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Nickel–bipyridine catalysed electrosynthesis of ketones from organic halides and carbon monoxide: kinetic and mechanistic investigations

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Abstract

The reactivity of zerovalent nickel-2,2′-bipyridine complexes towards carbon monoxide and organic halides was investigated by electroanalytical methods. The kinetic data obtained allow us to propose two pathways leading to the formation of an acylnickel complex by electroreduction of Nibpy^{2+} in the presence of both CO and a halocarbon. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Nickel carbonyl bipyridine complexes; Acylnickel complexes; Organic halides carbonylation catalysis

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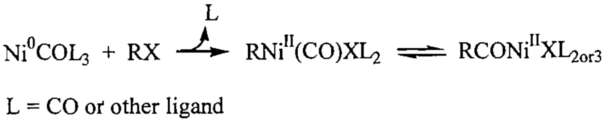
1. Introduction

We have previously reported [1,2] that ketones can be easily obtained by the electroreductive coupling of organic halides with carbon monoxide according to the following equation:

$$2\,RX + CO + 2e \xrightarrow{cat.} RCOR + 2X^-$$

The catalysis of this reaction is based on the electroreduction of the divalent nickel complex Nibpy^{2+} (bpy = 2,2′-bipyridine) in DMF solutions where the CO group is supplied either by bubbling carbon monoxide [1] or from a metal carbonyl [2].

The formation of an acylmetal complex RCOMX is commonly given as a key-step in the carbonylation of organic halides [3]. For chemical reactions involving low valent nickel complexes, two pathways have been proposed. The first route is the oxidative addition of the halocarbon onto a nickel–carbonyl complex followed by the alkyl group migration as shown in Scheme 1.



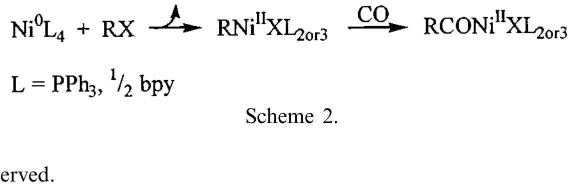
$$Ni^0COL_3 + RX \xrightarrow{L} RNi^{II}(CO)XL_2 \rightleftharpoons RCONi^{II}XL_{2or3}$$

L = CO or other ligand

Scheme 1.

Such a sequence has been proposed for $Ni(CO)_4$ [4] and $Ni(CO)_2(PPh_3)_2$ [5]. The second route is the insertion of CO in an alkyl- or arylnickel intermediate obtained by oxidative addition of the organic halide onto the zerovalent nickel complex, according to Scheme 2 [6–9].

These two routes have been established for different experimental conditions, where either CO or RX is first 'attached' to the nickel. No mechanistic investigation has ever been reported for conditions in which the two pathways can compete. Indeed, this can occur in our



$$Ni^0L_4 + RX \xrightarrow{L} RNi^{II}XL_{2or3} \xrightarrow{CO} RCONi^{II}XL_{2or3}$$

L = PPh$_3$, $^1/_2$ bpy

Scheme 2.

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experiments, where the electroreduction of the catalytic precursor $Nibpy^{2+}$ is achieved in solutions containing both carbon monoxide and an halocarbon. The aim of the present work was to try to determine which way induces, in our conditions, the formation of an acylnickel intermediate. For this purpose, we studied and compared the reactivity of CO towards Ni^0bpy on the one hand and the reactivity of organic halides towards the various Ni(0)–bpy and Ni(0)–bpy–CO complexes on the other hand.

