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Carbon Monoxide Oxidation by Molecular Oxygen in Presence of Nickel Complexes

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The Ni(0) carbonyl complexes of formula $NiL_x(CO)_{4-x}$ *(*$x = 1,2$*;* $L = PEt_3$*,* PEt_2Ph*,* $PEtPh_2$*) are oxidized by atmospheric oxygen, in acidic medium, to Ni(II) phosphine complexes, carbon dioxide and phosphine-oxide. Carbon dioxide and phosphine-oxide are the result of two independent reactions of Ni(II): one with CO and* H_2O *to produce* CO_2 *and Ni(0), the other, as a side reaction with dioxygen, to give phosphine-oxide. By carrying out the oxidation of Ni(0) in aqueous alcoholic solution under* CO/O_2 *mixture at 0 °C, the reaction* $CO + 1/2O_2 \rightarrow CO_2$ *is catalyzed. Under these conditions the Nickel complex catalyst is slowly destroyed by the side reaction; however carrying out the oxidation with stoichiometric oxygen at* -10 *°C and successively the carbonylation at room temperature, the catalyst is preserved. A possible mechanism for the catalytic cycle is discussed and evidence is given for the formation of a peroxo-species during the oxidation in neutral medium.*

Introduction

It is known that some Ni(0) complexes are able to bind molecular oxygen and to oxidize some substrates in catalytic or stoichiometric reactions [1a, b]. In particular the PPh_3 ligand has been oxidized catalytically by O_2 in very mild conditions [2]. During our studies on the carbon monoxide activation [3a, b, c], we have observed that the Ni(0) carbonyl–phosphine complexes of formula $NiL_x(CO)_{4-x}$ ($x = 1,2$; $L = PEt_3$, PEt_2Ph, $PEtPh_2$) are oxidized by atmospheric oxygen in acidic aqueous–alcoholic solution, to produce Ni(II) compounds, carbon dioxide and phosphine oxide. The CO oxidation, apparently in competition with the oxidation of the phosphine, has stimulated our interest. In particular we wanted to investigate the selective oxidation of the CO or of the phosphine ligand.

Results and Discussion

Recently we have reported [3b] that some Ni(II) tetraco-ordinated phosphine complexes are reduced by CO, via reductive carbonylation, in aqueous alcoholic solution (reaction 1):

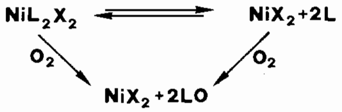
$$NiL_2X_2 + 3CO + H_2O \longrightarrow NiL_2(CO)_2 + CO_2 + 2HX \quad (1)$$

($L = PEt_3$, PEt_2Ph, $PEtPh_2$; $X = Cl$, Br).

During this study we observed that the acidic solution from the reaction, when exposed to the air, changed the colour from pale-yellow to red-violet owing to the oxidation of Ni(0) to Ni(II), as evidenced by electronic spectra. The gas chromatographic analysis revealed the presence of CO_2 in the gas-phase and the ^{31}P-NMR showed the presence of phosphine-oxide in solution. Furthermore, from potentiometric titration of the solution it was possible to deduce that two mol of H_3O^+ ion per mol of Ni(II) had been consumed. Several reactions can be in accordance with these experimental facts. However on the basis of some considerations (see below), we have established that the Ni(0) carbonyl complexes are first oxidized to Ni(II) by interaction with O_2 according to the stoichiometry of reaction (2), and that

$$NiL_2(CO)_2 + 2HX + 1/2O_2 \longrightarrow NiL_2X_2 + H_2O + 2CO \quad (2)$$

carbon dioxide and phosphine-oxide are produced successively by two independent reactions involving the Ni(II) complex. The CO_2 is only formed via reductive carbonylation of NiL_2X_2 (reaction 1), while phosphine-oxide is formed by direct interaction of dioxygen with Ni(II) complex or with free phosphine (Scheme I).



Scheme 1.

