

Electrochemical Synthesis of Tris(Tri-*o*-tolylphosphite)nickel(0)

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*An electrochemical procedure for the preparation of tris(tri-*o*-tolylphosphite)nickel(0) in acetonitrile solution is suggested. This procedure includes two steps: 1) the preliminary preparation of an extremely pure nickel(II) solution by anodic oxidation of metallic nickel and 2) the cathodic reduction of this solution on mercury in the presence of an excess of tri-*o*-tolylphosphite, this excess being necessary to prevent the formation of metallic nickel.*

*The electrochemical behaviours of a nickel electrode and of tris(tri-*o*-tolylphosphite)nickel(0) in acetonitrile are also reported.*

Introduction

The growing industrial demand for highly selective, low-cost homogeneous catalysts has recently stimulated considerable interest in the cathodic behaviour of coordination compounds.

Much research in this area is now in progress with the more or less remote perspective of generating electrochemically *in situ*, and possibly regenerating cyclically, the species properly suited for specific catalytic purposes.

It is known that nickel is one of the most important metals for homogeneous catalysis [1]. In particular, the complex tetrakis(tri-*p*-tolylphosphite)nickel(0), (Ni[P(O-*p*-tol)₃]₄), is a well recognized catalyst for the hydrocyanation of olefins [2]. The related complex tris(tri-*o*-tolylphosphite)nickel(0), (Ni[P(O-*o*-tol)₃]₃), is probably the most thoroughly investigated nickel(0) species and is currently prepared by chemical reduction of Ni(NO₃)₂·5H₂O with NaBH₄ in acetonitrile [3].

With the aim of contributing to the emerging trend to employ electrochemical methods in option to chemical ones for the generation of catalytically

interesting metal complexes, we report an electrochemical investigation on the Ni/nickel(II) and nickel(II)/Ni[P(O-*o*-tol)₃]₃ systems in acetonitrile, in which solvent Ni[P(O-*o*-tol)₃]₃ is known to exhibit its catalytic activity [2].

Experimental

Chemicals and Reagents

All the chemicals employed were of reagent grade quality. Reagent grade acetonitrile was further purified by distilling repeatedly from phosphorus pentoxide and stored over molecular sieves (3Å) in a nitrogen atmosphere. The supporting electrolyte tetrabutylammonium perchlorate (TBAP) was prepared from perchloric acid and tetrabutylammonium hydroxide and crystallized twice from methanol.

The chemical preparation of Ni[P(O-*o*-tol)₃]₃ was carried out according to the literature [3].

All operations were performed under 99.99% nitrogen, which, when used to remove the dissolved oxygen in acetonitrile, was previously equilibrated to the correct vapour pressure.

Apparatus and Procedure

All the electrochemical tests were carried out in a H-shaped cell with anodic and cathodic compartments separated by a sintered glass disk. In all cases the counter electrode was a mercury pool and the reference electrode was an aqueous SCE.

In coulometric and preparative experiments the working electrode was either a mercury pool or a nickel spiral. In voltammetric tests the working electrode was either a gold sphere freshly covered with mercury or a thin nickel wire.

The voltammetric unit was a three electrode system assembled with the MP-System 1000 equip-

ment in conjunction with a digital logic function generator [4]; the recording device was a Hewlett-Packard 7004 B X-Y recorder.

In the controlled potential electrolyses an Amel Model 557 SU potentiostat was used and the associated coulometer was an Amel integrator model 558.

Vis-u.v. spectra were recorded with a Optica CF4 spectrophotometer.

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 dimethylglyoxime test.

Results and Discussion

The accessible potential range for a nickel microelectrode in a 0.1 M TBAP, acetonitrile solution is illustrated in Fig. 1.

