Electroanalytical Investigation on Ligand-disproportionation and -exchange Equilibria in Nickel(II) and Nickel(I) Halide Phosphine Complexes in Acetonitrile

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Redox reactions of $[NiL_2X_2]$ complexes (L = PPh_3; X = Cl, Br, or I) at platinum electrodes in acetonitrile solution have been investigated by cyclic voltammetry, controlled-potential electrolysis, and spectrophotometry. The complexes undergo quantitative ligand disproportionation giving ionic species, and the nickel(I) complexes obtained as reduction products exhibit ligand-exchange equilibria. The nickel(0) species obtained in a further reduction process is not involved in any ligand-exchange reaction. The results demonstrate that the degree of reversibility of the redox processes depends markedly on the nature of the ligand set present in both the redox partners. The dependence of the reduction potentials on the nature of the halide ligands is discussed.

RECENTLY we reported an electroanalytical study of the Ni^{II}–Ni^{I}–Ni^{0}–PPh_3 system in acetonitrile.[1] The basic aim of this work was to get information on the mechanism of the electrocatalyzed coupling reaction of organic halides carried out in the presence of nickel(II) and triphenylphosphine.[2] In particular, it was observed that the halide ions released in the course of this process appeared to be able to modify the voltammetric behaviour described in ref. 1 as a consequence of their ability to form stable bonds with nickel in its higher oxidation states. The high degree of irreversibility of the nickel(II) reduction process in the presence of PPh_3 alone[1] was attributed by us to the molecular rearrangement required in the transformation of an octahedral tetrakis(acetonitrile)bis(phosphine)nickel(II) into a tetrahedral tetrakis(phosphine)nickel(I) complex, mainly due to the high steric hindrance of the phosphine ligand.

In order to shed further light on the role played by halide ions in the mechanism of the above electrocatalyzed coupling reaction and the influence of a configurational change on the degree of reversibility of the redox processes involving nickel, we have investigated the voltammetric behaviour of the complexes $[NiL_2X_2]$ (L = PPh_3; X = Cl, Br, or I) in acetonitrile at a platinum electrode.

EXPERIMENTAL

Chemicals.—All the chemicals employed were of reagent grade quality. Reagent-grade acetonitrile was further purified by repeated distillation from phosphorus pentaoxide and stored on molecular sieves (3 Å) under a nitrogen atmosphere. The supporting electrolyte tetrabutylammonium perchlorate was prepared from perchloric acid and tetrabutylammonium hydroxide and twice crystallized from methanol.

Stock solutions of anhydrous nickel(II) perchlorate in acetonitrile were prepared by anodic oxidation of metallic nickel in $[NBu_4][ClO_4]$–acetonitrile solutions as previously described.[3] Triphenylphosphine was crystallized from methanol and stored in a vacuum oven in the dark. The complexes $[NiL_2X_2]$ (L = PPh_3; X = Cl, Br, or I) were synthesized as reported in the literature;[4] $[NiL_4]$ and $[NiL_4][ClO_4]$ were electrochemically generated *in situ* as reported previously.[1]

Fully deoxygenated nitrogen, previously equilibrated to the vapour pressure of acetonitrile, was used to remove dissolved oxygen.

Apparatus and Procedure.—Voltammetric and chronoamperometric experiments were carried out in a three-electrode cell. The working electrode was a platinum disk surrounded by a platinum-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 a 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 counter electrode. In each case an aqueous saturated calomel electrode (s.c.e.) was used as reference.

The voltammetric unit employed was a three-electrode system assembled with the MP-System 1000 equipment and a digital logic function generator made in our laboratory.[5] The recording device was either a Hewlett-Packard 7040 A X–Y recorder or a Hewlett-Packard 1201 A memory scope. In the controlled-potential electrolyses an Amel model 552 potentiostat was used and the associated coulometer was an Amel model 558 integrator.

The electrochemical measurements were made, unless otherwise stated, at 20 °C.

Visible–near-i.r. spectra were recorded with a Cary 40 spectrophotometer.

