

Stabilization of Nickel(I) by a Mixed Phosphine–Olefin Coordination Sphere. An Electroanalytical Approach

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Abstract

The cathodic behaviour of both anhydrous nickel(II) perchlorate and of the nickel(II)–triphenylphosphine system in the presence of a variety of differently activated olefins has been investigated in acetonitrile. A combination of electroanalytical and spectrophotometric measurements have made possible the synthesis and the characterization of various nickel(0) and nickel(I) complexes.

The employed electroanalytical tools have also made it possible to demonstrate that a purely (see text) olefinic ligand coordination shell is able to stabilize only the zero oxidation state and not the +1 one. Two different situations are observed when a mixed coordination sphere PPh_3 –olefin is made available to the metal centres.

Moderately activated olefins such as ethyl acrylate and acrylonitrile stabilize the +1 oxidation state with respect to the zero and +2 ones, while very activated olefins (like diethyl fumarate, diethyl maleate and fumaronitrile) act in the opposite way.

Introduction

We previously reported on the influence of the nature of trivalent phosphorus ligands on the relative stability of nickel(II), nickel(I) and nickel(0) in acetonitrile [1]. As to the problem of the stability of nickel(I) towards disproportionation to nickel(II) and nickel(0), we concluded that this stems from a proper balance of σ -donor– π -acceptor properties of the phosphorus ligands present in the coordination sphere of the metal.

More recently, we became interested in testing the possibility of stabilizing nickel(I) by a mixed

phosphine–olefin coordination shell and found [2] that the triphenylphosphine–acrylonitrile pair is well suited to this purpose.

On the basis of these results, we have studied the cathodic behaviour of nickel(II) in the presence both of PPh_3 and of a number of olefins exhibiting various degrees of activation towards coordination to metal centres [3].

Experimental

Chemicals

All the chemicals employed were of reagent grade quality. Acetonitrile was further purified by distilling repeatedly from phosphorus pentoxide and was stored on molecular sieves (3 Å) 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 Ni(II) perchlorate in acetonitrile were prepared by anodic oxidation of metallic nickel in TBAP–acetonitrile solutions, as previously described [4]. Triphenylphosphine was crystallized from methanol and stored in a vacuum oven in the dark.

Nitrogen (99.99%), previously equilibrated to the vapour pressure of acetonitrile, was used in the removal of dissolved oxygen.

Apparatus and Procedure

Voltammetric and potential-dependent chronoamperometric experiments were carried out in a three-electrode cell. The working electrode was a platinum sphere or a glassy-carbon disk surrounded by a Pt-spiral counterelectrode. The potential of the

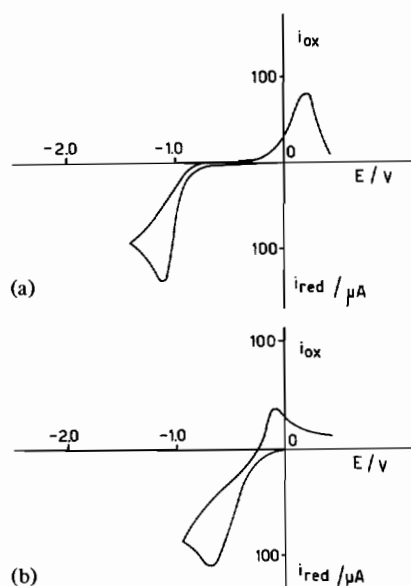


Fig. 1. a) Cyclic voltammetric curve recorded with a platinum microelectrode on a MeCN solution containing $\text{Ni}(\text{ClO}_4)_2$ (1.0×10^{-3} M) and TBAP (0.1 M). Scan rate 0.1 V s^{-1} . b) Cyclic voltammetric curve recorded with a platinum microelectrode on a MeCN solution containing $\text{Ni}(\text{ClO}_4)_2$ (1.0×10^{-3} M), FN (1.0×10^{-3} M) and TBAP (0.1 M). Scan rate 0.1 V s^{-1} .

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 platinum gauze while a mercury pool was used as counterelectrode.

In all cases an aqueous SCE was used as reference electrode.

The voltammetric unit employed was a three-electrode system assembled with the MP-System 1000 equipment in conjunction with a digital logic function generator made up in these laboratories [5]. 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 analogue 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 558. In the spectrophotometric measurements, a Zeiss PMQ II spectrophotometer and a Bruker Model ER 100-D ESR spectrometer were employed.

