

Olefin Hydrocarboxylation under Mild Conditions in Nickel Complex Solutions

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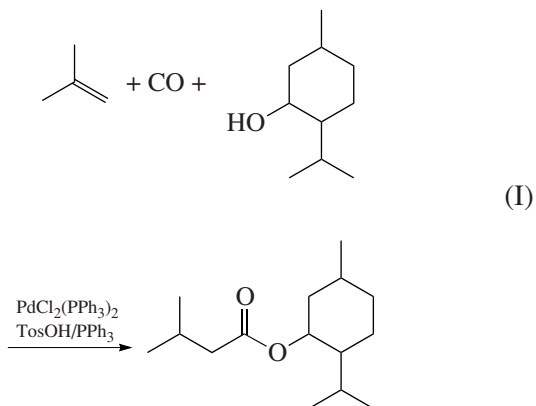
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Abstract—The hydrocarboxylation of α -olefins into carboxylic acids can be carried out in the presence of the dissolved complex $\text{NiCl}_2(\text{PPh}_3)_2$ at comparatively low CO pressures (below 0.8 MPa) with a fairly high product yield. Hexene-1 in acetic acid is converted into a mixture of heptanoic and 2-methylhexanoic acids, whose total yield is 40%. The molar ratio of the isomers is close to unity. However, the normal-chain product dominates at low CO pressures. Under the conditions examined, the catalyst is active only in the presence of a hydrogen (hydride ion) donor. The activity of the nickel complex can be markedly enhanced by preexposure of the reaction mixture to hydrogen pressure in the absence of CO. For the 0.8 MPa CO + 3.2 MPa H_2 gas mixture at 170°C, the turnover frequency of the catalyst is 28.5 and its activity is 4.8 h^{-1} .

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The most common catalysts for the synthesis of carboxylic acids by olefin carbonylation (hydrocarboxylation) are palladium complexes with the general formula PdL_n , including $\text{PdX}_2(\text{PPh}_3)_2$ (where X is an acido ligand, such as halogen and carboxylate) [1, 2]. These catalysts allow carbonylation reactions to be carried out under mild conditions (0.1–1.0 MPa CO_2 , 100–130°C). The activity of the Pd catalysts can be enhanced considerably by adding organic sulfoacids, which have recently found wide use [3–6]. The results obtained to date and the simple method developed for the recovery of the dissolved palladium complex [7] made it possible to commercialize a number of carbonylation processes, including the synthesis of mentyl isovalerate by isobutylene carbonylation (reaction (I)) for producing the active principle of Validol at a rate of 27 t/year (1995) [8–10].



Nickel compounds are much cheaper than palladium compounds and are often very active in similar

processes, including the hydrogenation of unsaturated compounds, coupling, cross-coupling, and the carbonylation of acetylenes. It is likely that the electronic structure of the metal is significant here: complexes of metals belonging to one family in the periodic table are known to be efficient catalysts for one kind of process. For example, Fe and Ru compounds are active catalysts for Fischer–Tropsch synthesis and for the selective carbonylation of alcohols and Co and Rh are classical catalysts for olefin hydroformylation [11, 12].

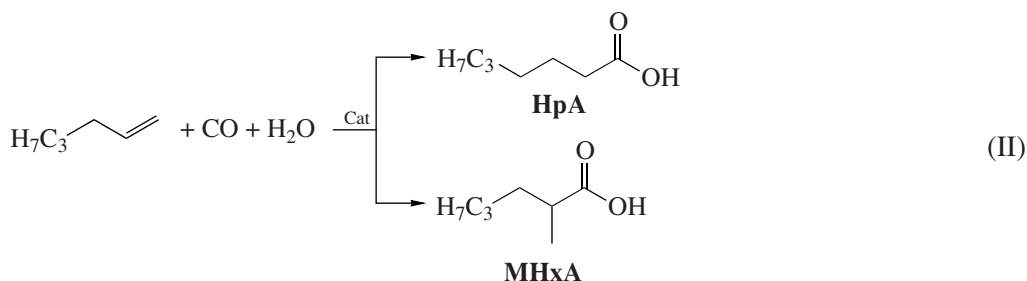
Nickel carbonyl, $\text{Ni}(\text{CO})_4$, and its salts were among the first catalysts suggested for carboxylic acid synthesis by olefin carbonylation [13, 14]. However, they were found to be active only under severe conditions ($P = 20\text{--}40$ MPa, $T = 250\text{--}300^\circ\text{C}$). For this reason, the catalysis of olefin carbonylation by nickel complexes has not been advanced since then.