RESULTS

Preliminary voltammetric tests showed that the same results could be obtained whether the $[NiL_2X_2]$ employed was chemically prepared or generated '*in situ*' upon addition of stoicheiometric amounts of triphenylphosphine and halide ions (as tetrabutylammonium halide) to solutions containing electrochemically generated nickel perchlorate.[3] The second method was generally preferred because of its greater feasibility.

Dibromobis(triphenylphosphine)nickel(II).—The cathodic behaviour of $[NiL_2Br_2]$ (L = PPh_3) has been studied at a stationary platinum microelectrode in acetonitrile by cyclic voltammetry (Figure 1).

Three cathodic peaks c_1, c_2, and c_3 were observed at *ca.* -0.46, -0.63, and -0.91 V, respectively. On the reverse scan two anodic peaks a_1 and a_2 were always exhibited which appear to be associated with c_3 and c_1, respectively, as shown by suitable restriction of the range of the potential scan. The third anodic peak a_3 appeared to be well defined only when the scan direction was reversed after traversing peak c_3 (full line); by reversing the cathodic scan soon after peak c_1 had been traversed (dashed line), peak a_3 could be observed, on the descending branch of peak a_2, only by employing very low scan rates (v = 0.04 V s^{-1}).

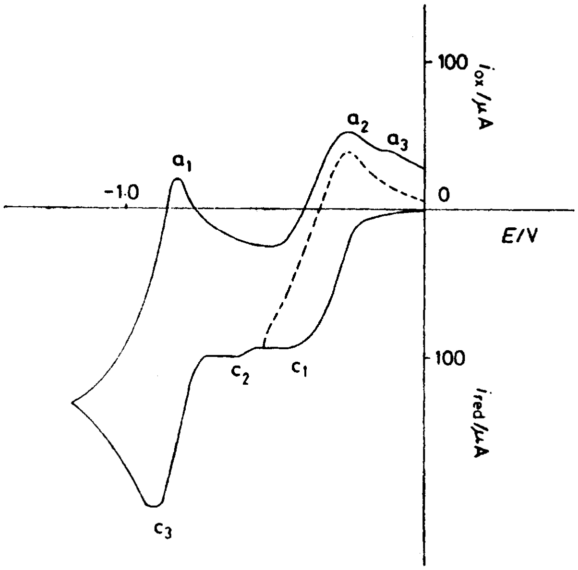


FIGURE 1 Cyclic voltammetric curve recorded at a platinum microelectrode in an acetonitrile solution of 5.0 × 10^{-3} mol dm^{-3} [NiL_2Br_2] and 0.1 mol dm^{-3} [NBu_4][ClO_4]. Scan rate 0.1 V s^{-1}

Since the observed voltammetric behaviour was markedly influenced by equilibria involving both the depolarizer, nickel(II), and one of the products, nickel(I), the peaks in Figure 1 will now be examined separately.

(*i*) ***First and second cathodic peaks*** (c_1 *and* c_2). The first cathodic peak exhibits a sigmoidal shape, typical of processes in which a charge transfer is preceded by a slow chemical reaction (c.e. process). This behaviour was confirmed by chronoamperometric and voltammetric experiments; the products $it^{\frac{1}{2}}$ and $i_pv^{\frac{1}{2}}$ were not constant, the first increasing with time, while the second increased with decreasing potential scan rate.

The stepwise addition of triphenylphosphine to the solution caused a progressive increase of the peak c_1 which reached its maximum height for a L : [NiL_2Br_2] mol ratio of 3 : 1 while, at the same time, peak c_2 disappeared. In these conditions peak c_1 was found to involve a one-electron reduction process by comparison of its height with that of the complex [$Ni(CN)_2(PEt_2Ph)_2$] for which the occurrence of such a process has been shown unambiguously.[6] Furthermore, the linear dependence of the peak current on the square root of the scan rate (0.025—2.00 V s^{-1}) in voltammetric tests and of the instantaneous current on the square root of the time in chronoamperometric experiments indicated a diffusive character for the process involved. It also appeared to assume a reversible character since E_p did not change upon increasing the potential scan rate and the difference $E_{p/2} - E_p$ was equal to 60 mV.