This work follows the one we reported in a recent paper [10] where we have shown that several zerovalent nickel complexes can be electrogenerated depending on the respective amounts of the metallic center, the ligands bpy and CO. If bpy, or CO, is in excess, a stable saturated 18-electron complex is obtained i.e. $Nibpy_2$ or $Ni(CO)_2bpy$. We noted that under these conditions, no ketone can be formed. Starting from solutions containing $Nibpy^{2+}$ without extra bpy, the generation of two unstable unsaturated complexes has been evidenced by electroanalytical methods. When there is a lack of CO (or no CO), the cathodic process is the well known generation of Ni^0bpy [11]. A new species Ni^0CObpy is formed when the ratio between the electrogenerated Ni^0bpy and the dissolved CO is 1:1. Only under these stoechiometric conditions, the quantitative formation of ketone can be observed.

In this paper, thanks to electroanalytical investigations, we can now explain the positive (or negative) results observed in our preparative electrosyntheses [1,10]. First, we proved that Ni^0bpy_2 and $Ni^0(CO)_2bpy$ do not allow the formation of an acylnickel complex and consequently the synthesis of ketones. Then, we established that the active species are the unsaturated complexes Ni^0bpy and Ni^0CObpy. Finally, these kinetic investigations allowed us to discuss about the two possible ways mentioned above and leading to an acylnickel intermediate.

2. Results and discussion

2.1. *Reactivity of zerovalent nickel complexes towards organic halides or carbon monoxide*

2.1.1. *Reactivity of Ni^0bpy_2*

The electroreduction of $Nibpy_2^{2+}$ into Ni^0bpy_2 is a well known reversible process [12,13]:

$$Nibpy_2^{+2} + 2e \rightleftharpoons Ni^0bpy_2$$

$$Ep_C = -1.2\ V/SCE,\ Ep_A = -1\ V/SCE$$

The addition of an organic halide RX (e.g. PhBr, $PhCH_2Cl$) to a solution of $Nibpy_2^{2+}$ does not really affect the voltammogram, which proves that the reaction between Ni^0bpy_2 and RX is not very fast. Only active aromatic halides (e.g. PhI) induced a partial lack of reversibility. This result was supported by chronoamperometric experiments which enabled the measure of the rate constants of the reaction when RX was added to a solution of Ni^0bpy_2, generated by exhaustive electrolysis of $Nibpy_2^{2+}$ [12]:

$$Ni^0bpy_2 + RX \xrightarrow{k_1} RNi^{II}Xbpy + bpy \qquad (1)$$

We found second order kinetics for this reaction (1). The rate constant k_1 depends on the nature of RX and on the concentration of extra bpy in the solution [12,14]. Thus, we found $k_1 = 25 \times 10^{-2}$ for PhBr [12] or $k_1 = 3.53\ l\ mol^{-1}\ s^{-1}$ for PhI [14] at 25°C, in solutions containing Ni^0bpy_2 (2×10^{-2} mol l^{-1}) plus bpy (2×10^{-2} mol l^{-1}).

On the contrary, when $Nibpy_2^{2+}$ was electroreduced in a DMF solution saturated with carbon monoxide, the Ni(II)/Ni(0) transition was radically modified. The bielectronic reduction occurred at a slightly less negative potential with loss of the reverse signal even at high sweep rate (50 V s^{-1}). The presence of extra bpy (1–15 bpy/Ni^{II}) had no influence. We can conclude that the complexation of Ni^0bpy_2 by CO, globally written according to the Eq. (2), is a very fast reaction, i.e. $v_2 \gg v_1$:

$$Nibpy_2^{2+} 2e \rightleftharpoons Ni^0bpy_2$$

$$Nibpy_2 + 2CO \xrightarrow{k_2} Ni^0(CO)_2bpy + bpy \qquad (2)$$

Chronoamperometric experiments achieved by adding CO in solutions containing Ni^0bpy_2 prepared by exhaustive electrolysis of $Nibpy_2^{2+}$ failed in the determination of v_2. Indeed, the pseudo zero-order kinetic then observed only expressed the slow rate of dissolution of CO.

