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Electrosynthesis of symmetrical ketones from organic halides and carbon dioxide catalysed by 2,2′-bipyridine-nickel complexes

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Abstract

The electrochemical reduction of a 2,2′-bipyridine-nickel complex, in the presence of carbon dioxide in *N*-methylpyrrolidone or dimethylformamide as solvent gives the corresponding nickel(0) complex associated with two molecules of CO. Oxidative addition of an alkyl halide to this complex, followed by an internal CO shift and reductive elimination, leads to the formation of a symmetrical ketone in high yield along with nickel(II), whereas aryl or vinyl halides mainly give acyl derivatives. The nickel(0) species is electrochemically regenerated, thus giving rise to an efficient catalytic process. The possible mechanism of these reactions is discussed.

Introduction

Many methods have been suggested for making ketones from organic halides or organometallic compounds. They all require the use of transition metal complexes in various ways. Thus carbonyl iron [1], nickel [2] and cobalt [3] complexes have been used for the synthesis of symmetrical ketones from aryl and benzyl halides or arylmercury halides [4]. These reactions are stoichiometric and require severe experimental conditions. Alternatively symmetrical ketones have been prepared by treating organometallic compounds with CO in the presence of transition metal catalysts [5]. Dialkyl- and diaryl-nickel or -palladium compounds also give ketones on treatment either with CO at normal pressure [6] or with oxalyl chloride [7].

Until now no electrochemical alternative to these reactions has been proposed.

We recently described [8] a nickel-catalysed electrochemical reduction of CO_2. This reaction is regarded as a two stage process: the Ni^0bpy_2 complex initially formed at -1.2 V/SCE [9] (bpy denotes 2,2′-bipyridyl) reacts stoichiometrically with CO_2 to yield the stable $Ni^0bpy(CO)_2$ complex (eq. 1). This complex is in turn reduced at −1.6 V/SCE to give the intermediate $Ni^0bpy(CO)_2^{\cdot -}$, which can further react with CO_2 via a catalytic process to give CO and CO_3^{2-} (eq. 2–4) (see Fig. 1).

$$Ni^{II}bpy_2^{2+} + 4\,CO_2 + 6e \xrightarrow{-1.2\text{ V}} Ni^0bpy(CO)_2 + 2\,CO_3^{2-} \qquad (1)$$

$$Ni^0bpy(CO)_2 + e \overset{-1.6\text{ V}}{\rightleftharpoons} Ni^0bpy(CO)_2^{\cdot -} \qquad (2)$$

$$Ni^0bpy(CO)_2^{\cdot -} + CO_2 \rightarrow Ni^0bpy(CO)_2 + CO_2^{\cdot -} \qquad (3)$$

$$2\,CO_2^{\cdot -} \rightarrow CO + CO_3^{2-} \qquad (4)$$

In the presence of Mg^{II} ions, the trapping of CO_3^{2-} prevents loss of the catalyst.

Since organic halides are also readily reduced by Ni^0 complexes, we conceived a one-pot process which would allow the nickel-catalysed eletrochemical synthesis of ketones from CO_2 and organic halides, and we describe here the scope and limitations of this approach [10].

The mechanistic investigation led us also to study the reaction under stoichiometric conditions. Comparison was also made between this new process and the chemical synthesis of ketones from organic halides and CO with either catalytic or stoichiometric amounts of nickel complexes.

Experimental

N-methylpyrrolidone (NMP) was distilled over alcoholic potassium hydroxide and *N,N*-dimethylformamide (DMF) over a mixture of barium oxide and copper sulfate. Reagents and supporting electrolytes were used as supplied.

The nickel complexes $NibpyBr_2$ and $Nibpy_3(BF_4)_2$ were obtained as precipitates after mixing 2,2′-bipyridyl with $NiBr_2 \cdot 2H_2O$ and $Ni(BF_4)_2 \cdot xH_2O$, respectively as previously described [11].

Voltamperometric and amperometric measurements involved are of a rotating gold disk microelectrode and conventional equipment (SOLEA-Tacussel); the electrochemical cell [12] was a cylindrical undivided glass cell with a Mg-rod as the anode, a cylindrical gold gauze as the cathode, and a SCE reference electrode. The electrolyses were carried out at room temperature under CO_2, the solubility of which in NMP was found to be 0.2 *M*.