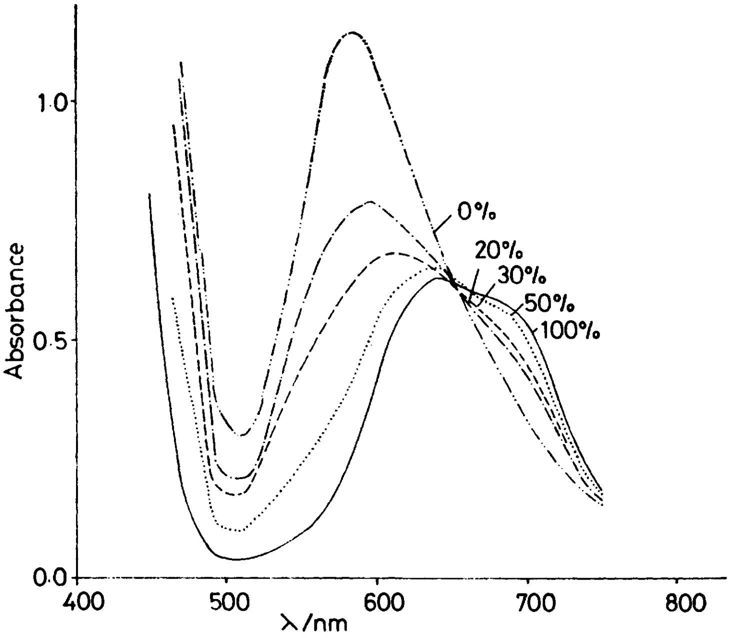


FIGURE 2 Visible spectra of 5.0 × 10^{-3} mol dm^{-3} [NiL_2Br_2] solution in acetonitrile–benzene mixtures. The percentages refer to the CH_3CN content

In contrast, addition of bromide ions to solutions containing either [NiL_2Br_2] alone or [NiL_2Br_2] in the presence of an excess of triphenylphosphine caused a progressive decrease of peak c_1 and a simultaneous increase of peak c_2 (the last appearing diffusive and irreversible in character). It must be noted, however, that peak c_1 did not disappear completely even in the presence of a large excess of bromide ions (100 : 1).

This peak 'conversion' shows that the depolarizers of both the first and the second cathodic peak are two nickel(II) species, in equilibrium with each other, and possessing different numbers of bromide and phosphine ligands. To confirm this, spectrophotometric investigations were carried out on $[NiL_2Br_2]$ solutions. In pure acetonitrile the electronic spectrum (Figure 2) exhibits two maxima in the region 630—700 nm (full line), but these change progressively to a single maximum at *ca.* 580 nm in benzene–acetonitrile mixtures containing decreasing fractions of CH_3CN. This suggests that the spectrum obtained in CH_3CN can be attributed to a nickel species formed by ionic dissociation of $[NiL_2Br_2]$ and which is increasingly suppressed with lowering of the dielectric constant of the medium (addition of benzene). This view is supported by the observation that on addition of bromide ions to the $[NiL_2Br_2]$-containing CH_3CN solution the absorbance in the region 630—700 nm progressively increased until it was twice its initial value. Furthermore, the addition of $[NBu_4]Br$ in a 1 : 1 mol ratio to benzene solutions of $[NiL_2Br_2]$ yields the spectrum as shown in Figure 3, which is similar to the spectrum recorded in pure acetonitrile. On standing, a blue-green precipitate was obtained to which the formula $[NBu_4][NiLBr_3]$ could be assigned on the basis of elemental analysis. Comparison of Figures 2 and 3 shows out that about half of the total nickel species in $[NiL_2Br_2]$–acetonitrile solutions is present as the $[NiLBr_3]^-$ complex. On the basis of simple mass balance, the remaining nickel has to be present as $[NiL_3Br]^+$ which cannot be easily detected spectrophotometrically as its absorbance in the region 550—600 nm is characterized by a very low molar absorption coefficient. Detection of this cationic complex was possible in the near-i.r. region where an isosbestic point at *ca.* 921 nm, is exhibited for equilibrium (1).