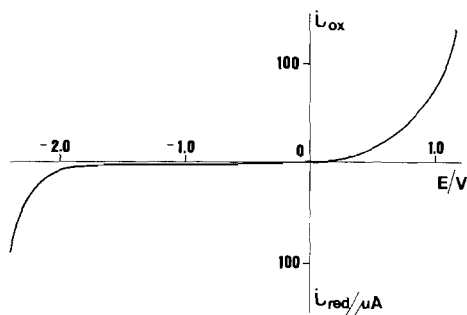


Fig. 1. Single sweep voltammogram obtained at a nickel microelectrode in a 0.1 M TBAP, CH_3CN solution. Scan rate: 0.1 Vs^{-1} . Potentials are scanned from 0.0 V both in cathodic and in anodic direction.

As the cathodic limit is very close to that found by employing a platinum microelectrode [5], we suggest that also in the present case the depolarizing process is the reduction of quaternary ammonium ions. In contrast, the anodic limit occurs at potential values at which neither the solvent nor the perchlorate ions could be oxidized [5], thus indicating that the depolarizing process must be the oxidation of the electrode material.

The shape of the anodic branch enables one to state that the anodic process exhibits a high irreversibility degree. To check whether the anodic process led to the formation of nickel(II) species, controlled potential coulometric experiments were carried out at +1.0 V by using a nickel anode and the resulting pale blue solutions were then titrated with EDTA after suitable addition of water [6]. The agreement between the coulombs used and the mol of

EDTA employed substantiated the quantitative yield in the nickel(II) production.

Voltammetric tests carried out on the solutions obtained after nickel oxidation revealed that the nickel(II) reduction is not detectable on a nickel microelectrode. On the contrary, cyclic voltammetric tests performed by using a stationary mercury microelectrode gave evidence of nickel(II) reduction as shown in Fig. 2.

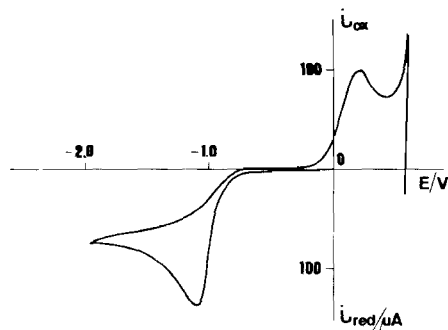


Fig. 2. Cyclic voltammogram recorded with a mercury microelectrode on a $3 \times 10^{-3} \text{ M}$ nickel(II), 0.1 M TBAP, CH_3CN soln. Scan rate 0.2 Vs^{-1} .

This figure shows that an anodic peak, located at about +0.20V, is associated to the nickel(II) reduction one at -1.1 V; this anodic peak can be reasonably attributed to the reoxidation of metallic nickel produced in the cathodic process.

The occurrence of the nickel(II) reduction process and the anticipated oxidation of metallic nickel (in comparison with that observed by using a nickel microelectrode) indicate that the nickel(II)/nickel couple exhibits a lower irreversibility degree on a mercury surface. However, no detailed electrochemical study of the electron transfer process could be performed owing to the jamming effect due to the formation of finely divided metallic nickel on the electrode surface as could be visually observed.

Controlled potential coulometric experiments carried out at -1.2 V on a mercury pool in solutions containing electrochemically generated nickel(II), allowed one to determine that the process required the same number of coulombs involved in the nickel oxidation. At the end of these cathodic reductions finely divided metallic nickel could be detected in the solutions. These findings appear as further supports for the quantitative yield in the nickel oxidation.

In order to explore the possibility of the electrochemical preparation of the tris(tri-*o*-tolylphosphite)-nickel(0) complex, a large excess (100:1) of tri-*o*-tolylphosphite was added to the acetonitrile solution containing nickel(II).

Cyclic voltammetric experiments carried out on a mercury electrode showed that the peak potential

relative to the nickel(II) reduction did not change. On the contrary, the associated anodic peak at +0.20 V (see Fig. 2) disappeared, while a new anodic peak located at more negative potentials (-0.05 V) could be observed after traversing the above mentioned cathodic peak.

