Catalytic hydrocyanation of α-ketoalkynes by Ni(CN)$_2$/CO/KCN system in alkaline aqueous media: Identification of the active species

Noé Rosas [a,*], Armando Cabrera [a], Pankaj Sharma [a], José Luis Arias [a], José Luis García [a,1], Henri Arzoumanian [b]

[a] *Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Circuito Exterior, Coyoacán, 04510 Mexico, D. F., Mexico*
[b] *Université D'Aix-Marseille III, Faculté des Sciences de Saint-Jérôme ENSSPICAM Marseille, France*

Abstract

5-Hydroxy-3-pyrrolin-2-ones are regioselectively synthesized in a good yield under very mild conditions by tetracyanonickelate (0) ion catalyzed hydrocyanation of α-ketoalkynes, in the absence of hydrogen cyanide. The catalyst is prepared in situ in a basic aqueous medium by reduction of Ni(CN)$_2$ with CO in the excess of KCN. From the IR spectroscopy studies and by evaluation of catalytic activity of some cyanonickelates it is proposed that $[Ni(CN)_4]^{-4}$ anion is the active species in the process. A possible mechanism is suggested for the conversion of nickel cyanide to $[Ni(CN)_4]^{-4}$. The effect of the reaction variables, e.g.: reaction time, temperature, absorption of carbon monoxide, the concentration of potassium cyanide, water, substrate, and sodium hydroxide were also examined. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrocyanation; Tetracyanonickelate; α-ketoalkynes; Pyrrolinone

1. Introduction

The hydrocyanation of alkenes and alkynes is an important industrial process since it leads to nitriles that are potentially useful intermediates in organic synthesis [1]. This reaction proceeds in the presence of a homogeneous or heterogeneous catalyst involving the use of highly poisonous hydrogen cyanide at elevated temperatures and pressures, which promotes other side reactions, e.g., isomerization and addition of protic solvents [2].

Transition metal complex catalyzed hydrocyanation of alkynes to yield nitriles are generally poorly understood. Some hydrocyanations in the absence of hydrogen cyanide have been accomplished by using $[Co(CN)_5]^{-3}$ in aqueous solution under H$_2$ atmosphere [3], or

---

* Corresponding author. Tel.: +52-5-616-2172; fax: +52-5-616-2217.
E-mail address: noe@servidor.unam.mx (N. Rosas).
[1] Also corresponding author.

$[Ni(CN)_4]^{-2}$ with a reductor media ($NaBH_4$) or by the use of zinc metal [4], in the presence of excess of KCN, in all cases the hydrocyanation is accompanied by other non-desirable reaction products.

Alper and Joó reported the carbonylation of allyl halides under phase-transfer conditions, using $Ni(CN)_2$ as precursor in order to generate the catalytically active specie $[Ni(CO)_3(CN)]^{-1}$ [5]. Subsequently, we have developed the hydrocarbonylation of alkynes [6,7] and allenes [8] catalyzed by the same system in the absence or presence of potassium cyanide respectively, these results lead to a new method for the hydrocyanation of α-ketoalkynes [9].

Here, we wish to report the improvement and the study of the regioselective synthesis of highly functionalized 3,5-substituted 5-hydroxy-3-pyrrolin-2-ones, by the hydrocyanation of α-ketoalkynes with potassium cyanide catalyzed by the $Ni(CN)_2/CO/KCN$ system in alkaline aqueous medium. From the IR spectroscopic data and the catalytic activity evaluated for some cyanocarbonylnickelates in the process, it is concluded that $[Ni(CN)_4]^{-4}$ anion is the active species. The effects of other reaction variables are also examined.

2. Experimental

2.1. General comments

Solvents and reagents were used as received from the suppliers unless otherwise stated. α-ketoalkynes [10], $K_2[Ni(CN)_4]$ [11], $K_4[Ni_2(CN)_6]$ [12], $Na_4[Ni(CN)_4]$ [4,11] $K_4[Ni_2(CN)_6(CO)_2]$ [12] and $[(Ph)_4P][Ni(CN)(CO)_3]$ [5] were synthesized by methods described in the literature, and their purities were checked by means of IR, MS and ^1H and ^{13}C NMR techniques [19]. IR spectra were recorded in $CHCl_3$, KBr or H_2O on a Nicolet FT 5SX spectrometer. NMR spectra were recorded on a Varian Unity Plus 500

using $(CH_3)_4Si$ as internal reference in $CDCl_3$ as solvent at 25°C. Mass spectra were obtained using a Jeol JMS-AX505 HA spectrometer. The reaction products were quantified by GC in a Hewlett Packard 5890 analyzer with a HP 225 (10 m × 0.53 mm) column packed. The absorption of carbon monoxide was estimated using a gas burette.