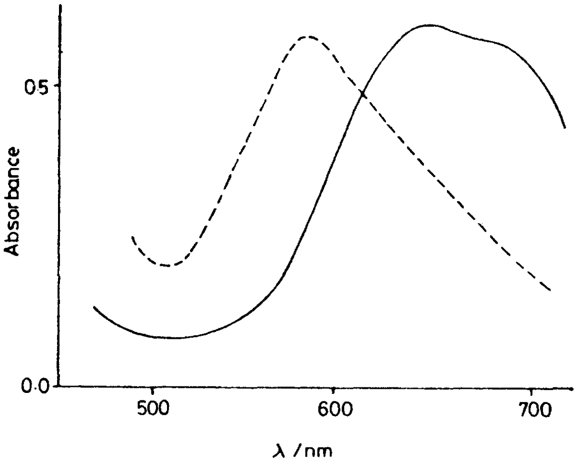


FIGURE 3 Visible spectra of 2.5×10^{-3} mol dm^{-3} $[NiL_2Br_2]$ in benzene: (– – – –), in absence of added $[NBu_4]Br$; (——), after addition of 2.5×10^{-3} mol dm^{-3} $[NBu_4]Br$

$$[NiL_3Br]^+ + 2\,Br^- \rightleftharpoons [NiLBr_3]^- + 2\,L \qquad (1)$$

All these experimental data indicate that the $[NiL_2Br_2]$ complex, in a polar solvent such as acetonitrile, undergoes the ligand disproportionation equilibrium (2) which is almost completely shifted towards the right-hand side. Thus, the cationic complex is the depolarizer of peak c_1, while the anionic species is reduced at c_2.

$$2\,[NiL_2Br_2] \rightleftharpoons [NiL_3Br]^+ + [NiLBr_3]^- \qquad (2)$$

Controlled-potential coulometric experiments carried out at potential values corresponding to c_1 gave a n_e value of 1 only when an excess of L, at least in a mol ratio 2 : 1, was present. In the absence of added phosphine n_e ranged from 0.4 to *ca.* 0.6, depending on the applied potential (the peak shifted cathodically during the electrolyses), and it became progressively lower upon electrolyzing the solution after addition of increasing amounts of $[NBu_4]Br$. In all cases the product was found to be the nickel(I) complex $[NiL_3Br]$ which separated slowly from the solution as yellow crystals. It could be identified by elemental analysis and by comparing the voltammetric behaviour obtained after electrolysis (which will be reported below) with that of freshly prepared acetonitrile solutions of an authentic sample of this species.[7]

By electrolyzing $[NiL_2Br_2]$ solutions directly at the potential corresponding to peak c_2 a n_e value of 0.66 was found and $[NiL_3Br]$ was again obtained as product.

These findings together with the observation that reaction (2) cannot be the rate-controlling process occurring at c_1 (spectrophotometric data indicate that this equilibrium lies 'quantitatively' to the right-hand side) suggest that $[NiLBr_3]^-$, in its turn, undergoes a slow ligand-exchange equilibrium (3) giving the $[NiL_3Br]^+$ species. This hypothesis agrees with the previously mentioned persistence of peak c_1 in $[NiL_2Br_2]$ solutions even after addition of a large excess of bromide ions, and it is consistent with the fact that solutions of $[NiBr_4]^{2-}$, prepared by adding suitable amounts of $[NBu_4]Br$ to solutions of electrogenerated nickel(II), have been found to undergo a two-electron reduction at potentials almost coincident with those at which peak c_3 is observed.

$$3\,[NiLBr_3]^- \rightleftharpoons [NiL_3Br]^+ + 2\,[NiBr_4]^{2-} \qquad (3)$$

(*ii*) *Third cathodic peak* (c_3) *and first anodic one* (a_1). Controlled-potential coulometric experiments carried out on $[NiL_2Br_2]$ solutions directly at potentials corresponding to the third cathodic peak (c_3) gave a n_e value of 2. The electrolyzed solutions turned from the initial green to red-brown and voltammetric tests revealed the presence of $[NiL_4]$ (peak a_1) at a concentration about half that of the initial starting nickel(II) species; the presence of finely divided metallic nickel could also be observed.

