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The Carboxylation Reaction using Nickel Catalysts. V.[1] The Catalytic Reaction of Propene with Nickel Carbonyl and Nickel Carbonyl-Triphenylphosphine

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The carboxylation reaction of propene catalyzed by nickel carbonyl was studied undeer various conditions. Iso- and *n*-butyric acids were obtained in good yields under mild conditions in the presence of a large amount of an organic acid. The catalytic carboxylation area was examined in detail. The carboxylation reaction proceeded smoothly in tetrahydrofuran, acetic acid, and dioxane. The proportion of isobutyric acid was largest in acetic acid (72.5–77.5%). Triphenylphosphine (TPP) had a great effect on the reaction rate, the catalytic reaction area, and the product distribution. On the reaction mechanism, an active species (HNi(CO)(TPP)X) was taken to account for the experimental results.

The preparation of carboxylic acids or their derivatives from unsaturated compounds and carbon monoxide in the presence of metal carbonyls is an important synthetic reaction known well as the carboxylation reaction. Numerous reports have been published on this reaction[2] besides the original works of Reppe *et al.* In our previous studies it was found that the carboxylation of propylne[3] and propadiene[4] in the presence of nickel carbonyl and organic acids takes place smoothly under a low carbon monoxide pressure.

It is said that the carboxylation of olefins except such reactive ones as bicyclo[2,2,1]heptene derivatives needs more stringent reaction conditions than does that of acetylenes.[2] Concerning the carboxylation reaction of olefins catalyzed by nickel catalysts, few detailed investigations have been published; all of them have used much more severe conditions than those for propyne and propadiene reported by us. In this report, the carboxylation of propene using a

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[1] Part I—IV are designated as follows: I, Y. Sakakibara, This Bulletin, **37**, 1601 (1964). II, S. Kunichika, Y. Sakakibara, and T. Okamoto, *ibid.*, **40**, 885 (1967). III, Y. Sakakibara, T. Okamoto, and H. Kurauchi, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 175 (1967). IV, S. Kunichika, Y. Sakakibara, and T. Nakamura, This Bulletin, **41**, 390 (1968).

[2] C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Logos Press, London (1967), p. 149.

[3] S. Kunichika, Y. Sakakibara, and T. Nakamura, This Bulletin, **41**, 390 (1968).

[4] S. Kunichika, Y. Sakakibara, and T. Okamoto, *ibid.*, **40**, 885 (1967).

nickel carbonyl catalyst has been investigated in detail with the aim of synthesizing butyric acid under milder conditions than those used in the literature.[5)]

$$CH_3CH{=}CH_2 + CO + H_2O \xrightarrow{Ni(CO)_4} CH_3CH_2CH_2CO_2H + (CH_3)_2CHCO_2H$$

The effects on the reaction processes of the reaction temperature, the carbon monoxide pressure, the solvent, and the addition of triphenylphosphine (TPP) were examined. As was seen in the case of the oxo reaction, two isomers were obtained. The nickel carbonyl catalyst and a catalyst system composed of nickel carbonyl and TPP both initiated the reaction smoothly under mild conditions and gave excellent yields of butyric acid. The presence of TPP in the reaction system contributed to obtaining a stable catalytic reaction and had a large influence on the product distribution.

Experimental

Materials. The propene, carbon monoxide, nickel carbonyl, TPP, and other compounds employed in this study were commercial products which were proved to be sufficiently pure by gas chromatography and/or elemental analysis.