2.2. General procedure

Preparation of the catalytic system: A stirred solution of 5 N NaOH (12.5 ml) was saturated with CO by slow bubbling of carbon monoxide at room temperature for a few minutes. To this solution was then added 1 mmol of $Ni(CN)_2$ and stirring was continued under CO atmosphere for 20 h, the resulting aqueous media yielded a yellowish green suspension. The addition of 15 mmol of KCN resulted in an immediate orange colored solution, which was used for some studies in the IR region.

2.3. Synthesis of 5-hydroxy-3-pyrrolin-2-ones

Ten micromolars of α-ketoalkyne was added to the catalytic solution previously prepared. The mixture was stirred at room temperature and under atmospheric pressure for 1 h. At the

Table 1
Catalytic hydrocyanation of α-ketoalkynes by $Ni(CN)_2/CO/$ KCN system in alkaline aqueous medium at 25°C for 1 h[a]

Reaction	α-ketoalkyne		Pyrrolinone yield (%)
	R	R^1	
1	Ph	Me	81
2	Ph	Et	82
3	Ph	Pr	73
4	Ph	t-Bu	70
5	Bu	Me	82
6	Bu	Et	80
7	Bu	Pr	80
8	Bu	t-Bu	73

[a]See Section 2 for general procedure.

Table 2
Hydrocyanation of 3-octyn-2-one by different nickel species formed in situ from $Ni(CN)_2$ and KCN
General conditions: 12.5 ml of H_2O, 10 mM 3-octyn-2-one at 25°C.

Reaction	Preparation of the catalytic system						Hydrocyanation of 3-octyn-2-one	
	$Ni(CN)_2$ (mM)	KCN (mM)	NaOH (mM)	Bubbling of CO (h)	KCN (mM)	IR absorption spectra[a]	Time (h)	Pyrrolinone yield (%)
9		15				1	9.0	30.62
10		15	62.5			1	9.0	15.85
11	8.5					2	9.0	11.13
12	8.5		62.5			3	9.0	13.23
13	1	15				7	9.0	16.17
14	1	15	62.5			7	9.0	13.53
15	1	15	62.5	20		7	9.0	16.53
16	1	15		20		7	9.0	16.21
17	1			20	15	7	9.0	18.22
18	1		62.5	20		8	20 min	6.15
19	1		62.5	20	3	9	20 min	12.13
20	1		62.5	20	15	11	9.0	89.10
21	1		62.5	20	15	11	20 min	42.27
22	1		62.5	20	20	11	20 min	27.10

[a] IR spectras were obtained before the addition of substrate.

end of the reaction, ethyl acetate $(3 \times 20$ ml) was used to extract the product. Evaporation of the solvent after drying over $MgSO_4$ yielded pure product.
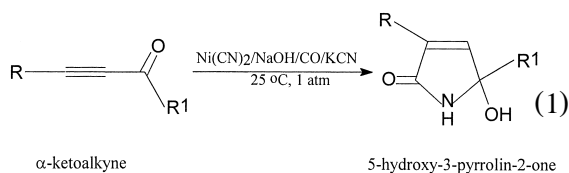
Table 3
Infrared absorption frequencies of cyanocarbonylnickelate species detected in the catalytic system and synthesized

Species	Medium	Absorption frequencies (cm^{-1})[a]	IR spectrum
NC^{-1}	KBr	2078	12
	KBr	2085 [13]	
	aqueous	2078	1
	aqueous	2080 [14]	
$Ni(CN)_2$ 1	KBr	2170	13
	KBr	2170 [15]	
	aqueous	2165	2
$[Ni(CN)_4]^{-2}$ 2	KBr	2124	14
	CsI	2122 [16]	
	aqueous	2123	3
	aqueous	2124 [14]	
$[Ni(CN)_5]^{-3}$ 3	aqueous	2103	5
	aqueous	2103 [14]	
$[Ni_2(CN)_6(CO)_2]^{-4}$ 8	aqueous	2123 2077 2057 1980 1919	8
	aqueous	2124 2077 2058 1981 1919 [12]	
$[Ni(CN)_4]^{-4}$ 9	KBr	1983	15
	Nujol	1985 [17]	
$[Ni_2(CN)_6]^{-4}$ 10	KBr	2125 2067 2045	16
	CsI	2124 2062 2032 [18]	
	aqueous	2122 2058 2025	11
$[Ni(CN)(CO)_3]^{-1}$ 11	KBr	2112 2048 1954	17
	CH_2Cl_2	2108 2045 1963 [5]	

[a] Absorption frequencies with superscript refer to literature data and numbers in parentheses to reference.