In 1971, the nickel complexes $\text{NiX}_2(\text{PPh}_3)_2$ ($X =$ halogen) were reported as catalysts for the hydrocarboxylation of propylene (P) at comparatively low CO pressures of 0.2–2.5 MPa [15]. The total yield of butyric and isobutyric acids was 76.1% in 6 h, but the selectivity with respect to either isomer was not high and was generally about 50% ($n/\text{iso} = 1 : 1$). The activity of nickel complexes increased in the order $\text{Cl} < \text{Br} < \text{I}$, and, under comparable conditions, the turnover frequency of the catalyst (the ratio of the number of moles of the product to the number of moles of the catalyst in a unit time) ranged between 3.4 and 6.0 h^{-1} . No other ligands were introduced, but hydroquinone (HQ) was used as an admixture. For $\text{NiCl}_2(\text{PPh}_3)_2$ (Ni), the molar ratios of the components were $\text{P}/\text{HQ}/\text{Ni} = 420 : 1 : 4$.

It is of interest to understand why the phosphine halide complexes of nickel are so active and to extend

the use of nickel catalysts in olefin carbonylation in order to design economically efficient catalysts for selective production of carboxylic acids or their deriva-

tives under mild conditions. We studied this process for hexene-1 (H-1) conversion into heptanoic acid (HpA) and 2-methylhexanoic acid (MHxA):



EXPERIMENTAL

Hydroquinone was purified by sublimation. Hexene-1 was distilled at atmospheric pressure, collecting the fraction boiling at 63–65°C. The complex $\text{NiCl}_2(\text{PPh}_3)_2$ (Acros) and the other chemicals were used as received.

Catalytic experiments were performed in a glass reactor placed in a temperature-controlled steel autoclave fitted with a sampler (the experimental procedure is reported elsewhere [8]). The components of the reaction mixture were charged into the reactor, the reactor was placed into the autoclave, the autoclave was sealed and purged with the gas, and the necessary pressure was established. Next, the stirrer and the heater were turned on. The instant the temperature reached the preset working value was taken to be the starting point of the reaction. The runs were conducted under the following conditions: $\text{NiCl}_2(\text{PPh}_3)_2$ concentration, 3.08×10^{-2} mol/l; hexene-1 concentration, 2.16 mol/l; water concentration, 2.16 mol/l; acetic acid as the solvent (16.6 ml); $T = 170^\circ\text{C}$; reaction time, 6 h.

The reaction products were identified by the GC-MS method with electron impact ionization using a PolarisQ instrument (Thermo Finnigan). Chromatographic separation was carried out in a Thermo TR-5ms capillary column (25 m \times 0.25 mm) under the following conditions: carrier gas (helium) flow rate of 1 ml/min; temperature-programmed column (5-min-long isotherm at 40°C followed by heating to 320°C at a rate of 20°C/min); flow ratio of 1 : 100; evaporator temperature of 250°C; ionizing electron energy of 70 eV.

Samples of the reaction mixture were analyzed by GLC using a packed column. The support contained 3% H_3PO_4 and was impregnated with 10% polyethylene glycol adipate [8].

RESULTS AND DISCUSSION

We began with experiments involving hydroquinone under conditions similar to the conditions examined by other authors (0.8 MPa CO, 170°C) [15]. At H-1 : HQ : Ni = 140 : 1 : 2, the total yield of heptanoic and 2-methylhexanoic acids was below 1% in 6 h. No other prod-

ucts were detected. For comparison, we carried out a run under the same conditions but without HQ and we found that the complex $\text{NiCl}_2(\text{PPh}_3)_2$ is absolutely inactive. Unfortunately, we failed to reproduce the results reported in [15].

Although the $\text{HQ}/\text{NiX}_2(\text{PPh}_3)_2$ system was found to be fairly active, the role of HQ was not discussed [15]. Hydroquinone is a rather strong reductant [16]. On the assumption that nickel hydride complexes form in the presence of HQ and that these complexes activate the olefin, it is pertinent to study the effect of hydrogen, which causes the formation of hydride complexes in various catalytic processes involving transition metal compounds [17]. The activation of hydrogen by Pd complexes in aprotic media is considered to be quite possible for olefin carbonylation [18]. A great increase in the activity of the $\text{PdCl}_2(\text{PPh}_3)_2/\text{PPh}_3$ system under the action of hydrogen is also observed for isobutylene hydrocarbalkoxylation in the absence of *p*-toluenesulfonic acid [8].