2.1.2. *Reactivity of $Ni^0(CO)_2bpy$*

We have prepared $Ni^0(CO)_2bpy$ solutions by electrolysis of $Nibpy^{2+}$ (or $Nibpy_2^{2+}$) in the presence of CO. We have shown that no reaction occurred after several hours when an organic halide such as $PhCH_2Cl$ was added to those solutions maintained under CO. We can then state that no acylnickel complex can be formed when $Nibpy_{1\ or\ 2}^{2+}$ is reduced in a solution of an organic halide in the presence of CO in excess. The fast binding of Ni(0) by CO only leads to the unreactive saturated complex $Ni^0(CO)_2bpy$.

However, this complex, as presented in Fig. 1 (curve a), can be reversibly electroreduced according to a one-electron process (C_2 and A_2 peaks):

$$Ni^0(CO)_2bpy + e \rightleftharpoons Ni^0(CO)_2bpy^{\bullet -}$$

$Ep(C_2) = -1.76$ V/SCE, $Ep(A_2) = -1.65$ V/SCE and irreversibly electrooxidised (A_3 peak):

$$Ni^0(CO)_2bpy \rightarrow Nibpy^{2+} + 2CO + 2e$$

$$Ep(A_3) = -0.16\ V/SCE$$

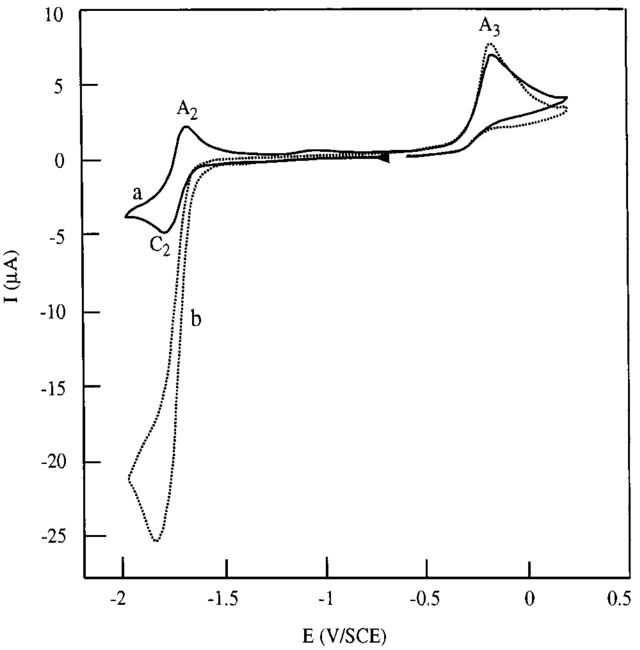


Fig. 1. Cyclic voltammograms of a solution of DMF plus Bu_4NBF_4 (0.1 mol l^{-1}). (a) Obtained after reduction of $Nibpy^{2+}$ (8×10^{-3} mol l^{-1}) under CO. (b) Addition of $PhCH_2Cl$ (4×10^{-2} mol l^{-1}). Gold microelectrode; $v = 0.1$ V s^{-1}, $E_{initial} = -0.5$ V/SCE.