3. Results and discussion

Table 1 shows the results of catalytic hydrocyanation of α-ketoalkynes with $Ni(CN)_2/CO/KCN$ system in alkaline aqueous medium Eq. (1). It was observed that in the range of conditions investigated here, the only product formed in a good yield was the 5-hydroxy-3-pyrrolin-2-one.

$$\text{R}-\!\!\!\equiv\!\!\!-\overset{\displaystyle O}{\underset{\displaystyle R1}{C}} \xrightarrow[\text{25 °C, 1 atm}]{\text{Ni(CN)2/NaOH/CO/KCN}} \quad (1)$$

α-ketoalkyne   5-hydroxy-3-pyrrolin-2-one

It was noted that the hydrocyanation reaction of α-ketoalkynes under very mild conditions occurs via the formation of the nitrile compound followed by its hydrolysis to amide, which on cyclization yield the pyrrolinone [9]. Introduction of substituents (R = Bu, Ph) into α-ketoalkynes has not appreciable effect on the hydrocyanation. In the case of substitution of R^1, yields of pyrrolinone decreased lightly with increasing of the size of the substituents.

In addition one showed underline that, when $[Co(CN)_5]^{-3}$ and $[Ni(CN)_4]^{-2}$ were used as catalytic precursors for the hydrocyanation of similar alkenes, isomerization, hydrogenation and other intermediate products were obtained.

3.1. Determination of the catalytic active specie

In order to determine that cyanocarbonylnickelates anions are formed in the catalytic system in the hydrocyanation reaction, we have examined hydrocyanation reaction of 3-octyn-2-one, and the results are summarized in Table 2. The IR spectra and the assignment of bands are shown in (Table 3) and Figs. 1–3. A detailed study of the catalytic system for the hydrocyanation process by IR spectroscopy revealed the formation of different ionic species of nickel with the following characteristics.
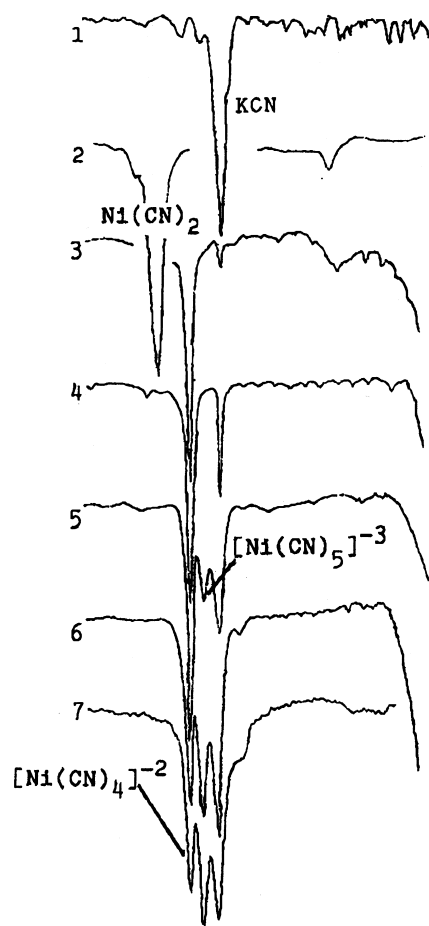

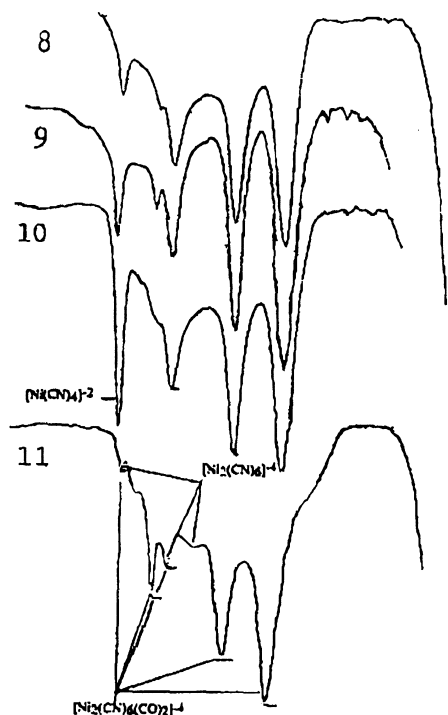Fig. 1. IR Absorption spectra measured in the preparation of differents catalytic systems formed from $Ni(CN)_2$ and KCN. See Table 2: (1) reactions 9 and 10. (2) Reactions 11 and 16 with 15 mM $Ni(CN)_2$ without KCN. (3) Reaction 12. (4) Reactions 13, 14, 16, 17 with 3 mM KCN. (5) Reaction 14 with 5 mM KCN. (6) Reaction 15 with 10 mM KCN. (7) Reactions 13, 17.

(1) The $Ni(CN)_2$ is very stable in aqueous solution, only negligible quantity is dissociated into CN^- and $[Ni(CN)_4]^{-2}$; this dissociation is not enhanced even with agitation for 20 h. (spectrum 2).

(2) In the presence of NaOH (2.5 g) or KCN, 3 mM., the $Ni(CN)_2$ is totally dissociated with formation of $[Ni(CN)_4]^{-2}$, spectra 3 and 4 respectively. An increase of KCN concentration (5–15 mmol) in the medium generates an equilibrium between $[Ni(CN)_4]^{-2}$ and $[Ni(CN)_5]^{-3}$ [14], spectra 5–7.

