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Promoting Effects of Metal Iodides in Ni(isoq)$_4$Cl$_2$-Catalyzed Carbonylation of Ethanol and *n*-Propanol[1]

Carbonylation of alcohols by homogeneous catalysis has been extensively studied (*1–4*) using Rh, Ir, Co, and Ni complex catalysts. Carbonylation of methanol using a Ni–PPh$_3$ catalyst system has been studied in detail by Rizkalla (*5*). Kelkar *et al.* (*6*) have shown that the Ni(isoq)$_4$Cl$_2$ (isoq = isoquinoline) complex catalyst is also equally active and selective in carbonylation of methanol. These studies indicated that Ni complexes with suitable ligands provide low pressure and selective catalysts for carbonylation of alcohols. However, detailed studies of the carbonylation of higher alcohols using Ni complex catalysts are very limited (*7, 8*). Therefore, in the present work carbonylation of ethanol and *n*-propanol was investigated with the aim of understanding the role of promoters in the activity and selectivity of Ni complex catalysts. Particularly, improved activity and selectivity in the presence of metal iodide promoters has been demonstrated in the carbonylation of ethanol and *n*-propanol.

The apparatus used and the procedure followed for the carbonylation experiments were similar to those described in our earlier work (*9*). Ni(isoq)$_4$Cl$_2$ was prepared by the method of Nelson and Shepherd (*10*).

To understand the role of iodide promoters in the activity and selectivity of Ni-catalyzed carbonylation of ethanol and *n*-propanol, several experiments were carried out using Ni(isoq)$_4$Cl$_2$ as a catalyst precursor with HI and alkali metal iodide (e.g., LiI) as promoters. The results are presented in Tables 1 and 2. The following important observations were made.

(1) In carbonylation of ethanol, propionic acid was the major product with ethylene and ethane as side products. With *n*-propanol as the substrate, *n*-butyric acid and isobutyric acids were the main products with propane and propylene as side products. The extent of side product formation was dependent on the type of promoter used and the reaction conditions. Unlike Rh-catalyzed carbonylation of ethanol and higher alcohols (*2, 3, 9*), in the case of Ni as a catalyst, significant by-product formation has been observed with HI as a promoter.

(2) Carboxylic acids were found to be the best solvents for these reactions. With noncarboxylic acid solvents, the activity of the catalyst, as well as the selectivity, was poor (see Table 3).

(3) In the presence of LiI as a promoter, the activity of nickel catalyst increases in the carbonylation of ethanol and *n*-propanol compared to aqueous HI as a promoter (compare run 1 with 4 and 3 with 6 from Table 1 and run 1 with 3 and 2 with 5 from Table 2).

(4) H$_2$ enhances the activity of the Ni(isoq)$_4$Cl$_2$–LiI catalyst system for carbonylation of alcohols.

(5) The formation of alkyl iodides was negligible when LiI promoter was used. In a typical carbonylation experiment at 498 K and 1000 psi total pressure, for liquid samples withdrawn after 30 and 60% conversion, GC analysis showed 1.5 and 2.5 mmol of ethyl iodide, which is comparable to ethyl iodide obtained at the end of the reaction.

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TABLE 1

Results on Carbonylation of Ethanol

Sr. No.	Time (min)	Promoter used (mmol)	CO consumed (mmol)	Products formed (mmol)					Conversion[b] (%)	Selectivity to propionic acid[c] (%)
				Propionic acid	Ethyl propionate	Ethyl iodide	Ethane	Ethylene		
1	178	HI(62)	208.00	205.00	62.00	50.00	20.00	3.80	67.10	89.83
2	268	HI(62)[a]	200.00	154.00	96.00	57.00	21.20	12.00	55.02	82.26
3	178	HI(124)	150.00	146.00	52.00	96.00	25.00	21.00	56.49	75.96
4	176	LiI(62)	298.00	290.00	41.11	1.09	5.00	3.00	87.59	97.31
5	252	LiI(62)[a]	228.00	227.40	99.30	1.50	8.00	4.00	70.37	94.98
6	102	LiI(124)	300.00	296.00	32.00	1.20	3.00	8.00	90.24	96.42

Note. Ni(isoq)$_4$Cl$_2$, 2.1 mmol; ethanol, 340.2 mmol; Temp., 498 K; P_{CO}, 420 psi. Isoquinoline, 8.4 mmol; solvent, propionic acid; P_H, 140 psi.

[a] No hydrogen was used in the feed.

[b] Conversion = (mmol of reactant charged − mmol of reactant remaining)/mmol of reactant charged, where mmol of reactant remaining = ethyl propionate + ethyliodide (noncarbonylation products).

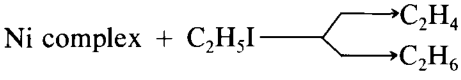
[c] Selectivity = mmol of propionic acid formed/mmol of ethyl propionate consumed.

This shows that the quantity of alkyl iodide formed in the experiments with LiI as a promoter is very low compared to the experiments with HI as a promoter.