Apparatus and Procedures of Carboxylation. A 200-m*l* rotational stirring-type stainless-steel autoclave (used at about 800 rpm) was charged under nitrogen with the solvent, an organic acid, hydroquinone, and a catalyst. The vessel was then cooled to about −40°C and the air was replaced completely by nitrogen. After evacuation, carbon monoxide was introduced until the specified pressure was reached. Then, propene was injected by an injection pump. Two reaction processes, the batch process (A) and the constant pressure process (B), were employed. The (A) process was used to search for the catalytic reaction conditions. The vessel was heated to the specified temperature with stirring, and the fall in the pressure was observed at that temperature. The (B) process was used to collect the kinetic data of the reaction. In this case, the pressure of the vessel was kept constant during the reaction by continuously supplying carbon monoxide from a gas storage tank. The relative reaction rate was calculated roughly from the absorption curve of carbon monoxide in the initial reaction period. The supply of carbon monoxide was stopped during the reaction, after which the vessel was cooled to room temperature. Then, the remaining gas was discharged through a mixture consisting of carbon tetrachloride, bromine, and water to decompose the nickel carbonyl and capture the residual propene.

Analytical Procedures. The reaction products, isobutyric acid and *n*-butyric acid, were determined by gas chromatography using a 2.5-m column of 21% dioctyl sebacate and 4% sebacic acid at 125°C. Acetophenone was used as the internal standard substance. The amount of residual propene trapped as 1,2-dibromopropane was determined gas-chromatographically by a 2.5-m column of 30% dioctyl phthalate at 120°C, using anisole as the internal standard substance. The amount of nickel carbonyl remaining after the reaction was determined by the nickel dimethylglyoxime method.

Results and Discussion

Carboxylation in the Presence of Nickel Carbonyl. At the beginning of this study, some attempts were made to determine the favorable conditions. The results are shown in Table 1. Under the same conditions as those used for the carboxylation of propyne,[3)] propene was unreactive and most of the propene and the nickel carbonyl were recovered (Run 1). The reaction under the carbon monoxide pressure using stoichiometric amounts of nickel carbonyl and an organic acid to propene (Run 2) showed a rapid pressure drop at 260°C; this drop indicated that the reaction was under way. In the next run (Run 3), where the amount of nickel carbonyl was reduced to a catalytic amount, the reaction started smoothly. When the amount of organic acid was reduced to a catalytic amount (Run 4), however, virtually no reaction was observed. It became apparent that a large amount of organic acid favored the carboxylation of propene. Therefore, subsequent experiments were carried out in the presence of a large amount of isobutyric acid or acetic acid.

TABLE 1. PRELIMINARY STUDY[a)]

Run No.	Solvent m*l*	C_3H_6 g	$Ni(CO)_4$ g	Cocatalyst g		$CO^{b)}$ atm	Reaction temp. °C	Reaction period, hr	Remarks
1	CH_3OH 70	8.4	2.0	H_2O AcOH	10 1.8	44— 45 (10)	160—163	1.5	recovered C_3H_6 96.2% recovered $Ni(CO)_4$ 90.6%
2	THF 25	9.0	9.0	H_2O IBA[c)]	25 11.2	154—108 (48)	260—270	5	
3	THF 25	10.2	2.0	H_2O IBA	25 11.2	153—140 (48)	250—270	5	
4	THF 25	13.8	2.0	H_2O IBA	25 1.9	164—180 (49)	260—277	5.5	

a) In every case, 0.05 g of hydroquinone was used for the reaction. Reaction process, (A).

b) The range of total pressure during the reaction period is shown. The value on the left shows the initial total pressure and on the right does the final one. The value in parenthesis shows the initial pressure of carbon monoxide at room temperature.

c) IBA; isobutyric acid

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5) W. Reppe, *Ann.*, **582**, 1 (1953); H. J. Hagemeyer, US 2739169 (1956); W. F. Gresham and R. E. Brooks, US 2448368 (1949).

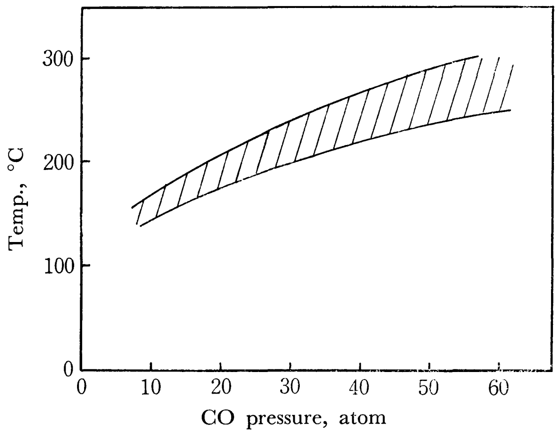

Fig. 1. Catalytic Reaction Area (Relation between the reaction temperature and the initial CO pressure at room temperature).
THF, 25 m*l*; H_2O, 25 m*l*; isobutyric acid, 11.2 g; Nickel carbonyl, 2.0 g; Propene, 4.3—12.5 g; Reaction process, (A).