Fig. 2. IR Absorption spectra measured in the preparation of differents catalytic systems formed from $Ni(CN)_2$ and KCN. See Table 2: (8) Reactions 18 and 32. (9) Reaction 19. (10) Reaction 19 with 5 mM KCN. (11) Reactions 21–22.

(3) When $Ni(CN)_2$ in alkaline media under CO atmosphere, it is observed that the quantity of CO absorbed depends on the concentrations of NaOH and on the time (Figs. 4 and 5), the principal species formed are $[Ni(CO)_2(CN)_2]$ [5] and $[Ni_2(CN)_6(CO)_2]^{-4}$ [6], Fig. 4 and spectrum 8. The $[Ni_2(CN)_6(CO)_2]^{-4}$ anion is in equilibrium with $[Ni(CN)_4]^{-2}$ and $[Ni(CN)_2(CO)_2]^{-2}$ species [16].

(4) We can observe from Scheme 1, that $[Ni(CO)_2(CN)_2]^{-2}$ ion is generated from the attack of hydroxide ion at one of the cyanocarbon atom of $[Ni(CO)_2(CN)_2]$ with the elimination of HCNO followed by the addition of CN^- [5,8]. It is also noted that the process is more efficient at high $-OH$ concentrations.

(5) At high KCN concentrations, the $[Ni(CO)_2(CN)_2]^{-2}$ ion generates: $[Ni(CN)_4]^{-4}$ and $[Ni_2(CN)_6]^{-4}$ species, spectra 9–11. The $[Ni(CN)_4]^{-4}$ ion is formed by the desplacement

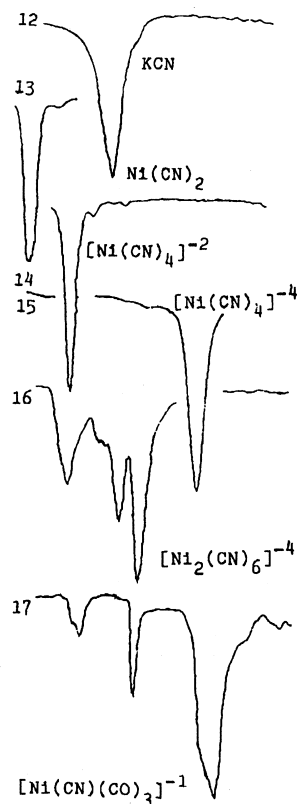

Fig. 3. IR Absorption spectra measured of cyanocarbonylNickelate complexes: (12) KCN. (13) $Ni(CN)_2$. (14) $[Ni(CN)_4]^{-4}$. (15) $[Ni(CN)_4]^{-4}$. (16)$[Ni_2(CN)_6]^{-4}$. (17) $[Ni(CN)(CO)_3]^{-1}$.

of CO ligands by CN^- in the $[Ni(CN)_2(CO)_2]^{-2}$ ion. The specie $[Ni_2(CN)_6]^{-4}$ is formed by oxidation of $[Ni(CN)_4]^{-4}$ [11,17].
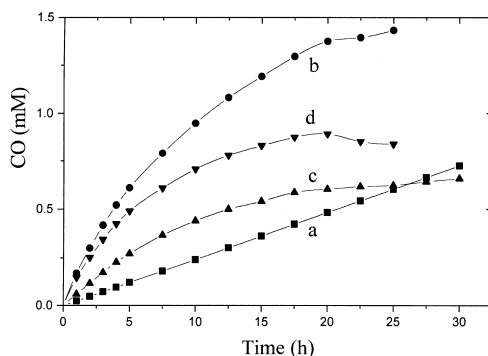

Fig. 4. Absorption of CO during preparation of catalytic system at 25°C Conditions: (a) 25 ml of 5 N NaOH. (b) 25 ml of 5 N NaOH, 0.5 mM $Ni(CN)_2$. (c) 5 ml of H_2O, 0.5 mM $Ni(CN)_2$. (d) [(b)–(a)] calculated.

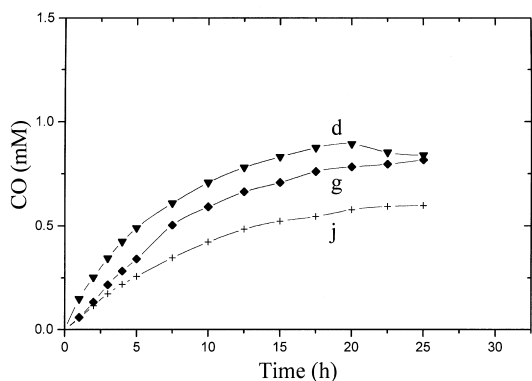Fig. 5. Absorption of CO by $Ni(CN)_2$ in alkaline aqueous media using different concentrations of NaOH at 25°C calculated. Conditions: (d) 5 N NaOH, see Fig. 4. (g) 1 N NaOH.(j) 0.5 N NaOH.
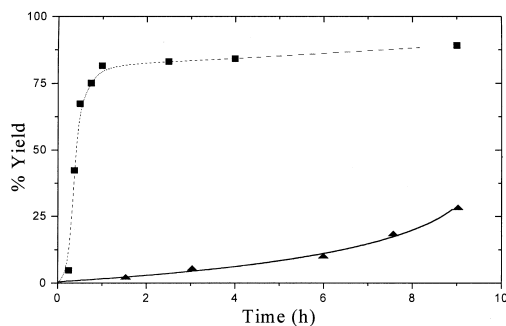