(6) With the increase in the concentration of HI, both the activity of the catalyst and the selectivity to carboxylic acids were found to decrease substantially due to the formation of side products consisting of ethane, ethylene, or propane and propylene from ethanol and *n*-propanol, respectively (see runs 1 and 3 in Table 1 and runs 1 and 2 from Table 2).

(7) In contrast, with an increase in the concentration of the LiI promoter, both the activity and the selectivity to carboxylic acids were improved. The formation of side products was substantially reduced (see runs 4 and 6 from Table 1 and runs 3 and 5 from Table 2). These observations indicate that LiI is a better promoter than HI in Ni(isoq)$_4$Cl$_2$-catalyzed carbonylation of ethanol and *n*-propanol.

The formation of alkane and alkene in these reactions can be explained by the following reaction *(11)*:



$$\text{Ni complex} + C_2H_5I \longrightarrow \begin{cases} C_2H_4 \\ C_2H_6 \end{cases} \quad (1)$$

The increase in the formation of alkane and alkene with increasing HI concentration is

TABLE 2

Results on Carbonylation of Propanol

Sr. No.	Time (min)	Promoter used (mmol)	CO consumed (mmol)	Products formed (mmol)							Conversion (%)	Selectivity to carboxylic acid (%)
				n-Butyric acid	Isobutyric acid	Propyl acetate	*n*-Propyl iodide	Isopropyl	Propane	Propylene		
1	298	HI(62)	129.12	48.00	77.00	47.50	27.00	32.00	20.00	10.00	60.18	77.60
2	348	HI(124)	100.37	41.20	65.80	33.70	30.00	36.30	40.00	18.00	62.61	63.88
3	199	LiI(62)	195.50	113.20	65.26	60.83	8.00	4.10	6.00	6.20	72.73	91.72
4	245	LiI(62)[a]	160.30	92.00	56.00	90.20	7.80	4.00	7.50	8.00	61.86	89.42
5	150	LiI(124)	190.50	108.45	74.60	52.00	4.90	3.10	7.20	6.10	77.57	88.21

Note. Ni(isoq)$_4$Cl$_2$, 2.1 mmol; *n*-propanol, 267.5 mmol; Temp., 498 K; P_{CO}, 420 psi. Isoquinoline, 8.4 mmol; solvent, acetic acid; P_H, 140 psi. Selectivity and conversion calculations are as shown in Table 1.

[a] No hydrogen was used in the feed.

TABLE 3

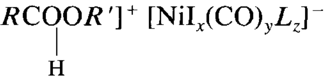
Effect of Solvents on the Activity and Selectivity in Carbonylation of Ethanol

Sr. No.	Solvent used	Time (min)	Average activity × 10^2 (mol/g/s)	Conversion (%)	Selectivity (%)
1	Acetic acid	180	13.40	70.00	87.22
2	Propionic acid	158	15.57	67.10	89.83
3	Water	200	—	—	—
4	Benzene	151	0.233	5.00	60.50

Note. $Ni(isoq)_4Cl_2$, 2.1 mmol; ethanol, 340.2 mmol; isoquinoline, 8.4 mmol; solvent, acetic acid; P_{CO}, 420 psi; P_H, 140 psi; temperature, 498 K.

consistent with the above reaction. The negligible concentration of alkyl iodide when LiI is used as a promoter explains the lower rates of formation of the side products and improved selectivity of carboxylic acids as products. On the other hand, a higher activity with metal iodide promoters, despite the relatively lower alkyl iodide concentrations (observed experimentally), in the system raises a question whether the oxidative addition of alkyl iodide is at all an important step in Ni-catalyzed carbonylation of alcohols. It is worthwhile noting that in carbonylation of ethanol and *n*-propanol with HI as a promoter the concentration of alkyl iodide is quite high (see runs 1, 2, and 3 in Table 1 and runs 1 and 2 in Table 2) throughout the reaction, while with metal iodide promoters it is negligible at any point of conversion (see runs 4, 5, and 6 in Table 1 and runs 4 and 5 in Table 2).

These results, the strong promoting effect of LiI and H_2, the observed necessity of a proton supplier such as carboxylic acid as a solvent, and improved rates of carbonylation despite negligible alkyl iodide concentration in the system, suggest that a protonated alkyl acetate form of a counterion of an anionic Ni iodocarbonyl derivative of the type $[NiI_x(CO)_yL_z]^-$ is likely to be an active species in the catalytic cycle:



$$[RC\underset{\displaystyle H}{\underset{|}{O}}OR']^+ [NiI_x(CO)_yL_z]^- \qquad (I)$$

Such anionic Ni complexes are known from the previous work of Cassar and Foa (*12*), wherein the formation of $M^+[NiI(CO)_3]^-$ is reported during the reaction of $Ni(CO)_4$ and MX (M = Li, Na; X = Cl^-, Br^-, I^-). However, there is no supporting evidence at this stage to strengthen the above speculation and discard the well-established mechanism wherein oxidative addition of alkyl iodide is the step leading to the formation of metal alkyl complex (*13*). The complexes of Ni carbonyl with N-containing ligands are known to be highly unstable (*14*) and hence, the characterization of such species is rather difficult. However, the observation of improved selectivity with metal iodide promoters compared to HI is particularly significant in view of its practical importance.

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