Catalytic Reaction Area: The catalytic carboxylation using nickel carbonyl was influenced by the reaction temperature and the carbon monoxide pressure. In other words, there is an area of smooth catalytic reaction (afterwards abbreviated as CRA) on the carbon monoxide pressure *versus* reaction temperature diagram. The CRA was examined for the reaction of propene in the presence of a large amount of isobutyric acid: the results are shown in Fig. 1.[6] For a given carbon monoxide pressure, no fall in pressure was observed at temperatures outside of the specified area. That is, all the nickel carbonyl and propene charged were recovered at temperatures below this area; on the other hand, at temperatures above this area, the propene was recovered unchanged, and the nickel carbonyl was decomposed completely. In this region, the catalytic reaction occurred after a short induction period, and almost all the charged nickel carbonyl was recovered after the reaction.

Effect of the Temperature and the Carbon Monoxide Pressure on the Reaction Rate: Several runs were made varying the temperature and the carbon monoxide pressure. The results are shown in Table 2. For the same carbon monoxide pressure, the carboxylation reaction proceeded faster at higher temperatures within CRA. For example, raising the temperature from 160°C to 170°C increased the initial carbon monoxide absorption rate by a factor of 2 (Runs 6 and 7). On the other hand, decreasing the carbon monoxide pressure also accelerated the reaction so much that the rate at 10.5 atm was about two times that at 15 atm (Runs 5 and 7). From these values, it was roughly estimated that the rate is reversely proportional to about a square of the carbon monoxide pressure, as was observed in the case of propyne.[3]

Effect of the Solvent on the Reaction Rate: Six solvents which give a homogeneous solution were ex-

TABLE 2. INFLUENCE OF TEMPERATURE AND CO PRESSURE FOR THE CARBOXYLATION OF PROPENE[a]

Run No.	CO[b] atm	Reaction temp., °C	Reaction period, hr	Relative rate[c]	Recovered $Ni(CO)_4$, %	Recovered C_3H_6, %	Product IBA g (%)[d]	NBA[e] g (%)	IBA/BA[f] %
5	15	169—171	11.5	1	78.1	25.6	9.3 (71.5)	3.5 (26.0)	72.5
6	10.5	159—165	9.5	1	95.6	36.6	6.0 (54.0)	1.7 (15.6)	77.5
7	10.5	168—172	11.5	2	85.4	27.3	9.3 (72.4)	3.4 (26.1)	73.5
8	8	159—162	7.5	4	82.4	41.7	7.1 (69.6)	2.5 (24.3)	74.1
9	7.5	169—170	1	—	12.4				

a) C_3H_6, 8.4 g; $Ni(CO)_4$, 2.0 g; AcOH, 50 m*l*; H_2O, 10 m*l*; Reaction process, (B).
b) The initial carbon monoxide pressure at room temperature.
c) The initial rate of Run 5 is taken as 1.
d) Yield based on consumed propene.
e) NBA; *n*-butyric acid.
f) BA; the sum of IBA and NBA.