The following is support for this pathway: We have not observed formation of CO_2 and phosphine-oxide by carrying out the oxidation of acidic mixture $NiL_x(CO)_{4-x}$ ($L = PEt_3$, PEt_2Ph) at low temperature (−20 °C); the only product obtained was NiL_2X_2 so that we have excluded the direct oxidation of both CO and phosphine ligand by O_2 via Ni(0) complex (reaction 3, 4, 5):

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$$NiL_2(CO)_2 + 1{,}5O_2 + 2HX \longrightarrow 0.5NiL_2X_2 + 0.5NiX_2 + CO_2 + CO + LO + H_2O \quad (3)$$

$$NiL_2(CO)_2 + O_2 + 2HX \longrightarrow 0.5NiL_2X_2 + 0.5NiX_2 + LO + 2CO + H_2O \quad (4)$$

$$NiL_2(CO)_2 + O_2 + 2HX \longrightarrow NiL_2X_2 + CO_2 + CO + H_2O \quad (5)$$

Furthermore, oxidizing a pure sample of $Ni(CO)_2(PEtPh_2)_2$ at room temperature and in acidic medium, CO_2 was not observed as expected, because with this ligand and under these conditions, the reaction (1) is very slow [3b].

The presence or absence of phosphine-oxide in the final reaction mixture was monitored by NMR spectroscopy. The ^{31}P-NMR spectrum of the $Ni(CO)_2(PEt_3)_2$ solution after oxidation at −20 °C did not show signals ascribable to phosphine-oxide, but exhibited two signals at 23.1 and 40.3 ppm which are assignable to the initial $Ni(CO)_2(PEt_3)_2$ [4] and $NiBr_2(PEt_3)_2CO$ [5] respectively (see below). On the contrary when the oxidation was carried out at room temperature the NMR spectra also displayed a broad signal at 61.3 ppm, which we have assigned to the coordinated oxidated ligand. In fact, a broad resonance at 61.3 ppm is the only one exhibited by a $NiBr_2(PEt_3)_2$ solution after oxidation at room temperature.

These data suggest that the $NiL_x(CO)_{4-x}$ complexes can catalyze the oxidation of CO to CO_2 through the two independent reactions (1–2). However the catalysis will be effective only when the concomitant oxidation of the phosphine ligand, via scheme I, is minimized. This has been realized by carrying out the oxidation with the stoichiometric amount of oxygen ($O_2/Ni = 0.5$) at −10 °C followed by the carbonylation at room temperature. In this way we have accomplished an oxidation–reduction cycle without phosphine-oxide formation.

In Tables I, II we have summarized some results, showing that the amount of CO_2 decreases after ten cycles only of 10% for PEt_3 and of 15% for PEt_2Ph complex. Several complexes of transition metals are able to catalyze the oxidation of CO. In most cases however, the oxidation of carbon monoxide is carried out by coordinated nitrite or nitro ligand [6]; few catalytic systems are able to effect CO oxidation by molecular oxygen via metal transfer [7]. The case described here is singular, since CO_2 is obtained by attack of a water molecule on the coordinated carbonyl. Halpern has reported a different procedure where CO was oxidized by attack with hydroxide ion [8].

When the oxidation of Ni(0) carbonyls was carried out at room temperature under CO/O_2 atmosphere in the molar ratio 2:1, loss of the catalyst, owing to phosphine oxidation, was observed. Under these conditions the amount of CO_2 formed is temperature-dependent; at 0 °C the maximum value of the CO_2/Ni ratio was 0.28. Table III lists the CO_2 at different temperatures for the NiL_2X_2 (L = PEt_3, PEt_2Ph) complexes. $NiCl_2(PEtPh_2)_2$ was not tested

TABLE I. CO_2 Developed Using $NiBr_2(PEt_3)_2$^{a} as Catalyst.

Cycle^b	mL O_2^{c}	CO_2 Mmol
1	2.5	0.18
2	3.0	0.21
3	2.0	0.15
4	2.5	0.17
5	2.5	0.17
6	2.5	0.16
7	2.5	0.17
8	3.0	0.19
9	2.5	0.16
10	2.5	0.16

^{a}0.38 mmol in 10 mL of ethanol–water (5%) solution. ^{b}A cycle was carried out putting the indicated volume of O_2 in the reactor vessel and adding CO until atmospheric pressure was achieved. ^{c}Volume of O_2 at 20 °C and atmospheric pressure.

TABLE II. CO_2 Developed Using $NiBr_2(PEt_2Ph)_2$ as Catalyst^a.

Cycle^1	mL O_2 ^{2}	CO_2 Mmol
1	2.5	0.15
2	3.0	0.18
3	2.0	0.12
4	2.5	0.14
5	2.5	0.14
6	3.0	0.16
7	2.5	0.13
8	2.5	0.13
9	2.5	0.13

^{a}0.38 mmol of $NiBr_2(PEt_2Ph)_2$ in 10 ml of ethanol–water (5%) solution. ^{1}See note b of Table I. ^{2}See note c of Table I.

TABLE III. CO_2 Developed at Different Temperatures and O_2/Nickel Ratios^a.