Fig. 6. Yield of pyrrolinone in the catalytic hydrocyanation of 3-octyn-2-one: ▲ absence of catalytic system, 15 mM KCN, 12.5 ml H_2O, 10 mM 3-octyn-2-one, CO at 25°C. ■ in presence of $Ni(CN)_2$ /CO/KCN in alkaline aqueous media with time. Conditions: 1 mM $Ni(CN)_2$, 62.5 mM NaOH, 12.5 ml H_2O, 15 mM KCN, 10 mM 3-octyn-2-one, CO at 25°C. See Section 2 for general procedure.

(6) Alper and Joó have mentioned the quantitative formation of $[Ni(CN)(CO)_3]^{-1}$ when $Ni(CN)_2/NaOH/H_2O$ system is kept under CO over a period of 3 h at 60°C. In this studiy at the same catalytic system and maintaining the temperature of 25°C, after 3 h the of $[Ni(CN)(CO)_3]^{-1}$ specie was not detected in the IR spectrum.

(7) The possibility of $[Ni(CN)_4]^{-2}$ and $[Ni(CN)_5]^{-3}$ to act as active species can be excluded because the hydrocyanation reaction of 3 octyn-2-one using the catalytic systems that generate these species gave lower yields of pyrrolinone (Table 2, Reactions 12 and 17). The formation of the product obtained can be explained by the nucleophilic attack of the CN^- to substrate without the participation of the cata-

lyst. (Table 2, Reactions 9–11 and Fig. 6). The result was further confirmed by carrying out the reaction using $K_2[Ni(CN)_4]$ as a catalyst under same conditions [11] (Table 4, Reactions 23–25).

(8) The specie $[Ni(CN)(CO)_3]^{-1}$ was synthesized as $[(Ph)_4P][Ni(CN)(CO)_3]$ [5], and its catalytic activity was evaluated in the hydrocyanation reaction, the product obtained was 16–18% at 9 h., the yield suggests that this is not the active specie, since it needs the CO atmosphere and its low solubility in water (Table 4, Reaction 30 and 31). Nevertheless these are not convincing arguments to eliminate the possibility that it can act as precursor of active specie (Scheme 1).
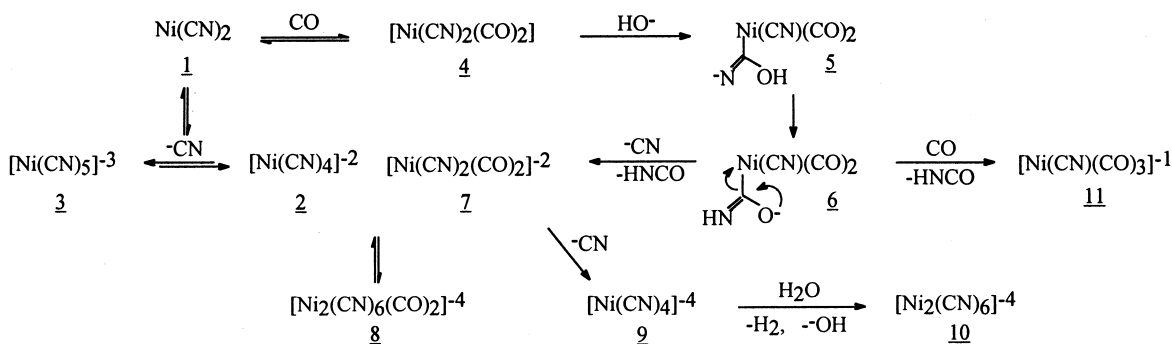
Scheme 1. A postulated reaction mechanism for reduction of $Ni(CN)_2$ with NaOH, CO and excess KCN in water.

Table 4
Evaluation of some cyanocarbonylnickelate anions synthesized as active specie in the catalytic hydrocyanation of 3-octyn-2-one
General conditions: 12.5 ml of H_2O, 15 mM KCN, 10 mM 3-octyn-2-one, under N_2 at 25°C.