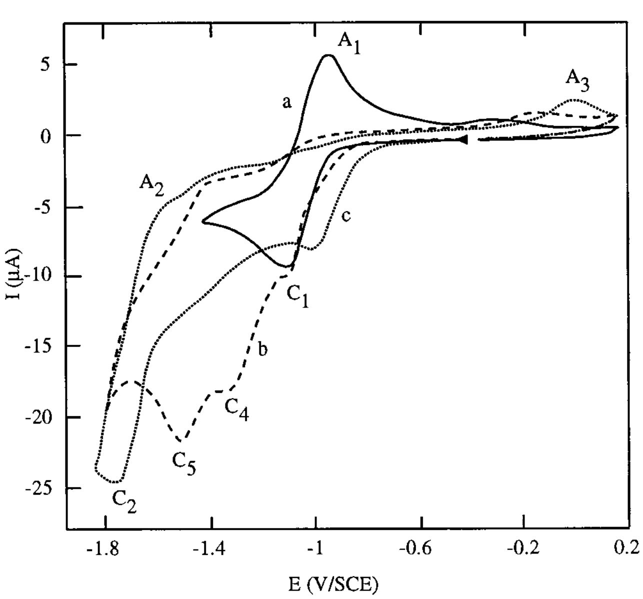


Fig. 2. Cyclic voltammograms of a solution of $Nibpy^{2+}$ (10^{-2} mol l^{-1}) in DMF plus Bu_4NBF_4 (0.1 mol l^{-1}) (a) Under argon. (b) Addition of PhI (2×10^{-2} mol l^{-1}) under argon. (c) With or without PhI, under CO. Gold microelectrode; $v = 0.1$ V s^{-1}; $E_{initial} = -0.5$ V/SCE.

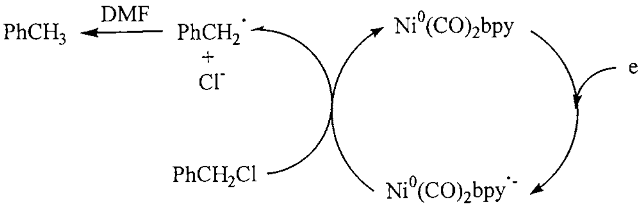
When $PhCH_2Cl$ was added to the $Ni^0(CO)_2bpy$ solution maintained under CO (Fig. 1, curve b), the anodic scan was not modified, which proved again that the organic halide does not react with $Ni^0(CO)_2bpy$. On the other hand, the cathodic scan exhibited at −1.76 V/SCE a catalytic current depending on the amount of $PhCH_2Cl$, and the reduction of $Ni^0(CO)_2bpy$ became irreversible. Then we carried out an exhaustive electrolysis of a solution containing $Ni^0(CO)_2bpy$ (8×10^{-3} mol l^{-1}) and $PhCH_2Cl$ (4×10^{-2} mol l^{-1}) at −1.76 V/SCE. We have found that benzyl chloride was consumed but the reaction only yielded toluene but no dibenzylketone. We assume that this behaviour can be explained by a redox catalysis reaction, as presented in Scheme 3, rather than by the formation of an alkyl- or an acylnickel complex.

$Ni^0(CO)_2bpy$ becomes unstable on dispelling carbon monoxide by bubbling the solution with an inert gas. The red solution of $Ni^0(CO)_2bpy$ turns pale green in a few minutes. If $PhCH_2Cl$ was preliminary introduced in the solution, we have shown that $Nibpy^{2+}$ was recovered and that dibenzylketone (0.8 mol per mol of $Ni^0(CO)_2bpy$) was formed. In connection with that, the formation of a symmetrical ketone was previously reported in solutions where $Ni^0(CO)_2bpy$ was prepared by electroreduction of $Nibpy^{2+}$ in the presence of carbon dioxide [15,16]. We can now explain that the species active towards the organic halide in this reaction is the transient unsaturated complex Ni^0CObpy, resulting from a loss of CO according to the following sequence:

$$Ni^0(CO)_2bpy \rightleftharpoons Ni^0CObpy + CO\uparrow$$

$$Ni^0CObpy + RX \xrightarrow{k_3} RNi^{II}(CO)Xbpy \rightleftharpoons RCONi^{II}Xbpy \quad (3)$$

$$RCONi^{II}Xbpy \xrightarrow{RX} RCOR + Nibpy^{2+} + 2\,X^-$$



Scheme 3. The source of “CO” can be either dissolved CO in the bulk of the solution or $Ni^0(CO)_2bpy$ or Ni^0CObpy at the level of the electrode.

