig. 3. Voltammetric curves recorded with a mercury covered gold microelectrode on a $CH_3CN$ solution containing $Ni(ClO_4)_2$ ($5 \times 10^{-3}$ M), TBAP (0.1 M) and TBA–acac added in the following molar ratios with respect to nickel(II): (——) 1 : 1; (– – –) 2 : 1; (· · · ·) 3 : 1. Scan rate 0.1 V $s^{-1}$.

with the following ligand-comproportionation reaction:

$$2[\mathrm{Ni(acac)_3}]^- + \mathrm{Ni}^{2+} \xrightarrow{6\ \mathrm{S}} 3[\mathrm{Ni(acac)_2S_2}] \tag{9}$$

Moreover, further addition of $Ni(ClO_4)_2$ up to ratios of 2 : 1 causes the further conversion of this profile into that relative to the mono(acetylacetonato) complex, the relevant peak exhibiting just the height expected on the basis of the reaction:

$$[\mathrm{Ni(acac)_2S_2}] + \mathrm{Ni}^{2+} \xrightarrow{6\ \mathrm{S}} 2[\mathrm{Ni(acac)S_4}]^+ \tag{10}$$

As to the reports mentioned in the Introduction section [7, 8] which claim that two mol of electrons per mol of nickel(II) complex are required in its reduction process, we wish to emphasize that such a result is obtained by us, as well as a pale-yellow soluble reduction product, only when not carefully purified acetonitrile is employed as the solvent. From our previous experience [19], we feel that metallic nickel is no longer formed in the reduction sequence (2–3) in that the 'bare' nickel atoms generated near the electrode surface in reaction (3) are trapped by activated olefins like acrylonitrile (which are known to be present as by-products in commercially available acetonitrile), before the metallic nickel lattice is allowed to grow up.

To substantiate this view, we have carried out some experiments on bis(acetylacetonato)nickel(II) solutions in carefully purified acetonitrile to which acrylonitrile was added in a molar ratio 2 : 1 with respect to nickel(II). Controlled potential electrolyses do not require in this case two mol of electrons per mol of nickel initially present, but lead to pale-yellow solutions in which metallic nickel is no longer observed. This finding is in agreement with the formation of a bisacrylonitrile nickel (0) complex whose existence is well established [20]. However, it points out also that acrylonitrile cannot be the only by-product causing the mentioned increase of the electron consumption when the reaction is performed in acetonitrile which was not carefully purified. Evidently, other impurities must be present which may interact with the acetylacetonato ion released in reaction (3), thus making it unable to subtract the electroactive species in reaction (4).

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