(a) Electrochemical synthesis of ketones from CO_2

Nickel catalyzed electrochemical synthesis of ketones: general procedure. A solution of $NibpyBr_2$ (224 mg, 0.6 mmol) or $Nibpy_3(BF_4)_2$ (420 mg, 0.6 mmol) and 2,2′-bipyridyl (140 mg, 0.9 mmol) in 30 ml of NMP, saturated with CO_2, containing NBu_4BF_4 (987 mg, 3 mmol) as supporting electrolyte, was first electrochemically reduced at −1.6 V/SCE until two mol of electron per mol of nickel complex had passed. The organic halide (6 mmol) was added in portions (10 × 0.6 mmol) after every cycle of 2 mol electron per mol of nickel. The mixture was then added to 1 *N* aqueous HCl and extracted with diethyl ether or pentane. Constant current electrolyses, with current density of 2.5 or 5 mA/cm^2, gave similar results.

Synthesis of ketones in stoichiometric conditions: general procedure. $NibpyBr_2$ (0.6 mmol) was totally reduced in NMP (30 ml) containing NBu_4BF_4 (3 mmol) at room temperature under CO_2 at −1.2 V/SCE using 6 F per mol of nickel to give

$Ni^0bpy(CO)_2$ quantitatively. The solution was then flushed with argon for 1 h to remove all the remaining CO_2. The organic halide RX (0.6 mmol) was then added and the reaction was carried out without passage of current until all the halide had disappeared. Work-up was as described above.

For mechanistic investigations, some reactions were performed either with two equivalents of organic halide relative to the nickel complex or in the presence of pyrrolidine (6 mmol) to trap the reactive intermediates.

(b) Electrochemical synthesis of ketones from CO

Catalytic experiments: typical procedure. A solution of $NibpyBr_2$ (0.6 mmol) and bpy (1.8 mmol) in 30 ml of NMP containing NBu_4BF_4 as supporting electrolyte was first electrochemically reduced under argon at −1.2 V/SCE until 1 F per mol of nickel had passed. A stream of a (10/90) mixture of CO and argon was then bubbled into the solution and RX (3 mmol) was added in portions (0.6 mmol) after each uptake of 1 F/mol of nickel).

Stoichiometric experiments: typical procedure. $Nibpy_3(BF_4)_2$ (0.6 mmol) and RX (1.2 mmol) were reduced at −1.2 V/SCE in NMP (30 ml) containing NBu_4BF_4 at room temperature under argon to form R_2Nibpy, as previously described [13]. The power was then turned off and CO was bubbled through the solutions at room temperature until all the organometallic was consumed. Work-up and analysis were performed as above.

Product analysis

All the products are known compounds. Their identifications were made on the basis of spectroscopic data by comparison with literature data or by comparison of their GLC data with those for authentic samples.

Yields of neutral products are those indicated by GLC using external standards. Yields of acid were obtained by acid–base titration [14].

Results

(1) Nickel-catalyzed electrosynthesis of ketones from organic halides and CO_2

The results of the electrosynthesis of various ketones from organic halides and CO_2 catalysed by $NibpyBr_2$ are given in Table 1.

In a typical reaction, a mixture of the catalyst $NibpyBr_2$ (2×10^{-2} *M*) and bpy (3×10^{-2} *M*) in NMP through which CO_2 was bubbled was first partly reduced by use of 2 F per mol of nickel at −1.6 V/SCE, at room temperature. The halide RX was then added in portions (2×10^{-2} *M*) after each passage of 2F/Ni, until 2×10^{-1} *M* of RX had been consumed. Yields of ketone were from good to high from allylic, benzylic, and aliphatic halides. The main side reactions give the dimer R–R and the hydrocarbon RH. In contrast, from vinyl (entries 8, 9) or aryl (entries 10, 11) halides no ketone was obtained; instead, the carboxylic acid and the dimer were formed along with the hydrocarbon. Aryl chlorides and non-activated aryl bromides (entries 12–14) reacted very slowly. The same results were obtained in DMF.

Electrolysis of a mixture of benzyl chloride and 1-hexyl bromide in 1/2 ratio gave a mixture of symmetrical and mixed ketones in statistical ratio.