2.1.3. *Reactivity of the unsaturated complex Ni^0bpy*

Starting from a solution of $Nibpy^{2+}$ (without extra bpy), the voltammogram (Fig. 2, curve a) exhibits a quite reversible system assigned to the Ni(II)/Ni(0) transition (C_1 and A_1 peaks) [14]:

$$Nibpy^{2+} + 2e \rightleftharpoons Ni^0bpy$$

$$Ep(C_1) = -1.1 \text{ V/SCE}, \; Ep(A_1) = -0.93 \text{ V/SCE}$$

For our purpose, we decided to compare the reactivity of Ni^0bpy towards respectively organic halides (Eq. (4)) or carbon monoxide (Eq. (5)):

$$\mathrm{Ni^0bpy} + \mathrm{RX} \xrightarrow{k_4} \mathrm{RNi^{II}Xbpy} \qquad (4)$$

$$\mathrm{Ni^0bpy} + 2\mathrm{CO} \xrightarrow{k_5} \mathrm{Ni^0(CO)_2bpy} \qquad (5)$$

Since $\mathrm{Ni^0bpy}$ is not stable in the solution, its reactivity can only be studied by transient cyclic voltammetry which allows investigation at short times.

When an organic halide was added to the solution of $\mathrm{Nibpy^{2+}}$, we observed (Fig. 2, curve b) for various RX (PhBr, $\mathrm{PhCH_2Cl}$, PhI) a loss of reversibility of the Ni(II)/Ni(0) transition. The electrochemical processes following the reduction of $\mathrm{Nibpy^{2+}}$ (C_4 and C_5 peaks) were assigned to the reduction of the aryl- or alkylnickel complex $\mathrm{RNi^{II}(X)bpy}$, issued from the oxidative addition reaction (Eq. (4)) [11,17,18]. By applying the Nicholson–Shain method [19][1], several values of k_4 were obtained at room temperature (r.t.) (20–22°C). For example, $k_4 = 60–70\ \mathrm{l\ mol^{-1}\ s^{-1}}$ for $\mathrm{PhCH_2Cl}$ and PhBr; $k_4 = 1–2 \times 10^3\ \mathrm{l\ mol^{-1}\ s^{-1}}$ for PhI [11].

When the solution contained carbon monoxide in excess ($\mathrm{Nibpy^{2+}} \leq 1.5 \times 10^{-2}$ mol $\mathrm{l^{-1}}$) [10], the voltammogram was the one presented on the Fig. 2, curve c. Even at high voltage sweep-rate (30 V $\mathrm{s^{-1}}$), the reduction of $\mathrm{Nibpy^{2+}}$ was fully irreversible and we only detected the monoelectronic reduction of $\mathrm{Ni^0(CO)_2bpy}$ at -1.76 V/SCE (C_2 peak) [10]. This behaviour was not modified when an organic halide was present in the CO saturated solution. We can conclude that the reaction of complexation of $\mathrm{Ni^0bpy}$ by two molecules of CO is a very fast reaction. So, $k_5 \gg k_4$ for all the tested RX (including PhI). This result is consistent with the one obtained from the saturated $\mathrm{Ni^0bpy_2}$ complex for which $k_2 \gg k_1$ (see above).

When CO is a limiting reactant, i.e. $\mathrm{Nibpy^{2+}} > 1.5 \times 10^{-2}$ mol $\mathrm{l^{-1}}$, we have previously shown [10] that the reduction of $\mathrm{Nibpy^{2+}}$ induced the simultaneous generation of $\mathrm{Ni^0(CO)_2bpy}$ and $\mathrm{Ni^0bpy}$. These two complexes then react according to a CO exchange reaction (Eq. (6)), leading to the formation of $\mathrm{Ni^0CObpy}$.

$$\mathrm{Ni^0bpy} + \mathrm{Ni^0(CO)_2bpy} \xrightarrow{k_6} 2\mathrm{Ni^0(CO)bpy} \qquad (6)$$