Unless otherwise stated, all the electroanalytical measurements were made at 20°C and in the experiments carried out in the presence of triphenyl-

TABLE I. Reduction Potentials (E_{pc}) of $\text{Ni}(\text{ClO}_4)_2$ in the Presence of the Employed Olefins together with Oxidation Potentials (E_{pa}) and Colour of the Obtained Nickel(0) Complexes. Peak potentials from cyclic voltammograms at a scan rate of 0.1 V s^{-1} are quoted vs. an aqueous SCE.

Olefin	E_{pc} (V)	E_{pa} (V)	Colour of the Ni^0 Complex
FN	-0.70	-0.10	red
FEt	-0.95	-0.15	red
MEt	-0.95	-0.15	red
AN	-1.05	-0.20	dark red

phosphine a PPh_3 to nickel molar ratio equal to 10:1 was employed.

Results and Discussion

The voltammetric picture exhibited by electro-generated nickel(II) perchlorate in acetonitrile is reported in Fig. 1a. As previously reported by us [4], the species $[\text{Ni}(\text{NCMe})_6]^{2+}$ is cathodically reduced in an irreversible two-electron process to metallic nickel which can be reoxidized to nickel(II) in the associated anodic peak. The addition of activated olefins or of mixtures of these olefins and PPh_3 causes profound changes in the observed voltammetric behaviour due to the formation of nickel complexes of the metal in low oxidation states.

The results obtained in the various conditions are reported in the following sections.

Nickel-Olefin Systems

We employed fumaronitrile (FN), diethyl fumarate (FEt), diethyl maleate (MEt) and acrylonitrile (AN). Investigations on more activated olefins such as tetracyanoethylene and maleic anhydride were precluded by the occurrence of their electrochemical reduction at potential values less cathodic than those required for reducing nickel(II). On the other hand, less activated olefins (for instance 3-methyl-2-butene) were not employed as they were found to be unable to modify appreciably the voltammetric profile reported in Fig. 1a.

The addition of increasing amounts of free olefin to a solution containing a known amount of the species $[\text{Ni}(\text{NCMe})_6]^{2+}$ causes a progressive lowering of the nickel(II) reduction peak and the appearance and concomitant increase of a new peak located at less cathodic potential values (see Table I). At the same time, the anodic peak in Fig. 1a decreases in height and a new peak develops at more negative potentials. This 'conversion' appears complete for an olefin to nickel(II) molar ratio equal to 2:1

TABLE II. Peak Potential Values (V) Recorded from Cyclic Voltammograms at a Scan Rate of 0.1 V s⁻¹ and Quoted vs. an Aqueous SCE.

System in MeCN	<u>E_{pc}</u>	<u>E_{pc}</u>	<u>E_{pa}</u>	<u>E_{pa}</u>	<u>E_{pa}</u>
	Ni ^{II} → Ni ⁰	Ni ^I → Ni ⁰	Ni ⁰ → Ni ^I	Ni ^I → Ni ^{II}	Ni ⁰ → Ni ^{II}
Ni-PPh ₃	-0.86	-0.81	-0.75	+0.12	-
Ni-PPh ₃ -AEt	-0.78	-0.72	-0.32	+0.15	-
Ni-PPh ₃ -AN	-0.76	-0.71	-0.20	+0.15	-
Ni-PPh ₃ -MEt	-0.77	-	-	-	+0.20
Ni-PPh ₃ -FEt	-0.77	-	-	-	+0.20
Ni-PPh ₃ -FN	-0.73	-	-	-	+0.23

(see Fig. 1b) and the height of the cathodic peak obtained under these conditions equals that relative to [Ni(NCMe)₆]²⁺, thus indicating that a two-electron process is again involved. The voltammetric picture is not affected by further addition of olefin up to ratios of 30:1.

Spectra recorded in the visible range on solutions containing [Ni(NCMe)₆]²⁺ show no change upon addition of excess olefin, thus indicating that the effect of this species on the voltammetric picture has to be due to its coordination to the metal in the zero oxidation state which is evidently the reduction product. Moreover, the fact that no further change in the voltammetric profile can be observed for olefin to nickel ratios higher than 2:1 indicates that just two molecules of olefin enter the coordination sphere of nickel(0)*.

Controlled potential coulometric experiments confirm that the cathodic process leads to nickel(0) without any indication of the existence of nickel(I) species and any formation of metallic nickel.