Table 1

Nickel-catalysed electroreductive synthesis of ketones from various halides and CO_2, at constant potential [a]

Entry	RX	Products yield (%)			
		RCOR [d]	RR [d]	RCOOH [e]	RH [d]
1	$PhCH_2Br$ [b]	85	15	–	–
2	$PhCH_2Cl$ [c]	70	5	–	25
3	$C_6H_{13}I$ [b]	60	5	20	–
4	$C_6H_{13}Br$ [c]	80	20	–	–
5	$C_{10}H_{21}Br$ [b]	80	15	–	5
6	$CH_3CH{=}CHCH_2Br$ [b]	70	–	–	[f]
7	$CH_3CH{=}CHCH_2Cl$ [b]	85	15	–	–
8	$PhCHBr{=}CH_2$ [c]	–	50	15	10
9	$CH_3CH_2CHBr{=}CH_2$ [c]	–	–	30	[f]
10	p-CF_3PhBr [c]	–	35	40	20
11	p-$FPhBr$ [c]	–	2	50	22
12	o-$FPhCl$	poor reactivity			
13	$PhCl$	poor reactivity			
14	p-CH_3OPhBr [c]	poor reactivity			

[a] NMP (30 ml); $NibpyBr_2$ (0.6 mmol); bpy (0.9 mmol); portionwise (0.6 mmol) addition of RX (6 mmol) (see text); Mg-anode; gold cathode; constant potential electrolysis (−1.6 V/SCE). [b] NBu_4BF_4 (3 mmol) as supporting electrolyte. [c] NBu_4Br (3 mmol) as supporting electrolyte. [d] GLC yields. [e] Yields determined by acid–base titration. [f] Not determined.

As pointed out previously [9] at least a two-fold excess of bipyridyl relative to the catalyst is necessary for quantitative reduction of Ni^{II} into $Nibpy^{2+}$ rather than $NibpyBr^+$. Both species are in fact reduced into Ni^0bpy_2; nevertheless, in the absence of extra bpy, half of the catalyst is lost according to eqs. 5 and 6.

$$Ni^{II}bpyBr^+ + 1e \rightleftharpoons Ni^{I}bpyBr \qquad (5)$$

$$2Ni^{I}bpyBr \rightarrow Ni\downarrow + Ni^0bpy_2 + 2Br^- \qquad (6)$$

However, as will be suggested in the Discussion, the reactive reductive species is probably Ni^0bpy, the concentration of which depends on that of bpy, in accord with equilibrium 7.

$$Ni^0bpy_2 \rightleftharpoons Ni^0bpy + bpy \qquad (7)$$

As expected if the amount of bpy is more than twice that of nickel the overall rate of reduction of CO_2 is lowered without change in the yield of ketone.

Some reactions were also conducted under constant current intensity with various solvents and supporting electrolytes as part of the mechanistic investigations and also to find a possible easier procedure for preparative work. The results are given in Table 2.

Bromine ions play a positive role in the reaction, more especially in reactions of benzyl chlorides (Table 2, entries 6, 7). As already noticed for the nickel-catalysed dimerisation of organic halides [9], in the presence of bromides the main species is the anion Ni^0bpyBr^- (eq. 8) which is more reactive towards both RX and CO_2.

$$Ni^0bpy_2 + Br^- \rightleftharpoons Ni^0bpyBr^- + bpy \qquad (8)$$

Additionally, in the presence of Br^- the formation of the acid is suppressed. This

Table 2

Ni-catalysed constant current electrosynthesis of ketones from benzyl halides [a]

Entry	RX	Solvent	Supporting electrolyte	Yield (%)		
				RCOR [d]	R–R [d]	RCOOH [e]
1	$PhCH_2Br$	NMP [b]	NBu_4BF_4	86	12	–
2		NMP [b]	NBu_4Br	88	10	–
3		DMF [b]	NBu_4BF_4	33	13	27
4		DMF [b]	NBu_4Br	77	21	–
5		DMF [c]	NBu_4BF_4	77	21	–
6	$PhCH_2Cl$	NMP [b]	NBu_4BF_4	40	1	40
7		NMP [b]	NBu_4Br	77	1	4
8		DMF [c]	NBu_4Br	100	–	–

[a] NMP (or DMF) (30 ml); $NiBr_2bpy$ (0.6 mmol); bpy (0.9 mmol); Mg-anode; gold cathode; portionwise (0.6 mmol) addition of RX (see text) (total amount 6 mmol); constant current electrolysis; CO_2 bubbling; room temperature; supporting electrolyte (3 mmol). [b] Current density: 5 mA/cm^2. [c] Current density: 2.5 mA/cm^2. [d] GLC yields relative to RX. [e] Yields determined by acid–base titration.

effect is interpreted in the Discussion below in terms of the stability of the intermediates.

The solvent effect can be understood as follows. We have found that the diffusion of the species is twice as rapid in DMF as in NMP, while the rates of the chemical reactions are roughly similar. As a consequence, the optimal current intensity should be lower for DMF than for NMP (Table 2, entries 1, 5), unless the rate of the chemical reactions is increased owing to the use of bromides (Table 2, entries 4), the effect of which has been mentioned above.