TABLE 3. INFLUENCE OF SOLVENTS FOR THE CARBOXYLATION OF PROPENE[a]

Run No.	Solvent[b]	Reaction period, hr	Recovered $Ni(CO)_4$, %	Recovered C_3H_6, %	Product IBA, g (%)	NBA, g (%)	IBA/BA, %
5	AcOH	11.5	78.1	25.6	9.3 (71.5)	3.5 (26.0)	72.5
10	THF	7.0	62.8	42.3	3.9 (38.6)	2.3 (23.9)	62.5
11	dioxane	9.5	59.4	54.8	2.7 (43.4)	1.2 (11.6)	66.9
12	diglyme	4.2	63.3	56.3	1.3 (16.2)	0.6 (7.8)	67.6
13	dimethyl cellosolve	5.0	93.8	89.5	1.2 (63.1)	0.6 (31.1)	67.1
14	methyl ethyl ketone	6.0	81.9	68.3	1.7 (30.6)	0.8 (15.1)	67.1

a) CO, 15 atm; 170°C; $Ni(CO)_4$, 2.0 g; AcOH, 10 m*l*; H_2O, 10 m*l*; C_3H_6, 8.4 g; Reaction process, (B).
b) Used 40 m*l*.

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6) CRA at the low carbon monoxide pressure is especially narrow. The appropriate temperature for 5 atm carbon monoxide pressure could not be found.

TABLE 4. CARBOXYLATION OF PROPENE IN THE PRESENCE OF TPP[a)]

Run No.	TPP P/Ni	CO atm	Reaction temp., °C	Reaction period, hr	Relative rate b)	Relative rate c)	Recovered C_3H_6, %	Product IBA, g(%)	Product NBA, g(%)	Product IBA/BA, %
5	0	15	169—171	11.5		1	25.6	9.3(71.5)	3.5(26.0)	72.5
15	1	7.5	167—172	11.0	1		32.5	5.4(45.1)	3.1(26.0)	63.3
16	2	4	170—173	5.5		2	42.8	3.4(34.0)	4.1(40.6)	45.6
17	2	7.5	168—173	12.0	2.5	1.4	28.7	4.2(33.6)	4.8(38.0)	46.9
18	2	15	169—173	13.0		1	21.7	4.8(34.7)	4.6(33.7)	50.8
19	3	7.5	168—170	11.0	3.5		24.2	4.3(31.8)	5.3(39.8)	44.4
20	2	8	160—163	9.0		1	46.5	3.4(35.0)	3.4(35.0)	50.0

a) C_3H_6, 8.4 g; $Ni(CO)_4$, 2.0 g; AcOH, 50 m*l*; H_2O, 10 m*l*; Reaction process, (B).
b) The initial rate of Run 15 is taken as 1.
c) The initial rate of Run 18 is taken as 1.

amined. The results are listed in Table 3. The initial carbon monoxide absorption rates were faster in tetrahydrofuran, acetic acid, and dioxane than those in diglyme, dimethyl cellosolve, and methyl ethyl ketone. For synthetic purposes, acetic acid was the most suitable solvent from the viewpoints of the recovery of nickel carbonyl (high catalytic level), and the yield, and also from the viewpoint of the selectivity of the products, as will be described later.

Product Distribution: Two isomeric butyric acids were obtained by the carboxylation of propene. In Tables 2 and 3, isobutyric acid is shown to have been formed predominantly in every case. Decreasing the temperature tended to increase the proportion of isobutyric acid (Run 6). The solvent also had a considerable effect on the distribution of the two isomers. In acetic acid, the ratio of isobutyric acid to *n*-butyric acid (i/n) was highest. The reported ratios in the literature are i/n=1 by nickel carbonyl,[5)] 1/3 by dicobalt octacarbonyl,[7)] 2/1 by palladium catalysts,[8)] and 1/3 by platinum chloride.[9)] The high values obtained here, 2/1—3/1, are thus worthy of note.

Carboxylation in the Presence of Nickel Carbonyl and TPP. A catalyst system composed of nickel carbonyl and TPP was examined, and the results obtained were compared with those obtained using nickel carbonyl alone in order to determine the effect of TPP. The results are summarized in Table 4.