Reaction	Preparation of the catalytic system				Hydrocyanation of 3-octyn-2-one	
	Nickel specie (1 mM)	NaOH (mM)	Bubbling of CO (h)	IR absorption spectra[a]	Time (h)	Pyrrolinone yield (%)
23	$[Ni(CN)_4]^{-2}$			14	9.0	12.11
24	ídem	62.5		14	9.0	14.92
25	ídem	62.5	20	14	9.0	12.33
26	$[Ni(CN)_4]^{-4}$			15	20 min	37.27
27	ídem			15	9.0	63.51
28	ídem	62.5		15	9.0	57.31
29	$[Ni_2(CN)_6]^{-4}$			16	9.0	14.27
30	$[Ni(CN)(CO)_3]^{-1}$			17	9.0	18.20
31	ídem[b,c]		20	17	9.0	16.14
32	$[Ni_2(CN)_6(CO)_2]^{-4}$ [d]			8	9.0	74.23
33	$[Ni(CN)_4]^{-4}$ [e]			11	20 min	53.46

[a] IR spectra refer to nickel specie synthesized.
[b] 4 ml of MeOH added to effect homogeneity.
[c] Under CO.
[d] Formed in aqueous medium with $K_2[Ni(CO)_4]$, NaOH, Zn and CO, see Ref. [12].
[e] Formed in aqueous medium with $K_2[Ni(CN)_4]$, $NaBH_4$ and KCN, see Ref. [4].

(9) The hydrocyanation reaction was carried out with the $[Ni_2(CN)_6]^{-4}$ species from $K_2Ni(CN)_4$, NaOH, and Zn powder, the dimeric specie was isolated and used as catalyst [12]. The yield of the product obtained was 14.3% at 9 h., indicating complete ineffectiveness of this complex as precursor (Table 4, Reaction 29).

(10) One can consider $[Ni(CN)_2(CO)_2]^{-2}$ as a precursor of the active species $[Ni(CN)_4]^{-4}$ which seems as an intermediate in the pathway of its transformation to $[Ni_2(CN)_6]^{-4}$. The hydrocyanation reaction proceeds very fast in the presence of NaOH, CO and KCN and forms the $[Ni(CN)_2(CO)_2]^{-2}$ (Table 2, Reactions 20 and 21). When this specie was synthesized by other method [12] and used as catalyst in hydrocyanation reaction, it yielded 74.2% of the product after 9 h, of reaction (Table 4, Reaction 32).

(11) In order to ratify that $[Ni(CN)_4]^{-4}$ is the active species in the hydrocyanation reactions, this anion was synthesized and isolated using $Na_2[Ni(CN)_4]$ and Na metal [11], when this specie was used as a catalyst, the pyrrolinone yields obtained were 37.3 and 63.5% after 0.37 and 9 h, respectively. (Table 4, Reactions 26 and 27). This lower yield after longer time

period may be due decomposition of $[Ni(CN)_4]^{-4}$ species in the pure form. However when $Ni(CN)_2$/NaOH/CO catalytic system was used in the presence of excess of KCN the pyrrolinone was obtained in good yield : 42.3 and 89.1% after 0.37 and 9 h, respectively. To confirm the activity of $[Ni(CN)_4]^{-4}$, it was synthesised by another method using $K_2[Ni(CN)_4]$, KCN and $NaBH_4$ as reductor in aqueous medium in the absence of CO [4]. The yield of pyrrolinone obtained was 53.5% after 0.37 h (Table 4, Reaction 33).

From the above facts we concluded that the $[Ni(CN)_4]^{-4}$ is the true catalytic active specie for hydrocyanation of α-ketoalkynes.

3.2. Evaluation of reaction variables

The adequate conditions for the hydrocyanation reaction were chosen after the study of the influence of different parameters in the process.

3.2.1. Effect of time

Fig. 6 presents the percent conversion of 3-octyn-2-one as a function of time. The results show that the $Ni(CN)_2$/CO/NaOH/KCN sys-
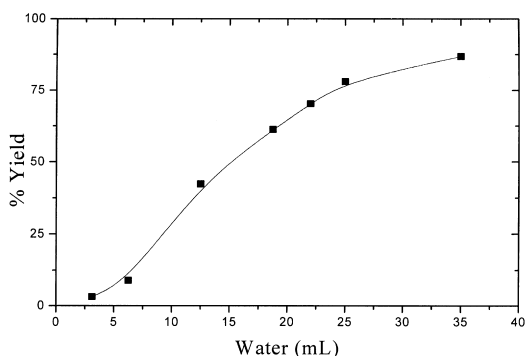
Fig. 7. Effect of the water concentration on the yield of pyrrolinone by the catalytic hydrocyanation of 3-octyn-2-one by $Ni(CN)_2$/CO/KCN in alkaline aqueous media Conditions: 1 mM $Ni(CN)_2$, 62.5 mM NaOH, 15 mM KCN, 10 mM 3-octyn-2-one, CO, for 20 min at 25°C.