There are important advantages in using a sacrificial anode of magnesium. This allows the reaction to be performed in a diaphragmless cell and, additionally prevents deactivation of the catalyst. In a divided cell, as soon as the reactions starts there is loss of the catalyst as precipitate. Mg^{II} ions prevent this side effect by forming the complex $Mg(CO_3)bpy$.

(2) *Nickel-mediated stoichiometric synthesis of ketones from organic halides and CO_2*

To a solution of electrochemically formed $Nibpy(CO)_2$ in NMP was added either a stoichiometric amount or a twofold excess of the halide. Benzyl, allyl, and vinyl halides reacted rapidly with the complex (within a few minutes) at room temperature, whereas the aliphatic or aryl halides reacted more slowly, requiring several hours. The products from various kinds of reagents are given in Table 3, with the corresponding experimental conditions.

As in the catalytic reactions, the ketone is formed in high yield in the case of alkyl halides, whereas the acid and the hydrocarbons RH and R–R are obtained from aryl and vinyl halides. The RX/Ni ratio has no effect except in the case of benzyl bromide, where an excess of the halide increases the yield of R–R because of the great reactivity of $PhCH_2Br$ towards $Nibpy(CO)_2$ as well as towards $(PhCH_2)_2Ni$, which is formed subsequently. The reductive elimination is promoted by addition of benzyl halide, which oxidatively adds to nickel to form a benzyl nickel halide complex and dibenzyl [15].

To aid in the mechanistic study some reactions were performed in the presence of pyrrolidine with the aim of trapping the intermediate leading to the carboxylic acid.

Table 3

Stoichiometric synthesis of ketones from RX and Nibpy(CO)$_2$ [a]

Entry	RX	Special conditions	Yield %				
			RCOR	RR	RCOOH	RH	RCO–N<
1	$PhCH_2Br$	[b,d]	85	14	–	–	–
2	$PhCH_2Br$	[b,e]	50	50	–	–	–
3	$PhCH_2Cl$	[c,d]	85	15	–	–	–
4	$PhCH_2Cl$	[c,e,f]	80	20	–	–	–
5	$C_6H_{13}Br$	[c,d] or [e]	70	–	–	30	–
6	$C_{10}H_{21}Br$	[b,d] or [e]	74	4	–	16	–
7	*trans*-$CH_3CH{=}CHCH_2Cl$	[b,d] or [e]	85	–	–	–	–
8	$PhCHBr{=}CH_2$	[b,e]	–	5	30	10	–
9	$PhCHBr{=}CH_2$	[b,e,f]	–	15	–	10	50
10	PhBr	[b,e]	–	–	20	20	–
11	PhBr	[c,e]	8	6	44	20	–
12	*p*-$CH_3OC_6H_4Br$	[c,d] or [e]	25	5	23	37	–
13	*p*-$CH_3OC_6H_4I$	[c,e,f]	–	–	–	36	60
14	*p*-$CF_3C_6H_4Br$	[c,e]	5	10	13	–	–

[a] NMP (30 ml) Nibpy(CO)$_2$ (0.6 mmol) (for synthesis see text). Argon bubbling, room temperature. [b] Supporting electrolyte NBu_4BF_4 (3 mmol). [c] Supporting electrolyte NBu_4Br (3 mmol). [d] Addition of RX (0.6 mmol). [e] Addition of RX (1.2 mmol). [f] Pyrrolidine (6 mmol).

It can be seen (Table 3) that the amide is formed only in the case of vinyl and aryl halides at the expense of the carboxylic acid. Such behaviour suggests that a common intermediate leading to either product.

(3) Synthesis of ketones from organic halides and CO in the presence of nickel complexes

These reactions were also carried out in a one compartment cell, in the presence of a magnesium rod as the anode, with R = alkyl or aryl in RX.

For the catalytic conditions, it is necesary to delay the bubbling of CO until one cycle of the catalytic reduction of RX has been performed, in order to avoid the loss of the catalyst as non-electroactive Ni(CO)$_4$. Yields of dialkyl ketone (RCOR, R = benzylic, aliphatic) are identical (around 80%) to those obtained using CO$_2$. The reaction is less efficient, however, than the catalytic reaction involving CO$_2$, in as much as the turnover of the catalyst is low, because of the poisoning effect of CO on the catalyst. Similarly, less than 10% of aromatic ketone can be obtained in this way, the hydrocarbons ArAr and ArH being preferentially formed. Similar results were obtained under stoichiometric conditions.

