## Homogeneous Catalysis of the Water-gas Shift Reaction Using 2,6-Bis(diphenylphosphinomethyl)pyridine Complexes of Nickel

By POTENZO GIANNOCCARO, GIUSEPPE VASAPOLLO, and ADRIANO SACCO\* (Istituto di Chimica Generale ed Inorganica dell'Università, Via Amendola 173, 70126 Bari, Italy)

Summary The water-gas shift reaction,  $\rm CO + H_2O = CO_2 + H_2$ , is effectively catalysed at low temperatures and pressures in water-alcohol (ethanol, propanol, or butanol) solutions by a catalyst system based on 2,6-bis(diphenylphosphinomethyl)pyridine complexes of nickel

Homogeneous catalyst systems capable of accelerating the water-gas shift reaction (1) are attracting considerable

$$CO(g) + H_2O(l) = H_2(g) + CO_2(g)$$
 (1)

interest because of the obvious benefits associated with carrying out the reaction at temperatures lower than those required by the available heterogeneous catalysts, and several reports concerning homogeneous catalysts for this reaction have been published recently  $^{1-3}$ 

We describe here an active, homogeneous catalyst system for reaction (1) based on water-alcohol solutions of 2,6bis(diphenylphosphinomethyl)pyridine (pnp, Hpnp = protonated form) complexes of nickel We have found that the already known<sup>4</sup> complexes (pnp)NiXY (X = Cl, Br, Y = Cl, ClO<sub>4</sub>) readily react with carbon monoxide in water-ethanol solution at room temperature and atmospheric pressure to give a nickel(0)-carbonyl complex, equation (2) In the presence of a base, like NaOH, Et<sub>3</sub>N, or pyridine, the reaction proceeds more rapidly, equation (3)

$$[(pnp)N_{1}X]^{+} + 3CO + H_{2}O = [(Hpnp)N_{1}(CO)_{2}]^{+}$$

$$(1) + CO_{2} + H^{+} + X^{-} \quad (2)$$

$$[(pnp)N_{1}X]^{+} + 3CO + 4OH^{-} = (pnp)N_{1}(CO)_{2}$$

$$(2)$$

$$+ CO_3^{2-} + X^- + 2H_2O$$
 (3)

The 1r spectrum of compound (2) in Nujol shows two strong absorptions at 1992 and 1930 cm<sup>-1</sup>, assignable to the C–O stretchings of the carbonyl ligand, and an absorption at 1590 cm<sup>-1</sup> characteristic of the unco-ordinated pyridyl group of the ligand  $^{4,5}$  The ir spectrum of compound (1) shows absorptions at 2335 and 1630 cm<sup>-1</sup>, assignable to the N-H stretching and to the ring vibrations of the protonated pyridyl group, besides strong absorptions at 2005 and 1945 cm<sup>-1</sup> assignable to the C-O stretchings The stoicheiometry of reactions (2) and (3) has been confirmed by both gas chromatography and acidimetric titration of the reaction products

The nickel(0)-carbonyl complex reacts with acids at temperatures > ca 40 °C, equation (4)

$$[(Hpnp)Ni(CO)_2]^+ + H^+ + X^- = [(pnp)NiX]^+ + H_2 + 2CO \quad (4)$$

Preliminary kinetic studies suggest that reaction (2) proceeds *via* the formation of a nickel(II)-carbonyl intermediate, which undergoes nucleophilic attack by water, giving an unstable hydroxycarbonyl that rapidly decarboxylates to give  $CO_2$  and the nickel(0)-complex, reactions (5), (6), (7) and (8)

$$[(pnp)NiCl]^{+} + CO \rightleftharpoons [(pnp)Ni(CO)Cl]^{+}$$
(5)

$$[(pnp)N_1(CO)Cl]^+ + H_2O \rightarrow [(Hpnp)N_1(CO_2H)Cl]^+$$
(6)  
$$[(Hpnp)N_1(CO_2H)Cl]^+ \rightarrow [(Hpnp)N_1]^+ + CO_2$$

$$+ H^{+} + Cl^{-} (7)$$
[(Hpnp)N<sub>1</sub>]<sup>+</sup> + 2CO  $\rightarrow$  [(Hpnp)N<sub>1</sub>(CO)<sub>2</sub>]<sup>+</sup> (8)

At 22 °C, a pseudo-first order rate constant of  $0.31 \text{ mm}^{-1}$ for the reaction of a Bu<sup>n</sup>OH-H<sub>2</sub>O(8%) solution of (pnp)NiCl<sub>2</sub> with carbon monoxide at a constant pressure of 0.94 atm has been found At higher temperatures the starting Ni<sup>m</sup>-complex is reformed according to reaction (4) and, when steady state conditions are reached, hydrogen and carbon dioxide are formed in a 1 1 molar ratio at rates depending on the temperature The rate reaches a maximum (turnover number *ca* 0.6 h<sup>-1</sup>) around 75 °C and decreases

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at higher temperatures, in agreement with the expected decrease, with the increasing temperature, of the nickel(II)carbonyl intermediate concentration.

The turnover number has been increased to about  $6 \ \rm h^{-1}$ by recycling the same solution, stirred at 90  $^{\circ}\mathrm{C}$  in a flask, through a column filled with glass beads and cooled at 30 °C, under a constant flow of CO at atmospheric pressure.

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Under these conditions, reaction (2) occurs in the cooled column section and reaction (4) in the heated flask section of the system.

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