In spite of the irreversible character of the electrochemical processes, an appreciable effect on the peak potential is caused by the differently activated olefins. Thus, the higher the activation of the olefin, the easier the reduction of nickel(II) and comparatively more difficult the oxidation of nickel(0).

Nickel-PPh₃-Moderately Activated Olefins (acrylonitrile, ethyl acrylate) Systems

The voltammetric picture exhibited by electro-generated nickel(II) perchlorate in acetonitrile in the presence of triphenylphosphine is reported in Fig. 2. As previously reported by us [6], nickel(II) is present in solution as [Ni^{II}(PPh₃)₂(NCMe)₄]²⁺ and it is directly reduced in a two-electron process to the complex [Ni⁰(PPh₃)₄]. The two anodic one-electron

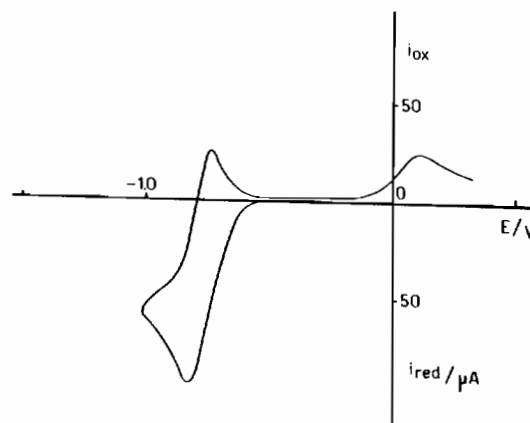


Fig. 2. Cyclic voltammogram recorded with a platinum microelectrode on a MeCN solution containing Ni(ClO₄)₂ (1.5 × 10⁻³ M), PPh₃ (1.5 × 10⁻² M) and TBAP (0.1 M). Scan rate 0.1 V s⁻¹.

peaks observed in the reverse scan have been found to be due to the stepwise oxidation of nickel(0) produced at the electrode surface to nickel(I) (as [Ni(PPh₃)₄]⁺) and nickel(II) respectively.

The presence of acrylonitrile (AN) or ethyl acrylate (AEt) modifies in the same way this voltammetric behaviour, the only difference being the potentials at which the electrochemical processes take place (see Table II). An anodic shift of both the irreversible two-electron reduction peak and of the two one-electron associated anodic ones is observed, and this change is complete when a 1:1 olefin to nickel molar ratio is achieved.

Cyclic voltammetric tests carried out with this molar ratio either at low temperature or at high scan rates (10 V s⁻¹) make possible the observation of a cathodic one-electron peak *d'* (easily distinguishable from the two-electron one *a'* which results to be shifted towards more cathodic potentials owing to its irreversibility; see Fig. 3), which gives rise to a cathodic-anodic irreversible system *b'*-*d'* with the first anodic peak.

*This statement does not exclude that the species [Ni⁰(olefin)₂] may exist in fast equilibrium with [Ni⁰(olefin)(NCMe)₂] (see reference [1]).

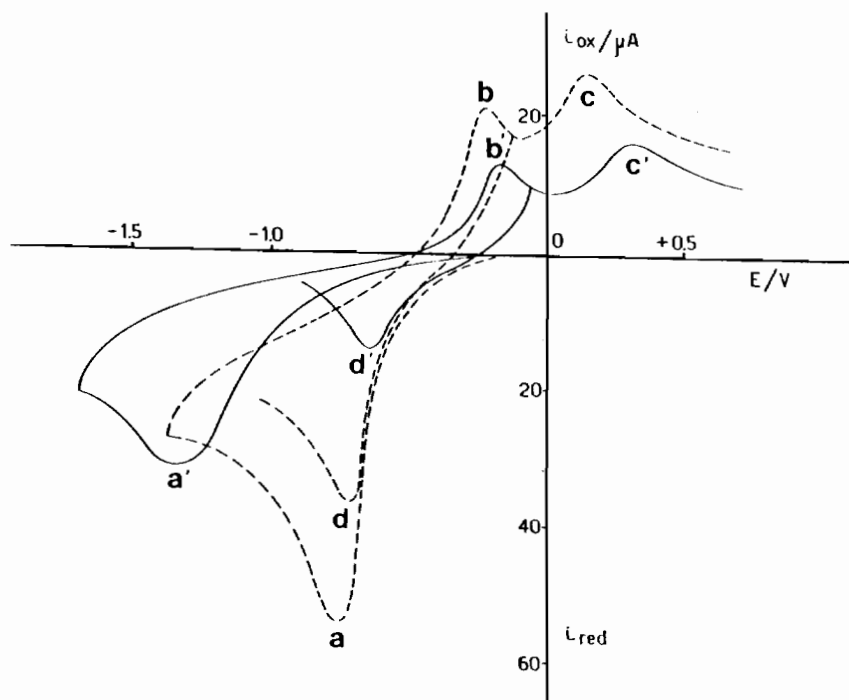
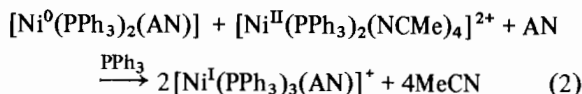
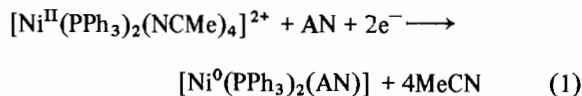


