The Carboxylation Reaction Using Nickel Catalysts, VI. The Catalytic Reaction of Propene with Dihalobis-(triphenylphosphine)nickel

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The carboxylation reaction of propene catalyzed by dihalobis(triphenylphosphine)nickel $(NiX_2(P\Phi_3)_2;$ X=Cl, Br, I) was studied under various conditions by comparison with nickel carbonyl catalyst systems reported previously by the present authors. The catalytic reaction proceeded under less restricted conditions than those of nickel carbonyl systems. For a fixed temperature of 170°C, the maximum reaction rate was obtained at 15 atm of carbon monoxide pressure. In that condition, the efficiency of $NiBr_2(P\Phi_3)_2$ catalyst was about 24 times that of nickel carbonyl catalyst. $NiI_2(P\Phi_3)_2$ catalyst started the reaction smoothly at 110°C and 2 atm of carbon monoxide pressure. Among the three catalysts the order of the reaction rate was as follows: $NiI_2(P\Phi_3)_2 > NiBr_2(P\Phi_3)_2 > NiCl_2(P\Phi_3)_2$. In every runs the ratio of isobutyric acid to n-butyric acid was approximately 1.

INTRODUCTION

In the previous paper,[1] the carboxylation of propene by the catalysis of nickel carbonyl was reported. The catalytic reaction started easily in the presence of a large amount of organic acids such as acetic acid and isobutyric acid under mild conditions and isobutyric acid and n-butyric acid, as the carboxylation products, were obtained in an excellent selectivity. It was also reported that the coexistence of triphenylphosphine has a considerable effect on the catalytic reaction area, the reaction rate, and the distribution of the two isomers. But both of the above catalyst systems did not give yet satisfactory reaction rates under our reaction conditions.

Dihalobis(triphenylphosphine)nickel $(NiX_2(P\Phi_3)_2)$ is a well known catalyst for homogeneous hydrogenation, isomerization, polymerization, and oligomerization of olefins[2] as well as carboxylation of acetylenes.[3] The carboxylation of olefins by this catalyst, however, has never been reported. In the present investigation, the carboxylation of propene by the catalysis of dihalobis(triphenylphosphine)nickel was examined with the aim of the synthesis of butyric acid under mild conditions.

$$CH_3CH=CH_2+CO+H_2O \xrightarrow[\text{NiX}_2(\text{P}\phi_3)_2]{} CH_3CH_2CH_2CO_2H+(CH_3)_2CHCO_2H$$
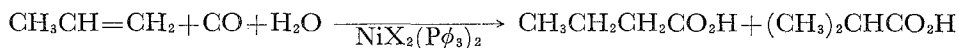
The effect of reaction conditions such as the reaction temperature, the carbon monoxide pressure, and the concentration of catalyst and also the difference in the halogen atom

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of the catalyst on the reaction rate, the catalytic reaction area, and the distribution of two isomers were examined and the catalytic activity of this catalyst was compared with that of nickel carbonyl systems.

EXPERIMENTAL

Materials. Propene, carbon monoxide, and the other compounds were commercial products which were proved to be sufficiently pure by gas chromatography and/or the elemental analysis. Dihalobis(triphenylphosphine)nickel complexes were prepared according to the method reported in literature.[4]

Apparatus and Procedures of Carboxylation. All reactions were carried out by using the same 200-ml stainless steel autoclave as was used in the previous study unless otherwise stated. Another 200-ml rotational stirring-type stainless steel autoclave was used for Runs 16–21. The procedure was the same as used previously. Acetic acid was chosen as the solvent.

Analytical Method. The products and the residual propene were analyzed by the same method as in the preceding experiment.

RESULTS AND DISCUSSION

Effect of the Temperature on the Reaction. Under the same carbon monoxide pressure (4 atm at room temperature), the reaction started smoothly at temperatures ranging from 120°C to 170°C by the catalysis of dibromobis(triphenylphosphine)nickel, as shown in Table 1. At 190°C, however, scarcely any absorption of carbon monoxide was observed during the reaction period (Run 5). The relative initial rates at 130°C, 150°C, and 170°C were 1, 1.7, and 3.1, respectively (Runs 2–4). In the case of diiodobis(triphenylphosphine)nickel, the reaction was initiated even at 110°C and 2 atm of carbon monoxide pressure and proceeded considerably quickly (Run 6).