Acid accumulation curves for experiments involving synthesis gas of composition $\text{CO}/\text{H}_2 = 1 : 1$ at a total pressure of 1.6 MPa are presented in Fig. 1.

As is clear from Fig. 1, the addition of hydrogen to CO allows the formation of the C_7 acids to be carried out at a noticeable rate: after 6 h, the total acid yield is 6.85% and the activity of the catalyst is 0.8 h^{-1} . As in the presence of hydroquinone [15], the *n/iso* ratio is close to unity. No aldehydes were detected. All subsequent experiments involved CO/H_2 mixtures. Their results are presented in Table 1.

As the total pressure of the $\text{CO}/\text{H}_2 = 1 : 1$ synthesis gas is raised (entries 1–4), the total acid yield passes through a maximum to become lower than 1% at CO pressures above 1.4 MPa. As the CO partial pressure is increased at a constant P_{H_2} value (entries 5, 2, 6, 7), the total acid yield decreases. Above 1.6 MPa, the reaction does not take place. At the same time, as the hydrogen partial pressure is raised (see entries 1 and 5 and entries 2, 8, and 9), the acid yield increases substantially and the activity of the catalyst increases to 2.7 h^{-1} (entry 9).

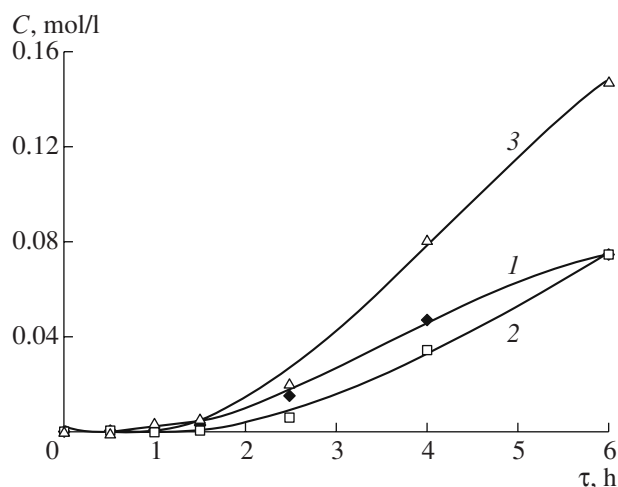


Fig. 1. C_7 acid accumulation curves: (1) HpA, (2) MHxA, and (3) total acid concentration.

These results demonstrate that hydrogen, which does not appear in chemical equation (II), markedly enhances the activity of the catalyst. This was assumed to be due to the formation of catalytically active complexes. In order to verify this assumption, we per-

Table 1. Dependence of the reaction outcomes on the CO and H_2 partial pressures

Entry	CO pressure, MPa	H_2 pressure, MPa	n_{iso}	Acid yield, %
1	0.5	0.5	1.05	5.27
2	0.8	0.8	1.05	6.85
3	1.4	1.4	0.52	0.88
4	2.0	2.0	0.69	0.98
5	0.4	0.8	1.30	8.24
6	1.6	0.8	—	0
7	3.2	0.8	—	0
8	0.8	1.6	0.70	8.94
9	0.8	3.2	0.84	22.69

Table 2. Effect of the preexposure of the reaction mixture to hydrogen pressure on the reaction outcomes

Entry	CO pressure, MPa	H_2 pressure, MPa	n_{iso}	Acid yield, %
2'	0.8	0.8	0.80	9.40
10	0.4	1.2	1.21	27.87
8'	0.8	1.6	1.10	32.41
9'	0.8	3.2	1.14	40.69

formed comparison experiments in which the reaction mixture was preexposed to hydrogen (4.0 MPa, 25°C, 17 h, no stirring). The results of these experiments are presented in Table 2.

A comparison between the data presented in Tables 1 and 2 suggests that the preexposure of the reaction mixture to hydrogen enhances the activity of the catalyst by a factor of 2–3 (compare entries 8 and 8' and entries 9 and 9'). The preactivation of the catalyst with hydrogen under the conditions examined allows the activity of the catalyst to be increased to 4.8 h^{-1} (entry 9'). The corresponding turnover frequency is 28.5. This activity is not the limit since the process is incomplete (Fig. 1) and the product yield increases as the hydrogen pressure is raised (Tables 1, 2). At the same time, the preexposure of the reaction mixture to synthesis gas (20 atm CO + 20 atm H_2 , 25°C, 17 h) followed by conduction of the reaction under the conditions of entry 8 (or 8') results in a decrease in catalytic activity, apparently because of the prolonged action of CO: the acid yield is 6.11%, and $n_{iso} = 0.67$.