In order to compare the rate of reactions 4 and 6, we have achieved the following experiments. A $\mathrm{Nibpy^{2+}}$ (3×10^{-2} mol $\mathrm{l^{-1}}$) solution maintained under CO was used to generate at the microelectrode equal amounts (1.5×10^{-2} mol $\mathrm{l^{-1}}$) of $\mathrm{Ni^0bpy}$ and $\mathrm{Ni^0(CO)_2bpy}$ [10]. Curve a of Fig. 3 shows that, at a low scan rate, Ni(II) was irreversibly electroreduced (C'_1 peak). For this Ni(II) concentration and at this time scale, the formation of $\mathrm{Ni^0CObpy}$ is quite quantitative [10]. The C_6 peak corresponds to the monoelectronic reduction of this complex [10]. Its intensity is lower than the one expected since the unstable complex $\mathrm{Ni^0CObpy}$ was partially decomposed. At a higher scan rate (Fig. 3, curve b), we distinguish the generation of $\mathrm{Ni^0(CO)_2bpy}$ (C''_1 peak) and $\mathrm{Ni^0bpy}$ (C_1 peak) and the C_6 peak is better defined. At this shorter time scale, the A_1 and C_2 peaks are detected with a small intensity, which shows the presence of residual $\mathrm{Ni^0bpy}$ (A_1 peak) and $\mathrm{Ni^0(CO)_2bpy}$ (C_2 peak) at the electrode [10]. This indicates that the reaction 6 is not extremely fast. The measurements of relative intensities of $C_1 + C''_1$, C_2, C_6 and A_1 peaks allow to conclude that reaction 6 has proceeded in only about 50%. We have verified that this ratio decreased along with the increase of the sweep rate. Unfortunately, the Nicholson–Shain method could not be applied in these conditions in order to determine precisely the value of the rate constant k_6. Nevertheless, we have shown that, for a same value of the sweep rate (0.6 V $\mathrm{s^{-1}}$), the $\mathrm{Nibpy^{2+}/Ni^0bpy}$ transition presents the same partial reversibility when the divalent nickel complex is placed under CO or in the presence of $\mathrm{PhCH_2Cl}$ in the ratio 3–5 mol of RX per mol of Ni(II). We then assume that at r.t. k_6/k_4 ca. 3–5 for RX = $\mathrm{PhCH_2Cl}$, i.e. k_6 ca. $2–4 \times 10^2\ \mathrm{l\ mol^{-1}\ s^{-1}}$, since $k_4 = 60–70\ \mathrm{l\ mol^{-1}\ s^{-1}}$. On the other hand, for a

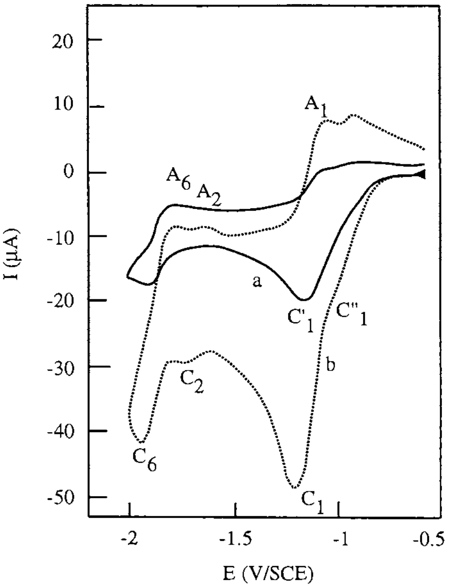


Fig. 3. Cyclic voltammograms of a solution of DMF plus $\mathrm{Bu_4NBF_4}$ (0.1 mol $\mathrm{l^{-1}}$). (a) $\mathrm{Nibpy^{2+}}$ (3×10^{-2} mol $\mathrm{l^{-1}}$), under CO; $v = 0.1$ V $\mathrm{s^{-1}}$. (b) $\mathrm{Nibpy^{2+}}$ (3×10^{-2} mol $\mathrm{l^{-1}}$), under CO; $v = 0.6$ V $\mathrm{s^{-1}}$ $E_{\mathrm{initial}} = -0.5$ V/SCE.