Discussion

Comparison of the data for the four electrochemical symmetrical ketone syntheses from alkyl halides and either CO$_2$ or CO described clearly reveals the potential of the new nickel-catalysed reaction involving CO$_2$. This reaction gives the ketones efficiently without direct use of CO, which is toxic, not easy to handle, and deactivates the catalyst.

The comparisons made also show that all four processes must have common intermediates at least at some stages: this helps in elucidating the mechanism of the new catalytic reaction.

If we focus on the two reactions with CO_2, we see that both the catalytic and the stoichiometric conditions give similar results in terms of the behaviour of the studied organic halides and the yields of products. There are however significant differences in the reaction rates. Indeed, the overall catalytic process being faster than the stoichiometric one, especially for the aliphatic and aryl halides. We can thus suggest that the two reactions proceed by the same pathway but with different reaction rates for the first step.

In both reactions involving CO_2 the first step is an oxidative addition of RX to a Ni^0 species formed by the electroreduction of Ni^{II} in the presence of CO_2 (eq. 1–4). A mixture of Ni^0 species is presumably thus obtained, the concentration of each being determined by the equilibria 9 and 10.

$$Ni^0bpy(CO)_2 \rightleftharpoons Ni^0bpyCO + CO \tag{9}$$

$$Ni^0bpy_2 + Ni^0bpy(CO)_2 \rightleftharpoons 2\ Ni^0bpyCO + bpy \tag{10}$$

As previously observed for many other reactions involving nickel catalysts, the most reactive Ni^0 species should be an incompletely coordinated one such as Ni^0bpyCO, which is more likely to be found in the catalytic process, where Ni^{II} is only partially reduced in the early stages, than in the stoichiometric process. The oxidation of Ni^0bpyCO is clearly revealed in cyclic (Fig. 1) and linear (Fig. 2) voltammetry at -0.2 V/SCE, that is, as expected, at a negative potential of $Ni^0bpy(CO)_2$ (0V/SCE).

This is in keeping with the fact that the optimum initial conditions for the catalytic process have been found to involve partial reduction of the starting Ni^{II}, thereby providing a mixture of nickel species, including the active one. As proof of this, we found that if we add to an electrochemically generated $Ni^0bpy(CO)_2$ an equal amount of Ni^{II}, the rate of formation of the ketone from RX (R = aliphatic) is greatly increased. This would reasonably account for the slower rate of disappearance of RX under stoichiometric rather than catalytic conditions. We thus assume that the first step is represented by eq. 11.

$$RX + \underset{(\mathbf{A})}{Ni^0bpyCO} \rightarrow \underset{(\mathbf{B})}{R\text{–}Ni(CO)bpyX} \tag{11}$$

To account for the differences in the behaviour of the studied halides, alkyl halides on one hand and aryl or vinyl halides on the other, it is necessary to detail the further steps.

The relative stability of the initially formed alkyl- or aryl-nickel derivative **B** is presumably the factor which determines the choice of reaction pathway (i.e.: formation of ketone or formation of acid). This intermediate is not very stable when R is an aliphatic, benzylic or allylic, group and it evolves into a dialkyl derivative by disproportionation (eq. 12) to give the dialkylnickel intermediate, which is easily characterized by cyclic voltammetry.

$$2\ \underset{(\mathbf{B})}{RNi(CO)bpyX} \rightarrow \underset{(\mathbf{C})}{R_2Ni(CO)bpy} + NibpyX_2 \tag{12}$$

