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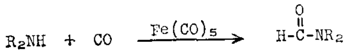
Pentacarbonyliron-Catalyzed Carbonylation of Amines to Formamides

Reactions of amines with CO are known (*1*, *2*) to be catalyzed by several different transition metal complexes. The products may be formamides (HCONHR), ureas [$(RNH)_2C{=}O$] or oxamides [RHNOC-CONHR) depending upon the catalyst and conditions. In extending our mechanistic studies (*3*) of the $Mn_2(CO)_{10}$-catalyzed formation of ureas from primary amines and CO, we have observed that $Fe(CO)_5$ catalyzes the formation of formamides from CO and primary and secondary amines according to Eq. (1):



$$R_2NH + CO \xrightarrow{Fe(CO)_5} H-\overset{O}{\overset{\|}{C}}-NR_2 \qquad (1)$$

This Note describes our results and mechanistic proposals for these $Fe(CO)_5$-catalyzed reactions.

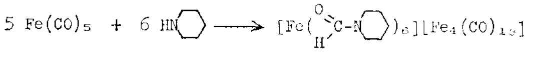
EXPERIMENTAL

Carbonylation of piperidine. A 300 ml stainless steel bomb was charged with 34.4 g of piperidine (distilled from KOH), 0.87 g of $Fe(CO)_5$ (used as obtained from Pressure Chemical Co.) and a magnetic stirring bar. The bomb was flushed with N_2, pressured with 95 atm of CO, and heated in an oil bath at 200°C for 12 hr with magnetic stirring. After cooling, the pressure was released and the contents of the bomb were fractionally distilled, yielding 30.0 g of *N*-formylpiperidine (*4*), bp 90°C/10 mm (66%, based on initial amine).

Carbonylation of cyclohexylamine. The bomb was charged with 21.6 g of cyclohexylamine, 25 ml of hydrocarbon solvent (hexane or cyclohexene), and 0.87 g $Fe(CO)_5$. It was flushed with N_2, pressured to 95 atm with CO, heated to 200°C for 20 hr with magnetic stirring, and allowed to cool to room temperature. Upon fractional distillation, 22.8 g of *N*-cyclohexylformamide (*4*) (83%) was collected, bp 135°C/10 mm.

RESULTS AND DISCUSSION

Pentacarbonyliron is known (*5*) to react with piperidine in benzene solvent at 85°C to give a complex with six *N*-formylpiperidine ligands coordinated to Fe(II) according to Eq. (2):



(2)

Its reaction with NH_3 at 20°C for several days, however, yields urea (*6*):

$$Fe(CO)_5 + 4\ NH_3 \longrightarrow (NH_4)_2[Fe(CO)_4] + (H_2N)_2C{=}O \qquad (3)$$

We now find that $Fe(CO)_5$ can catalyze the formation of formamides according to Eq. (1) from CO (~95 atm) and primary (cyclohexylamine) or secondary amines (piperidine) at 200°C in 66 to 83% yield, as detailed in the Experimental Methods section.

In Fig. 1 is given a possible mechanism

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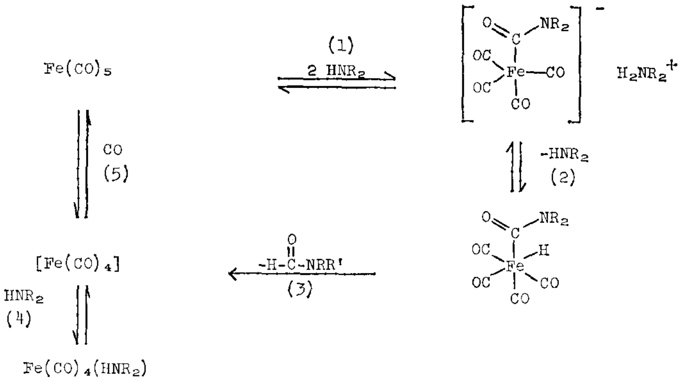

FIGURE 1

for this catalysis. Reaction (1) in this scheme involves the formation of a carbamoyl complex anion, $Fe(CO)_4[C(=O)NR_2]^-$. This reaction is known (*7*) to be rapid and reversible at room temperature with piperidine, pyrrolidine, and *n*-butylamine. In our catalytic reactions, this reaction will have already occurred before the bomb is pressured with a CO atmosphere. On heating at 50°C for 50 hr, the carbamoyl complex is known (*7*) to decompose yielding $Fe(CO)_4(HNR_2)$ and the formamide, $HC(=O)NR_2$. We propose that this occurs via steps (2), (3), and (4). Step (2) involves proton transfer from the ammonium cation to the iron atom yielding the hydride complex which reductively eliminates the formamide in step (3). The resulting coordinatively unsaturated species $Fe(CO)_4$ then reacts with excess amine to give the final observed product, $Fe(CO)_4(HNR_2)$. In the catalytic reaction under CO pressure, the $Fe(CO)_4$ intermediate could react with CO to regenerate $Fe(CO)_5$, according to step (5).

Since the hydride product of step (2) and the $Fe(CO)_4$ intermediate have not been experimentally detected, evidence of their probable existence must come from reactions of related systems. Such evidence may be found in the rapid reaction (*8*) of the acyl complexes, $Fe(CO)_4[C(=O)R]^-$, with acids such as acetic acid at room temperature to give aldehydes, RCHO. These reactions are believed to proceed by protonation of the metal to form $Fe(CO)_4[C(=O)R]H$ which reductively eliminates the aldehyde leaving the $Fe(CO)_4$ fragment. It is precisely this sequence which is proposed in steps (2), (3), and (4) in the carbonylation mechanism.

Because $H_2NR_2^+$ is a much weaker acid than acetic acid, the equilibrium associated with step (2) is undoubtedly much less favorable in the present system. If the enthalpy associated with this unfavorable equilibrium is positive, higher temperatures should make the equilibrium sufficiently favorable to allow the catalysis to proceed at a reasonable rate. This equilibrium may be the reason why such high temperatures are required for the catalysis.

While more detailed studies are required to confirm or discard this mechanism, it appears that the carbamoyl complex intermediate is central in the catalytic process, as was also found (*3*) in the $Mn_2(CO)_{10}$-catalyzed formation of ureas.

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