These results can be explained by considering that the phosphine is unable to keep in solution all the nickel(0) electrochemically generated, and that the cathodic reaction (4) occurs.

$$2\,[NiL_2Br_2] + 4\,e^- \longrightarrow [NiL_4] + Ni(s) + 4\,Br^- \qquad (4)$$

By carrying out the same electrolyses in the presence of triphenylphosphine in a ligand to $[NiL_2Br_2]$ mol ratio of at least 2 : 1, the same n_e value was found but in this case voltammetric tests indicated that all the nickel(II) originally present had been reduced to $[NiL_4]$ and the formation of metallic nickel could not be observed.

When the electrolyses were carried out on $[NiL_2Br_2]$ solutions previously electrolyzed at a potential corresponding to c_2 a n_e value of 1.33 was found and half of the nickel initially present was again (voltammetrically) $[NiL_4]$.

The formation of finely divided metallic nickel was also observed. This result can be explained by considering that at the working potential the one-electron reduction of nickel(I) obtained at c_2 (66% of the initial nickel content) and the two-electron reduction of $[NiBr_4]^{2-}$ (33% of the initial nickel content) occur concomitantly.

The potentials of the associated peaks c_3 and a_1 were affected by the presence in solution of an excess of both the ligands L and Br^-. In particular, the addition of L to $[NiL_2Br_2]$ solutions caused a shift of both peaks towards less cathodic potentials and a concomitant lowering of $(E_p)_{a1} - (E_p)_{c3}$, which approached the value (60 mV) expected for a reversible one-electron process with increasing L to $[NiL_2Br_2]$ mol ratio. On adding $[NBu_4]Br$, a shift in the opposite direction was observed and the process remained quasi-reversible in character ($\Delta E_p = 140$ mV).

In agreement with these results, cyclic voltammetric tests carried out on $[NiL_4]^+$ solutions, electrochemically prepared [1] in the presence of an excess of L, gave a peak c_3 which changed its character from reversible to quasi-reversible on addition of bromide ions; a shift of both peaks in the cathodic direction was also observed.

These shifts can be explained by considering that, in the presence of bromide ions, the Ni^I–Ni^0 process occurs *via* reaction (5).

$$[NiL_3Br] + L + e^- \longrightarrow [NiL_4] + Br^- \qquad (5)$$

We noted that the addition of L to $[NiL_2Br_2]$ solutions caused not only the anodic shifts but also a decrease of peak c_3. This fact can be explained by considering that the $[NiBr_4]^{2-}$ species is reducible in correspondence to this peak together with nickel(I) produced at c_1 and c_2. In the presence of L, $[NiBr_4]^{2-}$ is evidently converted into $[NiL_3Br]^+$ the reduction of which occurs at c_1 instead of at c_3. The height of this last peak, in fact, concomitantly increased as outlined above.

(*iii*) *Second and third anodic peaks* (a_2 *and* a_3). During the stepwise addition of L to $[NiL_2Br_2]$ solutions it was observed that, on reversing the potential scan after traversing either peak c_1 or c_2, peak a_2 decreased while the irreversible peak a_3 arose and progressively increased. The opposite peak 'conversion' was observed on adding bromide ions to $[NiL_2Br_2]$ solutions containing an excess of L.

To obtain information on this peak 'conversion,' bromide ions were added to solutions of electrochemically generated $[NiL_4]^+$.[1] Figure 4 shows that the anodic peak (full line), which is known [1] to correspond to process (6),

$$[NiL_4]^+ + 4\,CH_3CN \longrightarrow [NiL_2(NCCH_3)_4]^{2+} + 2\,L + 1\,e^- \qquad (6)$$

disappears completely and, at the same time, a new peak arises (dashed line) at potentials corresponding to peak a_3 when a Br^- to $[NiL_4]^+$ mol ratio of 1 : 1 is reached; moreover, in the reverse scan, peak c_1 appeared to be associated with this peak. As shown in Figure 4, further addition of bromide ions caused peak a_3 to decrease and the concomitant increase of peak a_2.