Temp., °C	O_2nickel^b mol ratio	Mmol CO_2
0	8.4	0.27
20	8.4	0.21
40	8.4	0.18
0	6.7^b	0.28
0	4.5	0.28

^{a}0.33 mmol of $NiBr_2(PEt_3)_2$ or $NiBr_2(PEt_2Ph)_2$ in 10 ml of ethanol–water (5%) solution. ^{b}A suitable volume of CO/O_2 mixture was put into the reactor vessel (197 mL) and Ar or N_2 was added to achieve atmospheric pressure.

because its reductive carbonylation takes place only at temperatures higher than 70 °C, at which the complex rapidly decays because of phosphine oxidation.

At 0 °C a pseudo first-order rate constant of 3.9×10^{-3} min^{-1} for the carbonylation of $NiBr_2(PEt_3)_2$, reaction (1), has been determinated spectroscopically, by bubbling a N_2/CO mixture in a 2:1 mol ratio; while at the same temperature by bubbling a N_2/O_2 mixture in a 2:1 mol ratio, a rate constant of 8.9×10^{-3} min^{-1} was found for the oxidation of $NiBr_2(PEt_3)_2$. The kinetic measurements, followed by monitoring the disappearance of the $NiBr_2(PEt_3)_2$ band at 525 nm in the electronic spectrum, are in agreement with the observed low CO_2/nickel ratio.

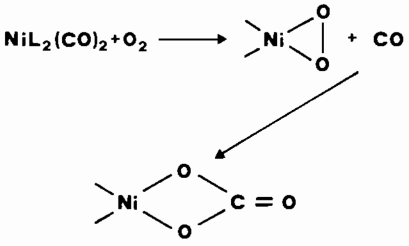
In order to obtain information about a possible mechanism for reaction (2), the $Ni(CO)_2(PEt_3)_2$ oxidation at 0 °C in hydrobromic acid was monitored by I.R. and UV–visible spectroscopy. UV–visible absorption of the solution after reaction with stoichiometric oxygen (30 min) displays, in the region 900–330 nm, bands ascribable to a mixture of $Ni(CO)_2(PEt_3)_2$, $NiBr_2(PEt_3)_2$ and $Ni(PEt_3)_2Br_2CO$, the last one being obtained by reaction (6) between $NiBr_2(PEt_3)_2$ and CO released from the oxidized Ni(0).

$$NiBr_2(PEt_3)_2 + CO \rightleftharpoons Ni(PEt_3)_2Br_2CO \qquad (6)$$

The IR spectra show a gradual decrease of the bands at 1990 and 1930 cm^{-1} assigned to initial $Ni(CO)_2(PEt_3)_2$, while a new band at 2018 cm^{-1} appears, assignable to the penta-coordinated $Ni(PEt_3)_2Br_2CO$ species.

This fact provides further support to the idea that reaction (1) is responsible for CO_2 formation. Attempts to identify by I.R. spectroscopy a peroxo or dioxygen compound as transient species were unsuccessful. Since the acid medium might be responsible for decomposition of the intermediate species, we have performed the oxidation in a neutral medium. Although we can offer no absolute proof for an oxygenated compound, the appearance in the electronic spectrum of a shoulder at 500 nm (not present in the starting Ni(0) carbonyl complex) suggests the existence of a Ni(II) species which we think to be a peroxo-species. An absorption band with a maximum at 600 nm in solution and at 680 nm in the solid state has been observed for the peroxo compound $Ni(O_2)(t\text{-}BuNC)_2$ [1a].

Support to the formation of this peroxo-species is provided by the behavior of the oxidized solution. In fact, by keeping the solution under dioxygen for 4 h at room temperature or for about 1 h at 40 °C, a green suspension of nickel carbonate was obtained, as emphasized by the CO_2 gas developed after reaction of the suspension with hydrochloric acid. Only the carbonyl complexes with PEt_3 and PEt_2Ph ligand are able to produce the carbonate; in the case of $PEtPh_2$ and PPh_3 we have not observed CO_2 evolution. On the basis of these data it is reasonable to suppose that the carbonate is formed by attack of a CO molecule on the peroxo-species as is outlined in scheme (II), where we have omitted the ligands for simplicity.