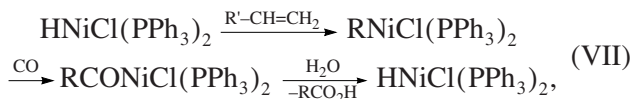
The retarding effect of CO, which is well known for carbonylation reactions, and the observed acceleration of the reaction by hydrogen are likely explained by the different natures of the complexes forming under the action of these gases. According to the literature, nickel carbonyl complexes, such as $Ni(CO)_4$ (detected by EXAFS) [19], and hydride complexes of composition $HNiL_n$ [20, 21] can form under the conditions examined:



The coordinatively saturated complex $Ni(CO)_4$ cannot activate an olefin and is obviously uninvolved in the catalytic cycle. Moreover, $Ni(CO)_4$ formation can reduce the concentration of the active forms of the catalyst, just as is observed for Co and Rh carbonyls [22]:



Nickel hydride complexes can apparently form under the action of hydrogen [23] because no strong protonic acid is present in the system. Reaction (II) can proceed via the Breslow–Heck mechanism, specifically, according to the following schemes:



where $R=R'-CH_2-CH_2-$.

Under the assumption that the hexene-1 hydrocarboxylation rate is determined by the $HNiCl(PPh_3)_2$ concentration, the observed dependence of the acid yield on the hydrogen partial pressure during the run (Table 2) for a fixed hydrogen exposure pressure

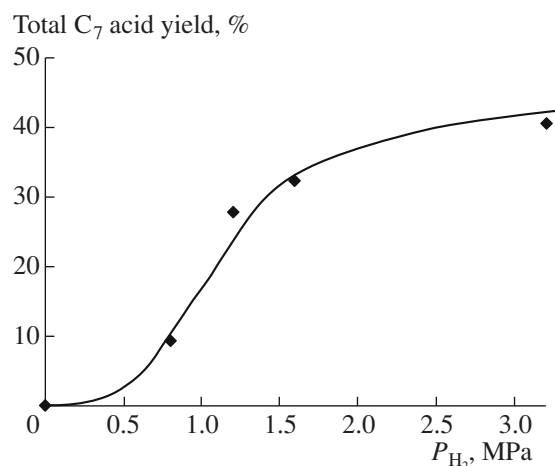


Fig. 2. Total acid yield as a function of the H_2 partial pressure.

($P_{H_2} = 4.0$ MPa) is evidence that reaction step (VI) is reversible and rapidly comes to equilibrium.

At the same time, the slowing-down effect of CO (Table 1) and the comparatively low product yield of 6.11% after the exposure of the reaction to synthesis gas (20 atm CO + 20 atm H_2) are evidence of the formation of inactive, coordinatively saturated nickel carbonyls. It is likely because of the absence of ligands capable of replacing CO in $Ni(CO)_4$ and the comparative high stability of this complex [24] that olefin carbonylation using this complex as the catalyst precursor was possible only under extremely severe conditions [13, 14]. For example, in the absence of protonic acids, the formation of active nickel complexes from $Ni(CO)_4$ in aqueous and alcoholic solutions is extremely hampered [20]. The prolonged action of CO can also cause the formation of inactive, polynuclear, nickel carbonyl clusters [25].

The catalytic inactiveness of $NiCl_2(PPh_3)_2$ in the absence of the hydride ion (observed in our experiments) suggests that this complex, unlike, e.g., Pd(II) complexes [18, 26, 27], cannot yield hydrides by reacting with CO and water.

In the experiments in which the catalyst was preactivated (Table 2), the yield of the C_7 acids increases with increasing H_2 pressure in a way described by an S-like curve (Fig. 2). Since no products other than acids were detected and reaction step (VI) is reversible, it can be assumed that the decline of the growth rate of catalytic activity is due to the $HNiL_n$ concentration approaching its maximum possible value under the given experimental conditions (temperature, solvent, etc.).

Thus, in order to activate the $NiCl_2(PPh_3)_2$ complex and make it work as an olefin carbonylation catalyst, it is necessary to introduce a hydrogen (hydride ion) donor favoring the formation of nickel hydride complexes. The formation of these complexes in the process examined needs further investigation.

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