These findings clearly indicate that the "bare" nickel atoms, generated at the electrode surface, are trapped by the tri-*o*-tolylphosphite ligand before the metallic nickel lattice is allowed to grow up. The fact that the nickel(II) reduction peak was not shifted towards more anodic potential values, as expected when a chemical reaction takes place after a charge transfer step, can be reasonably explained on taking into account the irreversibility degree of this cathodic process.

Controlled potential coulometric experiments were carried out on a mercury cathode at -1.20 V on nickel(II) acetonitrile solutions in the presence of a large excess of tri-*o*-tolylphosphite. These experiments indicated that two mol of electrons per mol of nickel(II) were again used. The electrolyzed solution appeared pale yellow in colour and no trace of metallic nickel could be observed.

The voltammetric picture exhibited by these electrolyzed solutions on a mercury microelectrode is reported in Fig. 3. It has to be pointed out that the height of both the cathodic and anodic peak was affected by the stirring of the solution, thus indicating that the product responsible of these peaks is present in the solution.

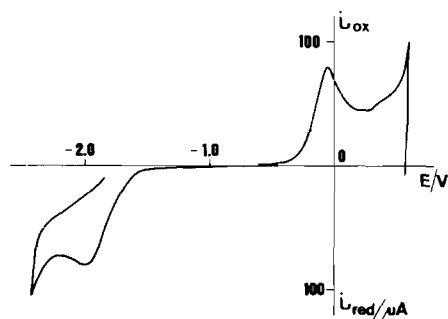


Fig. 3. Single sweep voltammogram obtained at a mercury microelectrode in a $2.5 \times 10^{-3} M$ $Ni[P(O-o-tol)_3]_3$, 0.1 M TBAP, CH_3CN soln. Scan rate $0.2 V s^{-1}$. Potentials are scanned from 1.0 V both in cathodic and in anodic direction.

The voltammetric behaviour shown in Fig. 3 was exhibited also by an acetonitrile solution of the chemically prepared $Ni[P(O-o-tol)_3]_3$, thus showing that this complex can be easily obtained by cathodic reduction of nickel(II) species in the presence of tri-*o*-tolylphosphite. A comparison of the vis.-u.v. spectra of an authentic sample of $Ni[P(O-o-tol)_3]_3$ in acetonitrile with the spectra of the solutions resulting from preparative electrolyses confirmed the success of the electrochemical preparation.

In this connection it has been reported that nickel atom in the complex $Ni[P(O-o-tol)_3]_3$ achieves tetra-coordination in acetonitrile by coordinating a solvent molecule [7], with consequent colour change from red to pale yellow. A further check of the effectiveness of our electrochemical preparation was obtained by evaporating the resulting solution under vacuum and dissolving the residual solid in benzene. The vis.-u.v. spectrum of the red-orange solution thus obtained exhibited the absorption peak at 407 nm, with a shoulder at 450 nm, characteristic of the three-coordinate compound [7].

The $Ni[P(O-o-tol)_3]_3$ yield was no longer quantitative when $P(O-o-tol)_3$ /nickel(II) mol ratios lower than 15:1 were employed, as revealed by some formation of finely divided metallic nickel, which could be visually observed. Even under these unfavourable conditions, however, quantitative yields could be obtained by lowering the nickel(II) reduction current. This could be achieved by shifting the potential value of the mercury electrode in the anodic direction just at the rising portion of the nickel(II) reduction peak (see Fig. 2). These findings clearly indicate that the reaction rate between the "bare" nickel(0) produced at the electrode surface and the ligand is comparable with that of metal lattice growth.

It is evident from the above reported results that $Ni[P(O-o-tol)_3]_3$ cannot be electrochemically prepared in a pure state, as a significant excess of free ligand is necessary to prevent the undesired reduction of nickel(II) to metallic nickel.