Fig. 9. Plot of the % conversion of pyrrolinone with NaOH concentration in the catalytic hydrocyanation of 3-octyn-2-one by $Ni(CN)_2$/CO/KCN in alkaline aqueous media. Conditions: 1 mM $Ni(CN)_2$, 12.5 mL H_2O, 15 mM KCN, 10 mmol 3-octyn-2-one, CO, for 20 min at 25°C.

tem is an effective catalyst for the hydrocyanation of α-ketoalkynes. The hydrocyanation of 3-octyn-2-one in the absence of catalytic system $Ni(CN)_2$/CO/NaOH was very slow, 30% conversion after 9 h (Table 2, Reaction 9), compared with reaction carried out in the presence of catalytic system, 42% conversion at 20 min and 81% of yield was obtained after 1 h, showing an induction time of 15 min.

3.2.2. Effect of water concentration

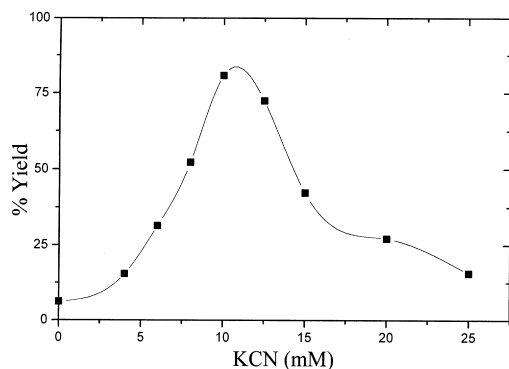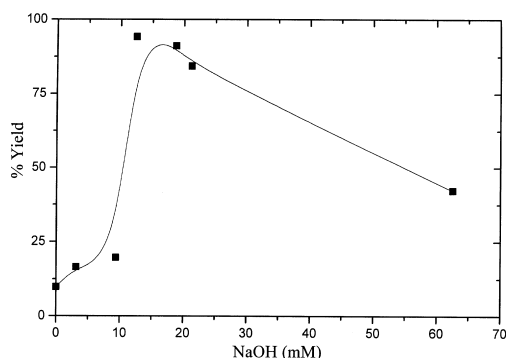In order to study the influence of water concentration in the hydrocyanation of 3-octyn-2-

one some experiments were performed in the range of 3 to 35 ml of water in the reaction medium. The results are shown in Fig. 7 as we can observe, a good correlation was found, which suggests an important role of water in the formation and stabilization of species 5, which evolutes to $[Ni(CN)_4]^{-4.}$

3.2.3. Effect of KCN concentration

Fig. 8 shows that the reaction is most favorable at 4.0–12.5 mM of KCN concentration, while KCN concentrations higher than 12.5 mM resulted in a decrease the pyrrolinone yield.
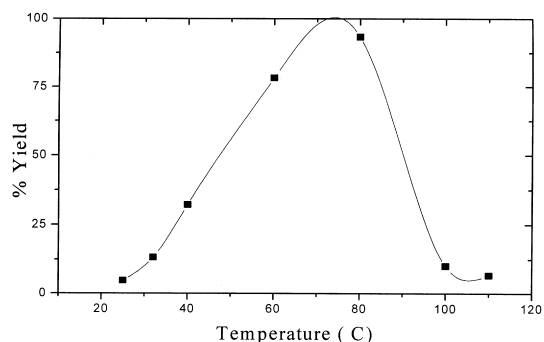

Fig. 8. Pyrrolinone formation as a funtion of KCN concentration in the catalytic hydrocyanation of 3-octyn-2-one by $Ni(CN)_2$/CO/KCN in alkaline aqueous media. Conditions: 1 mM $Ni(CN)_2$, 62.5 mM NaOH, 12.5 mL H_2O, 10 mM 3-octyn-2-one, CO, for 20 min at 25°C.

Fig. 10. Dependence of the yield of pyrrolinone on the temperature, in the catalytic hydrocyanation of 3-octyn-2-one by $Ni(CN)_2$/CO/KCN in alkaline aqueous media. Conditions: 1 mM $Ni(CN)_2$, 62.5 mM NaOH, 12.5 ml H_2O, 15 mM KCN, 10 mM 3-octyn-2-one, CO, for 20 min.

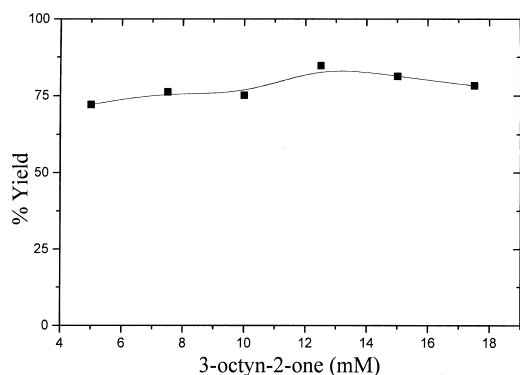Fig. 11. Yield of pyrrolinone in the catalytic hydrocyanation of 3-octyn-2-one by Ni(CN)$_2$/CO/KCN in alkaline aqueous media with 3-octyn-2-one concentration. Conditions: 1 mM Ni(CN)$_2$, 62.5 mM NaOH, 12.5 ml H$_2$O, 15 mM KCN, 10 mM 3-octyn-2-one, CO for 20 min at 25°C.