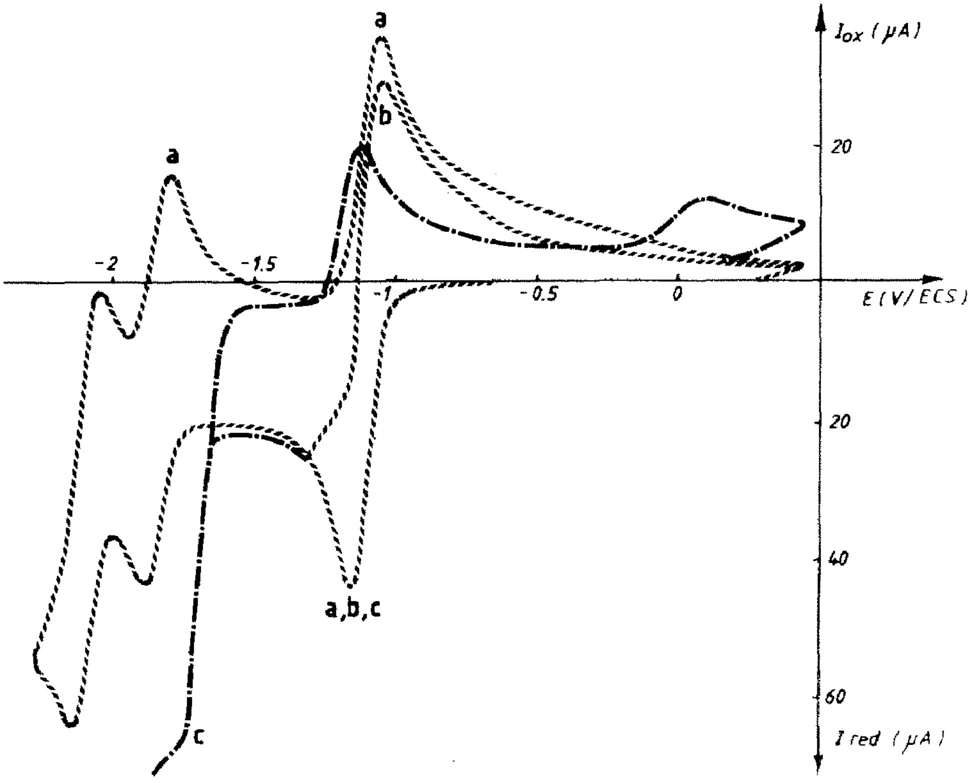

Fig. 1. Cyclic voltammogram (gold microelectrode 100 mV s^{-1}) of $Nibpy_3(BF_4)_2$ (10^{-2} *M*) in NMP with NBu_4BF_4 (10^{-1} *M*). Curve *a*: under argon [9]; curve *b*: under CO_2, potential sweep limits: 0.5 V; −1.3 V/SCE; curve *c*: under CO_2, potential sweep limits: 0.5 V; −2.3 V/SCE.

Evidence for such a disproportionation previously observed in similar systems [9], was obtained by chronoamperometric monitoring at the reduction potential of Ni^{II} (i.e.: −1.2 V/SCE) following the addition of 0.6 mmol of RX (R = benzyl and allyl), which showed the immediate regeneration of 50% of the initial Ni^{II} as given by the linear voltammetry. This rules out the possible alternative reaction of the organic halide with the monoalkyl nickel derivative **B** [16*].

The dialkylnickel derivative **C** formed (eq. 12) is identical to the intermediate obtained in the reactions involving CO. The linear voltammograms show identical waves (Fig. 3). Moreover, both reactions give the hydrocarbon RH by acid hydrolysis, whereas the dimer RR is formed in the presence of O_2.

The final steps are also common to all processes: the dialkyl intermediate **C** is slowly converted into an alkyl-acyl-nickel derivative **D**, as previously described [17], (eq. 13) and this rapidly decomposes by reductive elimination to give the ketone (eq. 14).

$$\underset{(\mathbf{C})}{R_2Ni(CO)bpy} \rightarrow \underset{(\mathbf{D})}{RCONibpyR} \qquad (13)$$

$$\underset{(\mathbf{D})}{RCONibpyR} \rightarrow RCOR + Ni^0bpy \qquad (14)$$

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* Reference number with asterisk indicates a note in the list of references.