The recovery of the nickel(0) complex from the solution requires of course the separation of the supporting electrolyte (TBAP) which is rather difficult owing to the high solubility of this compound in common organic solvent. This difficult can be overcome on using $NaClO_4$ as the supporting electrolyte. In this case the nickel(0) complex can be easily obtained by evaporating the acetonitrile under vacuum and extracting with an organic solvent with a low dielectric constant, in which $NaClO_4$ is sparingly soluble. When $NaClO_4$ is used as supporting electrolyte, the cathodic limit of the solvent is noticeably anticipated owing to the formation of sodium amalgam at about -1.7 V. This potential limit is however sufficiently cathodic to make possible the desired nickel(II) reduction.

The electrochemical synthesis of $Ni[P(O-o-tol)_3]_3$ using an electrochemical cell set up with a nickel anode and a mercury cathode was also attempted. These experiments were devised to avoid the nuisance of two distinct electrochemical processes: the first one to prepare nickel(II) in acetonitrile (Ni anode) and the second one to reduce it in the presence of $P(O-o-tol)_3$ (Hg cathode).

It has been preliminary checked by voltammetric analysis that the $Ni[P(O-o-tol)_3]_3$ oxidation on a nickel microelectrode is affected by a considerable

overvoltage, in that no oxidation peak could be detected in contrast with that observed by using a mercury microelectrode (Fig. 3). For this reason in carrying out the attempts of the electrochemical synthesis by the mentioned apparatus, the potential controlled was that of the Hg cathode, with the aim to prevent the possible reduction of $\text{Ni}[\text{P}(\text{O}-o\text{-tol})_3]_3$ (see Fig. 3).

In the solutions electrolyzed in this way, the presence of $\text{Ni}[\text{P}(\text{O}-o\text{-tol})_3]_3$ could be detected by voltammetric and spectrophotometric tests as described above.

However, in controlled potential coulometric experiments carried out on solutions containing suitable amounts ($5 \times 10^{-3} M$) of the nickel(0) complex chemically prepared, on using the same apparatus described above, we found that the current efficiency could not be equal to one. On applying, in fact, to the nickel anode the potential value at which it resulted polarized in the operative electrolyses, it could be ascertained that a not negligible oxidation of $\text{Ni}[\text{P}(\text{O}-o\text{-tol})_3]_3$ was concomitant with the nickel anode oxidation. This observation was based on the voltammetric response obtained on a mercury microelectrode after suitable amounts of coulombs were spent in the oxidation process: the height of the anodic peak relative to $\text{Ni}[\text{P}(\text{O}-o\text{-tol})_3]_3$ oxidation

(see Fig. 3) appeared, in fact, to decrease gradually with the progress of the anodic oxidation. It could be roughly estimated that about 90% of the current was due to the oxidation of the anode material to nickel(II), while the residual 10% was spent in the $\text{Ni}[\text{P}(\text{O}-o\text{-tol})_3]_3$ oxidation on assuming for it a one electron process.

It can be hence concluded that this last preparative procedure, although it allows one to accumulate the nickel(0) complex in the solution, does not produce the complex in a pure state but contaminated by its oxidation products.

References

- 1 F. W. Jolly and C. Wilke, "The Organic Chemistry of Nickel", vol. 2, Academic Press, New York, 1974.
- 2 B. W. Taylor and H. E. Swift, *J. Catal.*, **26**, 254 (1972).
- 3 W. C. Seidel and L. W. Gosser in G. W. Parshall (ed.), "Inorganic Syntheses", vol. 15, McGraw-Hill, New York, 1974.
- 4 F. Magno, G. Bontempelli, G. A. Mazzocchin and I. Patanè, *Chem. Instrum.*, **6**, 239 (1975).
- 5 C. K. Mann in A. J. Bard (ed.), "Electroanalytical Chemistry", vol. 3, M. Dekker, New York, 1969.
- 6 G. Schwarzenbach and H. Flaschka, "Complexometric Titrations", Methuen, London, 1969.
- 7 C. A. Tolman, *Inorg. Chem.*, **10**, 1540 (1971).