This may be due to the formation of inactive [Ni$_2$(CN)$_6$]$^{-4}$ species from [Ni(CN)$_4$]$^{-4}$ at higher KCN concentrations. It was found that the most active catalyst was formed at 11 mM of KCN.

3.2.4. Effect of NaOH concentration

As shown in Fig. 9, the base concentration significantly influences the yield. A low concentration of NaOH (0.375 g) gave a completely ineffective catalytic system which yielded the product ranging from 9.75–19.68%. A concentration higher than (18.7 g) of NaOH lowers the yield of hydocyanation product.

3.2.5. Effect of temperature

This study was carried out by varying the temperature in the range of 25 to 110°C. The temperature dependence is illustrated in Fig. 10. The results show a proportional increase of pyrrolinone formation in the range 25–80°C The maximum yield of product (93.31%) was obtained at 80°C, at higher this temperatures there is a pronounced decrease in the pyrrolinone formation probably due to the deactivation of the catalyst.

3.2.6. Effect of α-ketoalkyne concentration

This effect was studied by varying the concentration of substrate (3-octyn-2-one), the yield

of product is highest for concentration varing from 5 to 17 mM (72.10–84.73%.) (Fig. 11). After this range an increase in substrate concentration does not show a marked influence on the yield final product.

4. Conclusions

A simple catalytic hydrocyanation procedure under exceptionally mild conditions is described, which complements existing methods and would prove to be valuable to the synthetic organic chemist. The proposed oxidation–reduction mechanism for Ni(CN)$_2$/CO/KCN system in alkaline aqueous medium is the first reported example confirmed by IR spectroscopy studies, which enhances the scope of this catalytic system to carbonylation and hydrocyanaton reactions. It is claimed that the [Ni(CN)$_4$]$^{-4}$ ion is the active specie in the hydrocyanation reaction, This anion is obtained by replacement of CO ligands of [Ni(CN)$_2$(CO)$_2$]$^{-2}$ by CN$^-$. The mentioned facts prove the hydrocyanation reaction mechanism proposed earlier by our group [9]. In addition, this study provides an interesting example of some catalyzed organic reactions in aqueous media.

Acknowledgements

References

[1] J. March, in: Advance organic chemistry. rections, mechanics and structure, Wiley-Interscience, New York, 1992, p. 1293.
[2] B.R. James, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry 8 Pergamon, Oxford, 1982, p. 353.

[3] T. Funabiki, K. Tatsumi, S. Yoshida, J. Organomet. Chem. 384 (1990) 199.

[4] T. Funabiki, H. Sato, N. Tanaka, Y. Yamazaki, S. Yoshida, J. Mol. Catal. 62 (1990) 157.

[5] F. Joó, H. Alper, Organometallics 4 (1985) 1775.

[6] H. Arzoumanian, F. Cochini, D. Nuel, J.F. Petrignani, N. Rosas, Organometallics 11 (1992) 493.

[7] H. Arzoumanian, M. Jean, D. Nuel, J.L. Garcia, A. Cabrera, N. Rosas, Organometallics 14 (1995) 5458.

[8] H. Arzoumanian, F. Cochini, D. Nuel, N. Rosas, Organometallics 12 (1993) 1871.

[9] H. Arzoumanian, M. Jean, D. Nuel, J.L. García, N. Rosas, Organometallics 16 (1997) 2726.

[10] L. Brandsma, Preparative acetylenic chemistry, in: Studies in Organic Chemistry 34 Elsevier, New York, 1988, p. 105.

[11] J.W. Eastes, W.M. Burgess, J. Am. Chem. Soc. 64 (1942) 1187.

[12] M. Miura, N. Shimoura, M. Nomura, J. Chem. Soc. Perkin Trans. 1 (1998) 1993.

[13] S.K. De Hass, K.F. Fouché, Inorg. Chim. Acta 24 (1977) 269.

[14] R.A. Penneman, R. Bain, G. Gilbert, L.H. Jones, R.S. Nyholm, G.K.N. Reddy, J. Chem. Soc. (1963) 2266.

[15] A.G. Sharpe, in: The Chemistry of Cyano Complexes of the Transition Metals, Academic Press, London, 1976, p. 225.

[16] R. Nast, H. Schulz, D.H. Moerler, Chem. Ber. 103 (1970) 777.

[17] M.F.A. El Sayed, R.K. Sheline, J. Am. Chem. Soc. 80 (1958) 2047.

[18] W.P. Griffith, A.J. Wickham, J. Chem. Soc. A (1969) 834.

[19] N. Rosas, I. Chávez, L. García, P. Sharma, R. Le Lagadec, A. Cabrera, E. Díaz, Anal. Sci. 14 (1998) 585.