Effect of TPP on CRA: As has been described already, the catalytic carboxylation of propene in the presence of the nickel carbonyl catalyst was possible under the restricted conditions of Fig. 1. The presence of TPP made it possible to perform catalytic carboxylation smoothly under the conditions at which the carboxylation with nickel carbonyl alone did not occur because of the decomposition of the catalyst itself. For example, at 170°C and a carbon monoxide pressure of 7.5 atm, which lies outside the CRA for nickel carbonyl, the catalytic reaction proceeded smoothly in the presence of TPP (Runs 9 and 17). A smooth catalytic reaction was also obtained even at a carbon monoxide pressure of 4 atm (Run 16). This stability of the catalyst system is advantageous from the synthetic point of view.

Effect of TPP on the Reaction Rate: Although the presence of TPP acted to broaden the CRA, it did not accelerate the reaction. At 160°C and a carbon monoxide pressure of 8 atm, the presence of 2 mole equivalents of TPP to nickel carbonyl served to slow down the initial reaction rate to roughly one-fourth that in the absence of TPP (Runs 8 and 20). At 170°C and a carbon monoxide pressure of 15 atm, however, the above two catalyst systems showed approximately equal rates (Runs 5 and 18). Increasing the amount of TPP from 1 to 3 mole equivalents to nickel carbonyl raised the relative rate from 1 to 3.5 (Runs 15, 17, and 19).

Effect of the Carbon Monoxide Pressure on the Reaction Rate: In the presence of 2 mole equivalents of TPP to nickel carbonyl, the decrease in the carbon monoxide pressure raised the reaction rate. This tendency, however, is not so remarkable as that in the absence of TPP. The relative initial rates at carbon monoxide pressures of 15, 7.5, and 4 atm in the presence of 2 mole equivalents of TPP to nickel carbonyl were 1.0, 1.4, and 2.0 respectively (Runs 18, 17, and 16), while in the absence of TPP the initial reaction rate at a carbon monoxide pressure of 10.5 atm was about 2 times that at a carbon monoxide pressure of 15 atm (Runs 5 and 7).

Effect of TPP on the Product Distribution: The presence of TPP had a great influence on the distribution of two isomers. Increasing the ratio of TPP to nickel carbonyl (P/Ni) raised the proportion of *n*-butyric acid, as is shown in Table 4. In connection with such results, it was reported recently that, in the hydroformylation reaction using cobalt[10)] or rhodium[11)] carbonyl complexes, the presence of phos-

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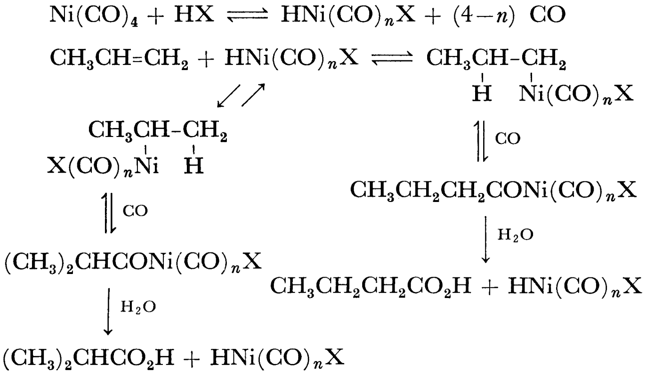
11) R. L. Pruett and J. A. Smith, *J. Org. Chem.*, **34**, 327 (1969); J. H. Craddock, A. Hershman, F. E. Paulik, and J. F. Roth, *Ind. Eng. Chem., Prod. Res. Develop.*, **8**, 291 (1969).

phorus compounds gives linear carboxylation products selectively. In the presence of 2 mole equivalents of TPP to nickel carbonyl, the isobutyric acid ratio seemed to increase slightly with an increase in the carbon monoxide pressure (Runs 16, 17, and 18), but the difference in the carbon monoxide pressure initially charged does not fully reflect the total isomer distribution, for the partial pressure of carbon monoxide is not constant during the reaction.