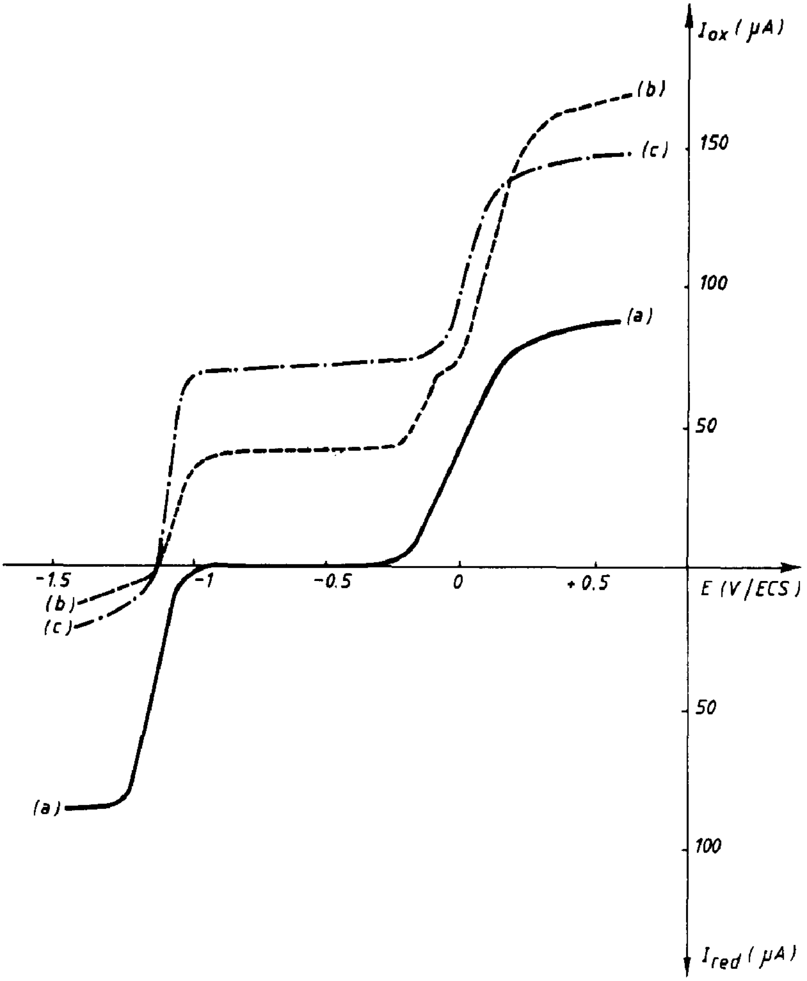


Fig. 2. Linear voltammogram in NMP with NBu_4BF_4 (10^{-1} M), at a rotating gold microelectrode (3 mm^2), under argon of: curve *a*: a mixture of $Nibpy_3(BF_4)_2$ (10^{-2} M) and $Nibpy(CO)_2$ (10^{-2} M), this latter having been formed by electroreduction (6 F/Ni) of $Nibpy_3(BF_4)_2$ under CO_2; curve *b*: same mixture after an electricity intake of 2 F/Ni at −1.2 V/SCE; curve *c*: after an intake of 2 F/Ni, at −1.2 V/SCE in the presence of additional (10^{-1} M) bipyridine.

When aromatic or vinylic compounds are involved, the oxidative addition (eq. 11) of the halide to Ni^0 leads to a more stable intermediate, presumably ArNi(CO)bpy which does not give a diaryl nickel complex.

This monoarylnickel slowly evolves into the less stable acylnickel derivative by CO insertion (eq. 15), and this decomposes by reductive elimination to form an acyl halide (eq. 16).

$$\text{ArNi(CO)bpyX} \rightarrow \text{ArCONibpyX} \tag{15}$$

$$\text{ArCONibpyX} \rightarrow \text{ArCOX} + \text{Ni}^0\text{bpy} \tag{16}$$

Hydrolysis converts this product into the corresponding carboxylic acid. When the reaction is performed in the presence of an amine (stoichiometric condition)

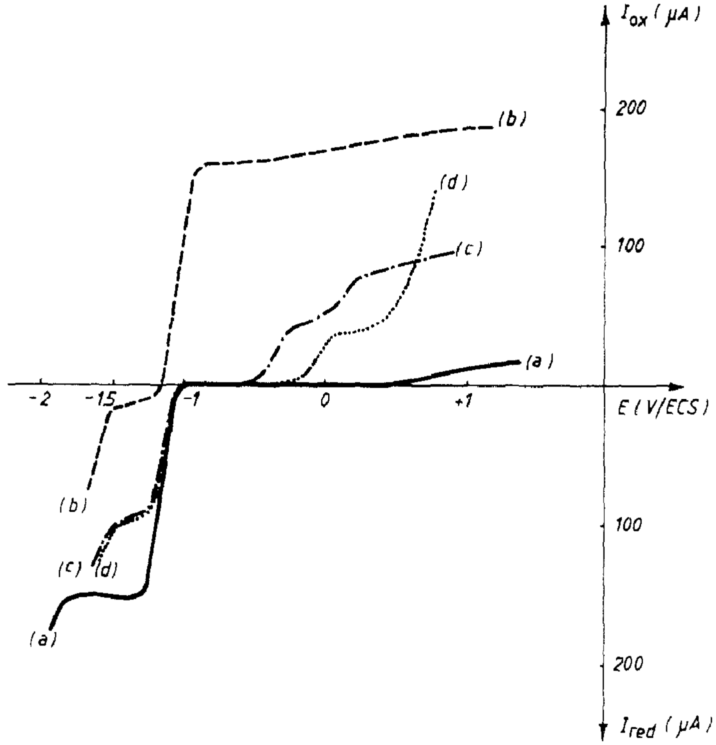
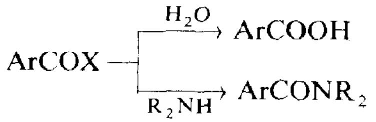