Fig. 3. Cyclic voltammetric curves recorded with a platinum microelectrode on a MeCN solution containing $\text{Ni}(\text{ClO}_4)_2$ (2.0×10^{-3} M), PPh_3 2.0×10^{-2} M AN (2.0×10^{-3} M) and TBAP (0.1 M); (---) at 20°C; (—) at -30°C. Scan rate 0.1 V s^{-1} . See the text for the meaning of the reported letters. Peaks *d* and *d'* are observed on the second cathodic sweep after reversing the scan near -0.1 V.

We have previously demonstrated [2] on the basis of electroanalytical results that the reduction of nickel(II) in the presence of PPh_3 -AN mixtures can give mixed-coordination sphere complexes both of nickel(I) and nickel(0). Thus, nickel(0) is directly obtained by a two-electron reduction at peak *a*, while nickel(I) can be obtained either by one-electron oxidation of nickel(0) at peak *b*, or by an apparently one-electron reduction at peak *b*, which actually masks an E.C. process implying a two-electron reduction of fifty per cent nickel(II) to nickel(0) and a fast comproportionation of this product with the depolarizer, according to the following sequence:



We confirm here this electrochemical pattern for the nickel- PPh_3 system also when a similarly activated olefin ligand like ethyl acrylate is present, and we offer a further chemical evidence for the stabilizing effect of PPh_3 and AN or AEt on the oxidation state +1 for nickel as a coordination centre. We

could in fact demonstrate the occurrence of reaction (2) by mixing equimolar amounts of the electro-generated nickel(0) and nickel(II) reagents and by detecting the nickel(I) product by cyclic voltammetric

TABLE III. Visible and Near-infrared Spectral Data.

System in CH_3CN	λ_{max} (nm)	
	Ni^{I} complex	Ni^0 complex
Ni- PPh_3	1525	undetermined
Ni- PPh_3 -AEt	1500	undetermined
Ni- PPh_3 -AN	1450	undetermined
Ni- PPh_3 -MEt	-	430
Ni- PPh_3 -FEt	-	430
Ni- PPh_3 -FN	-	≤ 410

tests (peaks *c* and *d* in Fig. 3 by direct anodic and cathodic scans).

Spectrometric evidence for the formation of nickel(I) species and for their geometric configuration is given by near-infrared spectrophotometry and ESR spectrometry. The presence of a ligand field band in the range 1400-1500 nm [1, 7, 8] (see Table III) coupled with the observation of a broad frozen solution ESR signal with no