The cathodic shift of the anodic peak corresponding to the oxidation of $[NiL_4]^+$ observed after the initial addition of Br^- ions can easily be explained by taking into account the fact that the oxidation product in the new experimental conditions is the species $[NiL_3Br]^+$, which is more stable than the $[NiL_2(NCCH_3)_4]^{2+}$ complex obtained in the absence of Br^-. The subsequent peak 'conversion' can be interpreted in terms of the ligand-exchange equilibrium (7), the cationic complex being the depolarizer of peak a_3,

$$[NiL_4]^+ + Br^- \rightleftharpoons [NiL_3Br] + L \qquad (7)$$

while the neutral complex is oxidized at a_2. In this connection, we note that peak a_2 gave rise with c_1 ($[NiL_3Br]^+$ reduction) to a reversible catho-anodic system when the concentration of the phosphine added was sufficient [equilibrium (1)] to make peak c_1 reversible and the scan rate was high enough. This result indicates that the high scan rate is necessary to cancel the effect of the chemical reaction (7) which we feel follows the charge-transfer step and which hence appears to be a rather slow ligand exchange.

The slowness of this ligand exchange has been confirmed by carrying out cyclic voltammetric tests at different potential scan rates and temperatures. When L was added to $[NiL_2Br_2]$ solutions, peak a_2, which was observed by reversing the scan direction after traversing peak c_1, increased with increasing scan rate (more than a diffusive peak) and with decreasing temperature. Moreover, on adding bromide ions to $[NiL_4]^+$ at −30 °C, the peak 'conversion' which took place at room temperature was no longer observed, but peak a_2 was clearly detectable in the second and successive cycles by using a switching potential more cathodic than that of peak c_1. On lowering the temperature and increasing the scan rate, the nickel(I) complex $[NiL_3Br]$ produced at peak c_1 cannot undergo the ligand exchange (7) on the time scale of the experiment.

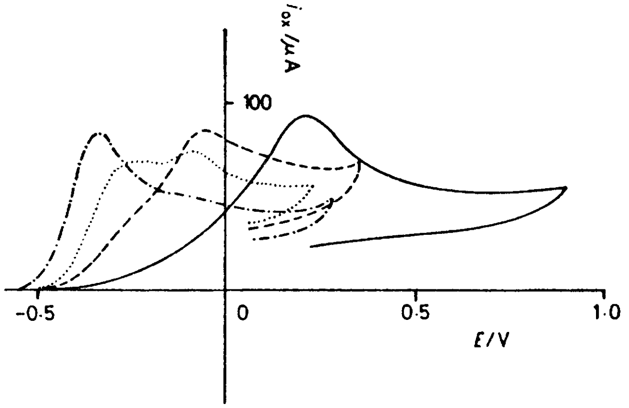


FIGURE 4 Voltammetric curves recorded at a platinum microelectrode in an acetonitrile solution of 4.0×10^{-3} mol dm^{-3} $[NiL_4][ClO_4]$ and 0.1 mol dm^{-3} $[NBu_4][ClO_4]$. Mol ratio of $[NBu_4]Br$ added: (——), 0 : 1; (– – – –), 1 : 1; (· · · ·), 2 : 1; and (— · — · —) 4 : 1. Scan rate 0.1 V s^{-1}

Similar arguments allow one to explain the presence of peak a_3 in the cyclic voltammetric profiles recorded on traversing peak c_3 (see Figure 1). In the process operative at peak a_1, $[NiL_4]^+$ is formed by anodic oxidation of $[NiL_4]$ generated at peak c_3 and the slowness of the reaction (7), allowing only a limited ligand exchange, accounts for the presence of peak a_3 which corresponds to the oxidation of the cationic nickel(I) species. In agreement with this, by using a switching potential beyond c_3 in cyclic voltammetric experiments, a peak 'conversion' from a_2 to a_3 was observed either on increasing the scan rate or on lowering the temperature.