Fig. 3. Linear voltammogram in NMP with NBu_4BF_4 (10^{-1} *M*) at a rotating gold microelectrode (3 mm^2) of: curve *a*: $Nibpy_3(BF_4)_2$ (2×10^{-2} *M*) under argon; curve *b*: after an electricity intake of 2 F/Ni at −1.2 V under argon; curve *c*: after addition of $PhCH_2Br$ (2×10^{-2} *M*) (oxidation of $(PhCH_2)_2Nibpy$) curve *d*: after bubbling of CO (oxidation of $Nibpy(CO)_2$, formation of $(PhCH_2)_2CO$).

corresponding amide is formed in comparable amount:



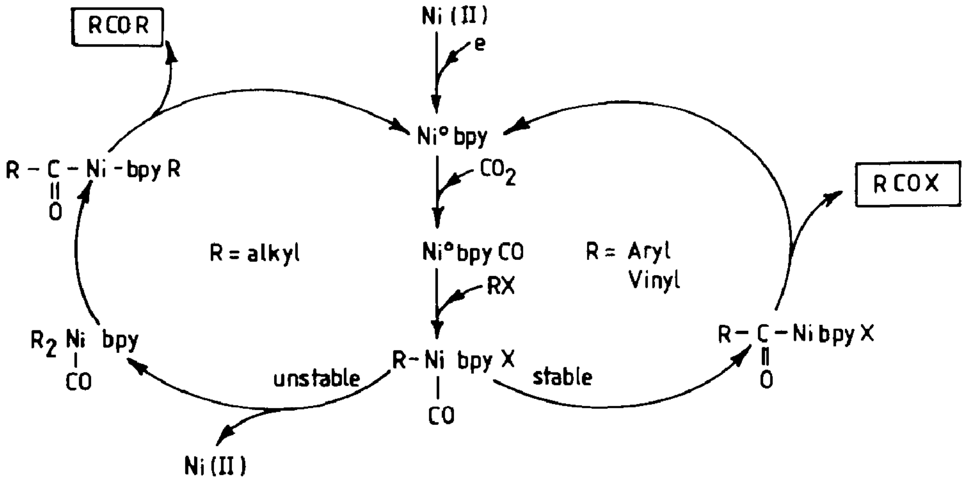
$$ArCOX \xrightarrow{H_2O} ArCOOH$$

$$ArCOX \xrightarrow[R_2NH]{} ArCONR_2$$

The formation of the dimer ArAr indicates the possible formation of the diarylnickel complex (Ar_2Nibpy), but in contrast to the monoaryl derivative this diaryl complex does not undergo CO insertion, as shown by the stoichiometric experiments in the presence of CO.

Amide formation was never observed with alkyl derivatives. This means that the carboxylic acid obtained in some experiments (see entry 3, Table 2) is not formed through the same pathway. Indeed, the monoalkyl $PhCH_2NibpyX$ is not stable enough to allow the insertion of CO into the C–Ni bond. On the other hand such a complex can be reduced at a not very low potential to give $PhCH_2Ni^-$, which can react with CO_2 to give the acid. The possibility would depend on the nature of the associated halide, the sequence of stability of RNiX being as follows [18] RNiCl > RNiBr > RNiI. This can account for the difference between the results from runs 1 and 6, in Table 2.

Scheme 1 summarises the various steps of the nickel-catalysed electrochemical synthesis of ketones or acyl derivatives from organic halides and CO_2.



Scheme 1

In conclusion, we have shown in this study that the bpy-nickel complex is an efficient catalyst in the electroassisted activation of both CO_2 and organic halides RX to give symmetrical ketones in high yields when R in RX is an alkyl group (aliphatic, allyl or benzyl), whereas acyl derivatives are formed when R is an aryl or vinyl group. The main advantage of the process lies in the use of CO_2 as an in situ source of CO, in controlled amounts to avoid the deactivation of the catalyst as $Ni(CO)_4$. The use of consumable anode of magnesium in a diaphragmless cell not only provides a very simple procedure but also progressively provides the amount of Mg^{2+} necessary to trap the undesirable CO_3^{2-} formed in the reduction of CO_2.

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16 *Note added in proof.* The reduction of complex *B*, suggested by a referee, has been ruled out as main pathway in controlled potential electrolyses for it should lead mainly to the carboxylic acid. This mechanism is probably operative in constant current electrolyses at high current densities.

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