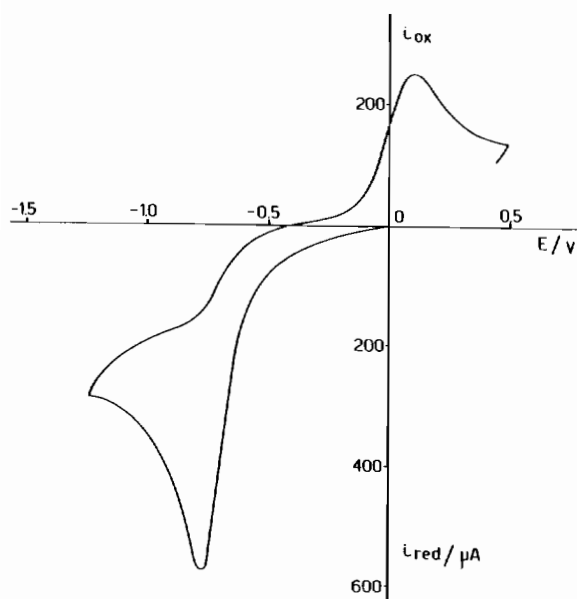


Fig. 4. Cyclic voltammogram recorded with a platinum microelectrode in a MeCN solution containing Ni(ClO₄)₂ (5.5×10^{-3} M), PPh₃ (5.5×10^{-2} M), FEt (5.5×10^{-3} M) and TBAP (0.1 M). Scan rate 0.1 V s^{-1} .

³¹P hyperfine structure not only confirm the formation in the solution of nickel(I) complexes, but also indicate that they exhibit an essentially tetrahedral configuration [8, 9].

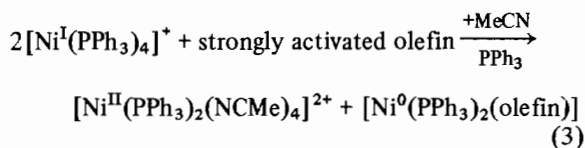
Nickel-PPh₃-Very Activated Olefins (diethyl fumarate, diethyl maleate, fumaronitrile) Systems

Voltammetric tests carried out on nickel(II) solutions containing a 10:1 PPh₃ to nickel ratio and increasing concentrations of added activated olefin show that the cathodic peak relative to the reduction of [Ni(PPh₃)₂(NCMe)₄]²⁺ (see Fig. 2) decreases, while a new cathodic two-electron peak located at less negative potentials arises (see Table II). This 'peak conversion' is complete for the olefin to nickel ratio equal to 1:1 (see Fig. 4). Further olefin addition (up to 30:1) does not affect this voltammetric picture.

Parallel spectrophotometric measurements show that the addition of olefin does not modify the coordination sphere of nickel(II), thus indicating that the anodic shift of the two-electron irreversible cathodic peak is due to the coordination of the olefin to nickel(0) which is evidently produced in the reduction process. No evidence for the formation of nickel(I) species could in fact be obtained by: (i) cyclic voltammetric tests, (ii) potential dependent chronoamperometry [10], and (iii), controlled potential coulometric experiments combined with both spectrophotometric monitoring and cyclic voltammetric control on the solutions during the electrolyses. The electronic spectra recorded under these

conditions show in fact the direct conversion of nickel(II) into [Ni⁰(PPh₃)₂(olefin)] (spectral data in Table III).

The instability of the +1 oxidation state of nickel in the presence of PPh₃ and strongly activated olefins has been proved by two other tests. In contrast with the findings obtained when moderately activated olefins are employed (see earlier), by letting equimolar amounts of electrogenerated [Ni⁰(PPh₃)₂(olefin)] and [Ni^{II}(PPh₃)₂(NCMe)₄]²⁺ to interact in acetonitrile, no comproportionation reaction (see eqn. 2) is found to occur. Moreover, addition of any strongly activated olefin to acetonitrile solutions of electrogenerated [6] [Ni^I(PPh₃)₄]⁺ in molar ratio 0.5:1, causes the immediate valence disproportionation depicted in the following equation:



as seen by cyclic voltammetric tests performed on the obtained solution.

Conclusions

We support and confirm in this paper the general conclusion drawn in ref. 1 concerning the role played by the ligand in the stabilization of nickel(I) towards valence disproportionation to nickel(0) and nickel(II). Thus, if only essentially π-acceptor ligands like olefins are allowed to enter the coordination sphere of the reduced nickel centres, the oxidation state zero and not the +1 is stabilized. The same happens when a mixed coordination sphere, *i.e.* PPh₃-very activated olefin, is made available to the reduced nickel centres. In fact, according to our reasoning [1], this can be expected in that the co-existence of a moderate σ-donor-π-acceptor ligand like PPh₃ with very good π-acceptor ones (strongly activated olefins) destabilizes nickel(I) in favour of nickel(0) and nickel(II). On the contrary, when a well-suited mixed coordination sphere (*i.e.* PPh₃-moderately activated olefins) is offered to nickel(I), a complete thermodynamic stabilization of this oxidation state is obtained. Therefore, we conclude that an average suitably soft coordination sphere is really the most convenient one for stabilizing nickel(I).

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