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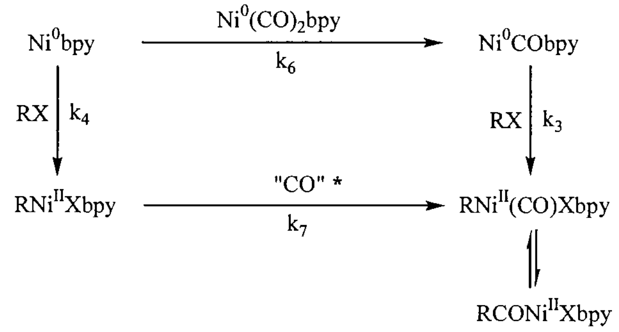
[1] The $\mathrm{Nibpy^{2+}}$ reduction in the presence of an organic halide undergoes an E_rC_i mechanism (fast electron transfert followed by irreversible chemical reaction) according to:

$$\mathrm{Nibpy^{2+}} + 2\mathrm{e} \rightleftharpoons \mathrm{Ni^0bpy},\ E_r$$

$$\mathrm{Ni^0bpy} + \mathrm{RX} \xrightarrow{k_4} \mathrm{RNi^{II}Xbpy},\ C_i$$

We have used the E_rC_i Nicholson–Shain abacus representing the ratio $\mathrm{ip(A_1)/ip(C_1)}$ in a function of $\log(k\tau)$. τ is the time necessary to go from E_λ (inversion potential) to $E_{\frac{1}{2}}$ [$E_{\frac{1}{2}} = 1/2\ E\mathrm{p(A_1)} + 1/2\ E\mathrm{p(C_1)}$]. τ is calculated from the voltage scan rate v according to the formulae: $\tau = 1/v|E_\lambda - E_{1/2}|$.For this purpose, RX must be in excess towards $\mathrm{Nibpy^{2+}}$, so $k = k_4$ [RX]. Then, by measuring $\mathrm{ip(A_1)/ip(C_1)}$, we determined the value of k_4.



Scheme 4.

reactive organic halide such as PhI, the rate constant k_6 is presumably lower than k_4, since $k_4 = 10^3 – 2 \times 10^3$ l mol^{-1} s^{-1}.

3. Formation of an acylnickel complex

Our results (see above) have clearly shown that the reduction of Nibpy^{2+} in the presence of CO in excess only led to the formation of the unreactive Ni^0(CO)$_2$bpy complex according to the very fast reaction 5:

$$\mathrm{Ni^0bpy} + 2\mathrm{CO} \xrightarrow{k_5} \mathrm{Ni^0(CO)_2bpy}$$

In accordance with this fact, we have noticed that organic halides were not converted when electrolyses of Nibpy^{2+} and RX solutions, set under CO bubbling, were carried out at low current intensity, which involved the solution being continuously saturated in CO [1].

The conversion of organic halides into ketones can only be effective if CO is limiting, in order to generate a mixture of Ni^0(CO)$_2$bpy and Ni^{0}bpy. In these conditions, two ways can be considered for the formation of the required acylnickel intermediate (Scheme 4).

The first way is an oxidative addition of the organic halide on the zerovalent nickel complex bound to both bpy and CO (Eqs. 6 and 3).

A second way is an oxidative addition of the halocarbon on the Ni^{0}bpy complex, followed by a CO capture from the mixed complexes Ni^0(CO)$_2$ bpy or Ni^{0}CObpy or from dissolved CO (Eqs. 4 and 7).

Very reactive organic halides such as aryl iodides for which $k_4 > k_6$ will react according to the second way. On the contrary, a number of organic halides (benzylchlorides, arylbromides, alkylbromides or iodides) have a moderate reactivity towards Ni^{0}bpy and the respective values of k_4 are not much lower than the value of k_6 (see above). Furthermore, preparative electrolyses yielding the ketone were conducted in solutions where Nibpy^{2+} was in a catalytic amount (5% vs. RX) [1]. In these conditions, the rates of the reactions 4 and 6 are presumably close to each other and the two routes leading to the acylnickel complex can be simultaneously involved.