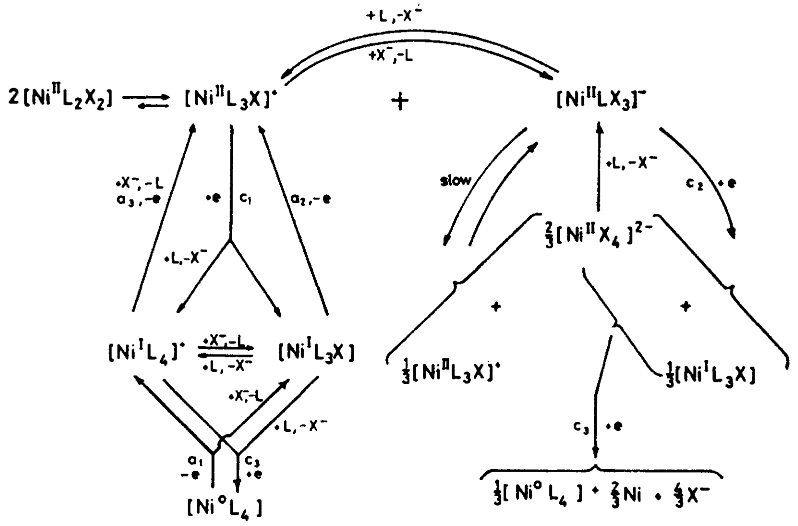
Dichlorobis(triphenylphosphine)nickel(II) *and Di-iodobis-(triphenylphosphine)nickel*(II).—The voltammetric behaviour of acetonitrile solutions of $[NiL_2Cl_2]$ was quite similar to that reported in Figure 1 for the dibromo-analogue, the only difference being the potentials at which both the cathodic and the anodic peaks occurred (Table). Moreover voltammetric tests, carried out under the same experimental conditions, showed that reactions (3) and (7) (*i.e.* the kinetic steps determining peaks c_1 and a_2 respectively) are characterized by a slower rate.

Peak potential values from cyclic voltammograms at a scan rate of 0.1 V s^{-1} for $[NiL_2X_2]$ complexes, quoted *versus* an aqueous s.c.e.

Complex	Peak potential/V					
	c_1 *	c_2 †	c_3 *	a_1 *	a_2 *	a_3 *
$[Ni(PPh_3)_2Cl_2]$	−0.42	−0.81	−0.90	−0.76	−0.36	−0.08
$[Ni(PPh_3)_2Br_2]$	−0.35	−0.72	−0.88	−0.77	−0.29	−0.02
$[Ni(PPh_3)_2I_2]$	−0.27		−0.84	−0.78	−0.21	

* Potentials quoted for a L : Ni^{II} mol ratio of 5 : 1. † Potentials quoted for a X^- : Ni^{II} mol ratio of 5 : 1.

As far as the di-iodo-complex is concerned, a considerable difference is observed in that peaks c_2 and a_3 could not be observed under any experimental conditions. Moreover, the cathodic peak c_1 appeared to be always essentially diffusive in character (voltammetric and chronoamperometric tests) even when an excess of L was not present. The presence of L caused, however, an increase of peak c_1 which exhibited a height equal to *ca.* two thirds that of a one-electron peak in solutions of $[NiL_2I_2]$ alone, becoming a one-electron peak in the presence of L at ratios of at least 1 : 1. At the same time the addition of phosphine lowered peak c_3 from a height corresponding to a diffusive process involving 1.33 e^- per mol of depolarizer to that typical of a one-electron process. This partial peak 'conversion' can be explained, once more, on the basis of the ligand disproportionation equilibria (2) and (3), the only difference being that now reaction (3) is faster.



SCHEME

We note that solutions in which both L and I^- were added to electrogenerated nickel(II) in the ratios 1 : 1 and 3 : 1 respectively (stoicheiometric ratios for the formation of $[NiLI_3]^-$) exhibited the same voltammetric behaviour as that observed for $[NiL_2I_2]$, the only difference being in the heights of peak c_1 and c_3 which were lower and greater respectively. This suggests that the cationic and anionic complexes obtained in the ligand-disproportionation reaction (1) are reduced, in this case, at the same potential value.