Effect of the Carbon Monoxide Pressure on the Reaction Rate. The influence of the carbon monoxide pressure on the catalytic reaction was examined in the presence of dibromobis(triphenylphosphine)nickel catalyst. The reaction started at carbon monoxide pressures of 4 atm to 20 atm (Runs 7–11). The results are shown in Fig. 1, together with the results of nickel carbonyl catalyst and nickel carbonyl-triphenylphosphine system for comparison. As was seen in Fig. 1, the dependence of the reaction rate on the carbon monoxide pressure was completely different from that of nickel carbonyl or nickel carbonyl-triphenylphosphine. In the latter case the reaction rate decreased monotonously with the increase in the carbon monoxide pressure. As for dibromobis(triphenylphosphine)nickel catalyst, however, the maximum rate was obtained at about 15 atm of carbon monoxide pressure. Under the relatively high pressures of carbon monoxide such as 25 atm, the reaction did not start similarly to the nickel carbonyl systems (Run 12). The relative rates at 4, 8, 11, 15 and 20 atm of carbon monoxide pressure were 2.5, 2.5, 3.0, 3.5 and 1, respectively. Such a maximum in the reaction rate was also observed in the carboxylation reaction of 1-hexyne

Table 1. Influence of Temperature and CO Pressure for the Carboxylation of Propene.
C_3H_6, 8.4 g (0.2 mole); AcOH, 50 ml; H_2O, 10 ml; Hydroquinone, 0.05 g.

Run No.	NiX$_2$(PΦ$_3$)$_2$ mmole		Reaction temp. °C	CO[a] atm	Reaction period hr.	Relative rate[b]			Recovered C$_3$H$_6$ %	IBA[d] g(%)	NBA[e] g (%)	IBA/BA[f] %
1[g]	X=Br	1.9	118–122	4	8.0				58.0	1.9 (25.1)	1.6 (22.9)	53.7
2		1.9	129–132	4	9.5	1			61.5	2.0 (30.5)	1.9 (28.6)	51.6
3		1.9	148–151	4	10.0	1.7			35.0	4.2 (36.7)	3.9 (33.7)	52.1
4		1.9	168–173	4	10.5	3.1	2.5		21.9	4.0 (29.3)	3.8 (27.5)	51.6
5		1.9	188–191	4	2.5				56.5	1.4 (18.4)	1.3 (16.8)	52.4
6	X=I	1.9	108–111	2	9.5	1.3			21.0	5.9 (42,2)	4.3 (30.6)	58.0
7	X=Br	1.9	169–172	2	1				68.0	0.7 (12.3)	0.8 (14.4)	46.0
8		1.9	169–172	8	10.0		2.5	1	18.8	5.2 (36.1)	4.7 (33.1)	52.2
9		1.9	170–173	11	8.5		3.0		18.9	5.3 (37.2)	4.4 (30.9)	54.7
10		1.9	169–173	15	8		3.5		22.2	4.7 (34.6)	4.1 (29.6)	53.8
11		1.9	168–172	20	9		1		37.5	4.5 (41.0)	3.4 (31.3)	56.8
12		1.9	169–173	25	1				58.5	1.8 (23.9)	1.6 (21.6)	52.7
13		1.9	188–191	8	8.5				18.5	4.7 (36.7)	4.2 (23.8)	52.6
14		3.8	169–172	7.5	6			1.9	9.0	6.7 (41.8)	6.7 (41.8)	50.0
15		3.8	159–162	8	6			1.6	17,0	6.6 (45.2)	5.1 (34.9)	56.5

[a] The initial carbon monoxide pressure at room temperature is shown.

[b] For a series of experiments where the influence of the reaction temperature was examined, the initial rate of Run 2 is taken as 1 (absorption rate 5.5%/hr.), and for CO pressure, that of Run 11 is taken as 1, and for concentration of catalyst, that of Run 8 is taken as 1.

[c] Yield based on consumed propene

[d] IBA; isobutyric acid

[e] NBA; n-butyric acid

[f] BA; the sum of IBA and NBA

[g] In this run, 2 atm of H_2 was added.

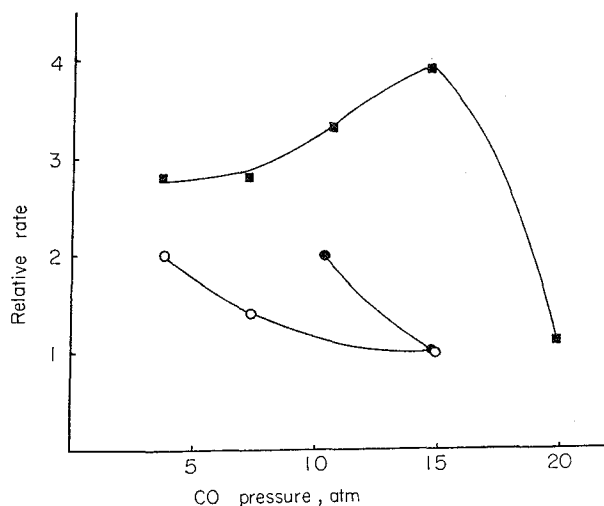Fig. 1. Effect of CO pressure on the reaction rate.
C_3H_6, 8.4g; AcOH, 50 ml; H_2O, 10 ml; Temp., 170°C