At present, we have no sufficient data to give more accurate informations on the formation and on the evolution of the acylnickel complexes. So, the mechanism explaining the conversion of an organic halide into ketone is not yet fully elucidated. Only a few data are available in the literature concerning acylnickel complexes and particularly their evolution into ketones. Acylnickel complexes are known to be unstable since they evolve by decarbonylation, reductive elimination or reaction with organometallic compounds [6,7,20,21]. Under our conditions, another possible way is the electroreduction of the acylnickel complex, which way has not been fully investigated.

4. Conclusion

This study of the reactivity of zerovalent nickel complexes towards CO and organic halides has allowed us to establish the following points: Whatever is the halocarbon, CO is the most reactive species towards the complexes Ni^{0}bpy or Ni^{0}bpy$_2$. The reaction leads to the stable, inactive complex Ni^0(CO)$_2$bpy. The conversion of the organic halide into a ketone requires well adapted experimental conditions. Ni^{0}bpy and CO have to be present in the same amount to simultaneously generate equal amounts of Ni^0(CO)$_2$bpy and Ni^{0}bpy in order to avoid either the loss of the catalytic activity or the formation of the dimmer RR induced by the sole Ni^{0}bpy [11,12,17,18,22–24]. The electrochemical method has proved to be quite convenient to easily adjust the rate of production of Ni^{0}bpy versus the rate of dissolution of CO [25]. Two ways can be considered to explain the formation of a transient acylnickel species from the mixture Ni^0(CO)$_2$bpy + Ni^{0}bpy + RX.

5. Experimental

DMF (Merck), PhI (Aldrich), PhCH$_2$Cl (Aldrich) and 2,2′-bipyridine (Aldrich) were used as received. Bu$_4$NBF$_4$ used as supporting electrolyte was purchased from Fluka and further purified by recrystallisation from 1,1,1-trichloro-ethane/diethylether and dried in vacuum (30 mmHg) at 70°C. Nibpy^{2+} was obtained starting from the mixture Ni(CH$_3$SO$_3$)$_2$ plus bpy in the ratio 1:1 or from the NiBr$_2$bpy complex. The complexes Ni(CH$_3$SO$_3$)$_2$ and NiBr$_2$bpy were prepared according to reported procedures [10,12].

5.1. Preparation of $Ni(CO)_2bpy$ in DMF solution

An exhaustive coulometric reduction at controlled current (0.2 A) of $Ni(CH_3SO_3)_2$ (8×10^{-3} mol l^{-1}) plus bpy (8×10^{-3} mol l^{-1}) plus Bu_4NBF_4 (0.1 mol l^{-1}) in DMF solution was carried out under CO bubbling. The undivided cell was fitted with a magnesium rod as the anode, which was surrounded by a nickel grid as the cathode. The initial pale green solution turned to red during the electrolysis, which involves 2 mol of electrons per mol of divalent nickel.

Alternatively, Ni^0bpy_2 complex was formed by electrolysing a $Ni(CH_3SO_3)_2$ solution under argon and in the presence of excess bpy. The dark green solution then obtained led to the red solution of $Ni(CO)_2bpy$ after CO bubbling.

Voltammetric experiments were carried out using a three-electrode configuration cell under argon or CO, in DMF solution plus Bu_4NBF_4 (0.1 mol l^{-1}). The working electrode was a gold disk electrode ($\phi = 0.5$ mm). A two compartment system (saturated calomel reference electrode and DMF plus 0.1 mol l^{-1} Bu_4NBF_4 solution) separated by alumina fritted disks was used to probe the working electrode potential.

The electrochemical experiments with ohmic drop compensations were performed with an EG&G PAR model 173 potentiostat interfaced with a microcomputer.

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