The absence of peak a_3 can be explained if the ligand-exchange equilibrium (7) is very fast in the presence of iodide ions (unlike the cases of X = Cl or Br), although the hypothesis that both the nickel(I) complexes involved can be oxidized at the same potential value cannot be disregarded.

DISCUSSION

The results reported in this paper for the $[NiL_2X_2]$ complexes indicate clearly that in a polar solvent such as acetonitrile these nickel(II) compounds undergo quantitative ligand disproportionation leading to ionic species as in the Scheme, which also shows all the other electrochemical processes when X = Cl or Br. In this connection we note that the ligand disproportionation proposed and the ligand exchange involving nickel(I) were not reported for the $[NiL_2Cl_2]$ complex in tetrahydrofuran and 1,2-dimethoxyethane.[8]

Arguing by analogy, the same hypothesis of a preliminary ionic dissociation of the nickel(II) complex can be advanced also for $[NiL_2I_2]$, but no definitive evidence has been obtained from the spectrophotometric data.

The degrees of reversibility of the investigated electrochemical processes appear to be markedly affected by the ligand displacement involved, especially those for the nickel(I) oxidation and reduction processes. Thus the nickel(I) oxidation appears to be reversible when the nickel atom is present in the ligand set L_3X which is not modified in the charge-transfer reaction (the oxidation product is $[NiL_3X]^+$), while the oxidation of $[NiL_4]^+$, which involves the substitution of one molecule of L by a X atom, has a rather high overvoltage. In contrast the reduction of the two nickel(I) species always leads to the $[NiL_4]$ complex. The reduction of $[NiL_4]^+$ occurs in a reversible charge-transfer process where the nature of the ligands is the same for the redox partners, while the change of the chemical environment involved in the reduction of $[NiL_3X]$ makes it quasi-reversible.

In this connection we note that the peak c_1 recorded for $[NiL_2I_2]$ solutions appeared to be reversible in the presence of an excess of L, but its degree of reversibility decreased on adding iodide ions, thus suggesting that also in this case the ligand-disproportionation reaction is operative.

All the nickel complexes involved in the investigated redox processes are known to exhibit a tetrahedral configuration; it is therefore of interest that electroanalytical techniques can be used not only for inferring structural properties of the co-ordination compounds [9,10] but also to obtain valuable information concerning these species in the solution state.

The potentials (Table) corresponding to the cathodic processes occurring at c_1 and c_3 appear to depend on the nature of the halide ligand co-ordinated to the nickel atom, the reduction process becoming easier with increasing softness of the anionic ligand. A tentative explanation of this trend can be advanced by taking into account the greater 'softness' of nickel(I) compared to nickel(II) which is classified as a borderline Lewis acid. Therefore the softer is the halide ion the more stable is the relevant nickel(I) complex obtained in the cathodic reduction, while a much smaller difference in stability is expected for the corresponding nickel(II) compounds. Similar arguments can be advanced to account for the trend observed for the peaks c_3 if nickel(0) is considered to be softer than nickel(I). Consequently the trend in these potentials is mainly determined by the stability of the reduced species involved.

The effect of the nature of the halide ligands on the rates of both the ligand-disproportionation reaction (2) involving nickel(II) and the ligand-exchange equilibrium (7) concerning nickel(I) deserves a short comment. The trend of the rates of the reaction involving Ni^{II} as metal centre could be explained on the basis of a bimolecular mechanism in which a halide ligand acts as a bridge in the activated complex, and the known order of bridging ability $I^- > Br^- > Cl^-$. It is more difficult to explain the observed kinetic trend for the nickel(I) complexes, owing to the lack of knowledge of the kinetics of complexes of this metal centre. A tentative explanation, however, cannot be based on a purely dissociative mechanism considering the very likely class b character of nickel(I). An essentially associative interchange mechanism, with an important bond-breaking contribution, may be involved. On increasing the bulkiness of the halide leaving group one would expect a decreasing activation energy for the removal of the leaving group in the transition state relative to the dissociation of the reactive five-co-ordinate intermediate.

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