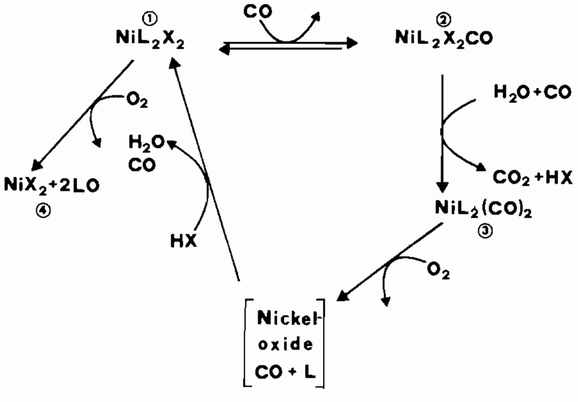
Scheme II.

The absence of spectroscopic evidence for the peroxo-species in acid medium probably is attributable to the fast decomposition as indicated in reactions (7) and (8):

$$2NiL_2(CO)_2 + O_2 \longrightarrow 2NiO + 2L + 4CO \qquad (7)$$

$$2L + NiO + 2HX \longrightarrow NiL_2X_2 + H_2O \qquad (8)$$

A green mixture of nickel oxide and nickel carbonate has been obtained when the oxidation of $Ni(CO)_2(PEt_3)_2$ was carried out by bubbling dioxygen in neutral solution so that the carbon monoxide is removed prior to reacting with the peroxo-species. Finally in Scheme III we have summarized the key steps for the catalytic cycle together with the side reaction responsible for the catalyst's destruction.



Scheme III.

Experimental

All the solvents, of reagent-grade quality, were distilled and stored under nitrogen atmosphere. All solutions were prepared and manipulated in an atmosphere of the specified gas by standard vacuum-line techniques. Gas chromatographic determinations were carried out on Porapak Q 3.5 m and molecular sieve (5A) 2 m columns using a Carlo Erba Fractovap

C connected to a Hewlett Packard 3380 A integrator. I.R. spectra were recorded on a Perkin-Elmer 577 spectrophotometer; electronic spectra on a Varian Cary 219. Potentiometric titrations were carried out on a Potentiograph E 336 Metrohm-Herisau. ^{31}P NMR spectra were recorded with a Varian XL 200 spectrometer operating in FT mode. The solution of the sample was placed in a nitrogen or carbon monoxide filled 8-mm NMR tube held coaxially in 10-mm tube containing D_2O which served as an external lock.

Preparation of the Ni(0) Carbonyls

The acidic mixtures of Ni(0) carbonyl complexes were prepared *in situ* by carbonylation in aqueous alcoholic solution of the related NiL_2X_2 ($X = Br$, $L = PEt_3$, PEt_2Ph). The reactions were carried out in a glass reactor vessel (60 ml) provided with a jacket for thermostatting. In a typical experiment 0.150 g (0.33 mmol) of $NiBr_2(PEt_3)_2$ were dissolved in 10 ml of an ethanol–water (5%) solution under CO. After 2 h argon was bubbled through the solution to remove the CO_2 dissolved. The resulting solution was utilized directly without manipulation.

Oxidation–Reduction Cycles

10 ml of the above mentioned Ni(0) carbonyl solution was cooled at –10 °C. The reactor was evacuated, a measured volume of O_2 was added (Table I, II) and CO was added to give atmospheric pressure. The solution was stirred for 1 h at –10 °C and then at room temperature until it became pale yellow. The gas was analyzed for CO_2. This solution after bubbling argon was utilized for a new catalytic cycle.

Catalytic Conversion of CO/O_2 Mixture in CO_2

0.150 g (0.33 mmol) of $NiBr_2(PEt_3)_2$ was reduced to Ni(0) carbonyl in a reactor vessel (197 ml). Argon was bubbled and a mixture of (2:1) CO/O_2 was introduced. The solution was stirred at the selected temperature and CO_2 analyzed after it became green (see Table III).

Preparation of Ni(0) Carbonyl Complexes in Neutral Solution

The Ni(0) carbonyl complexes in neutral solution were prepared *in situ* in the following mode: 0.450 g (0.99 mmol) of $NiBr_2(PEt_3)_2$ dissolved in 30 ml of an ethanol–water (5%) solution was reduced under CO atmosphere. The resulting acidic solution was neutralized with CaO, stirred under CO atmosphere for 1 h and then filtered. This solution was utilized for the reaction with O_2.

Reaction with Dioxygen

20 ml of the above solution was cooled at –20 °C and O_2 was introduced into the evacuated reactor vessel. The solution became yellow-orange and successively decomposed to give, slowly at room temperature (4 h), rapidly at temperatures higher than 40 °C, a green suspension. When this suspension was treated with hydrochloric acid, CO_2 developed (87% with respect to the Ni complex).

Acknowledgments

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