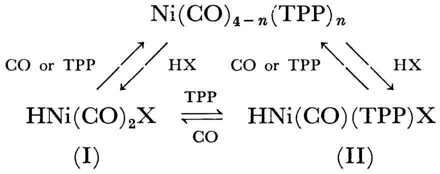
Carboxylation Reaction Path. The active species of catalyst for the carboxylation using nickel carbonyl is speculated to be $HNi(CO)_nX$ (I) (n; maybe 2), which is probably formed by the addition to nickel carbonyl of an active hydrogen compounds (HX) such as hydrogen halide, organic acid, and water. The reaction path is believed to be as follows:[3,12]



$$\mathrm{Ni(CO)_4 + HX \rightleftharpoons HNi(CO)_nX + (4-}n\mathrm{)\ CO}$$

$$\begin{tikzcd}
\mathrm{CH_3CH{=}CH_2 + HNi(CO)_nX} \arrow[r, shift left] \arrow[d, shift left] & \mathrm{\underset{H}{CH_3CH}\text{-}\underset{Ni(CO)_nX}{CH_2}} \arrow[l, shift left] \arrow[d, shift left, "CO"] \\
\mathrm{\underset{X(CO)_nNi}{CH_3CH}\text{-}\underset{H}{CH_2}} \arrow[u, shift left] \arrow[d, shift left, "CO"] & \mathrm{CH_3CH_2CH_2CONi(CO)_nX} \arrow[u, shift left] \arrow[d, "H_2O"] \\
\mathrm{(CH_3)_2CHCONi(CO)_nX} \arrow[u, shift left] \arrow[d, "H_2O"] & \mathrm{CH_3CH_2CH_2CO_2H + HNi(CO)_nX} \\
\mathrm{(CH_3)_2CHCO_2H + HNi(CO)_nX} &
\end{tikzcd}$$

In the presence of TPP, nickel carbonyl would exist as its TPP derivatives formed by replacing some carbon monoxide by TPP, depending on the reaction conditions. The results of the rate and the product distrubution suggest that the active species, different from that in the absence of TPP, also works in the reaction. As recent articles have reported the existence of $HNi[P(C_6H_{11})_3]_2Cl$[13] and $HNi[P(C_6H_{11})_3]_2(OAc)$,[14] it would be reasonable to consider the $HNi(CO)(TPP)X$ (II) species as corresponding to the $HNi(CO)_2X$ (I) of the nickel carbonyl catalyst. Concerning the formation of II, the following scheme may be considered:



$$\begin{tikzcd}
 & \mathrm{Ni(CO)_{4-}}{}_n\mathrm{(TPP)}_n \arrow[dl, shift left, "HX"] \arrow[dr, shift left, "HX"] & \\
\mathrm{HNi(CO)_2X} \arrow[ur, shift left, "\text{CO or TPP}"] \arrow[rr, shift left, "TPP"] & & \mathrm{HNi(CO)(TPP)X} \arrow[ll, shift left, "CO"] \arrow[ul, shift left, "\text{CO or TPP}"]
\end{tikzcd}$$

(I) (II)

It has been reported that TPP has a strong field-stabilizing power as a ligand.[15] Therefore, both the active species, II, and the Ni-alkyl complexes derived from II would have higher thermal stability than I and its alkyl derivatives. This is in accordance with the finding that, in the presence of TPP, the catalytic carboxylation proceeds under a low carbon monoxide pressure at a high temperature. As for the results of the reaction rate in the presence of TPP, a clear explanation is difficult at the present time. The rate of carboxylation reaction is probably determined by the step of the reaction between propene and the active species, such as I and II.[3] The rate is, then, determined by the reactivity and the concentration of active species. However, their dependence on the reaction conditions is very complicated because of the presence of the many equilibrium steps described in the above scheme. The increase in the proportion of n-butyric acid is caused mainly by two factors, both of which are in good accordance with the effect of TPP on the product distribution. One is the increase in the hydride character of Ni–H,[16] which facilitates the anti-Markownikoff addition to olefin. The other is the steric bulkiness of TPP, which facilitates the formation of the n-alkyl complex rather than that of the more crowded iso-alkyl complex.

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[16] TPP has a greater σ-donar character compared with carbon monoxide.