● ; $P\phi_3/Ni(CO)_4=0$ (Ni(CO)$_4$; 0.012 mole)
○ ; $P\phi_3/Ni(CO)_4=2$ (Ni(CO)$_4$; 0.012 mole)
■ ; $NiBr_2(P\phi_3)_2$ (0.0019 mole)

catalyzed by the same catalyst.[3c]   The result may be explained by considering the situation that the substitution of carbon monoxide for the ligand of the catalyst occurs at the low carbon monoxide pressure and a resulting compound or its derivatives act as an active catalytic species without requiring such a dissociation of carbon monoxide prior to the slow step of carboxylation as was proposed for the nickel carbonyl catalyst.[5] The decrease in the reaction rate after the pressure (~15 atm) would be explained by the modification of the catalyst due to the high pressure of carbon monoxide.   When twofold amount of catalyst was used, the rate increased by a factor of about 2 (Runs 8, 14, and 15).   Assuming that the proportionality would be continued in higher concentration of the catalyst, it may be said that dibromobis(triphenylphosphine)nickel is more active than nickel carbonyl by a factor of about 24 at 170°C and 15 atm of carbon monoxide pressure.

   Catalytic Reaction Area.   The catalytic carboxylation of propene by nickel carbonyl proceeded only under the restricted area which was determined by both the reaction temperature and the carbon monoxide pressure.   This phenomenon was partly due to the instability of the nickel carbonyl catalyst and partly to the depression of the formation of the active species by the carbon monoxide pressure.   When dibromobis(triphenylphosphine)nickel was used, the catalytic reaction proceeded smoothly over a far wide range.   The result is shown in Fig. 2.   A similar tendency was also observed in the catalytic reaction by nickel carbonyl with the coexistence of triphenylphosphine.   These results show that the catalyst or the organo-nickel species derived from it has a high thermal stability owing to the presence of triphenylphosphine compared with nickel carbonyl and its unstable derivatives.   The result would be
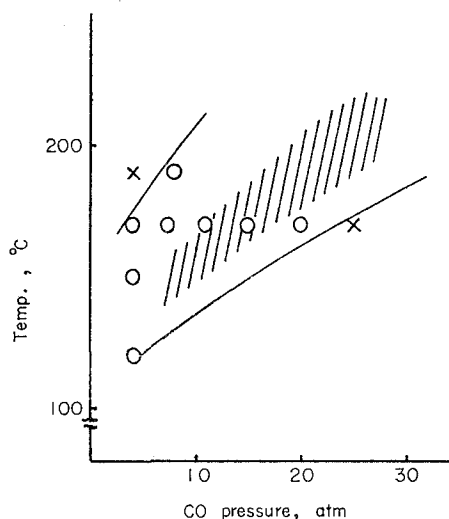
Fig. 2. Catalytic reaction area (dibromobis(triphenylphosphine)nickel catalysis).
C$_3$H$_6$, 8.4 g; AcOH, 50 ml; H$_2$O, 10ml; NiBr$_2$(Pϕ_3)$_2$, 1.70 g

○ ; Reaction occurs

✕ ; No reaction

Oblique lines represent catalytic reaction area by nickel carbonyl catalyst.

reasonable since triphenylphosphine has a strong ligand field stabilizing power compared with carbon monoxide.[6]

Effect of the Halogen Atoms of Catalyst on the Reaction Rate. The reaction was tried by the three catalysts, NiX$_2$(Pϕ_3)$_2$ (X=Cl, Br, and I). The results are shown in Table 2. The order of the reaction rates were; NiI$_2$(Pϕ_3)$_2$>NiBr$_2$(Pϕ_3)$_2$>NiCl$_2$(Pϕ_3)$_2$. The relative rates at 170°C and 10 atm of carbon monoxide pressure were roughly as follows; I: Br: Cl=1.7: 1.4: 1 (Runs 16–18). The order accord with the π-polarizability of the ligands and also the oxidation potentials of the halogen ions. The same tendency was also reported for the polymerization of allene by these catalysts.[7]

Product Distribution. As shown in Tables 1 and 2, the proportion of

Table 2. Influence of Halogen Atom in the Catalyst for the Carboxylation of Propene. AcOH, 50 ml; H$_2$O, 10 ml; Hydroquinone, 0.05 g.

Run No.	NiX$_2$(Pϕ_3)$_2$ mmole	Reaction temp. °C	CO atm	C$_3$H$_6$ g	Reaction period hr.	Recovered C$_3$H$_6$ %	Product IBA g(%)	Product NBA g(%)	IBA/BA %
16	X=I 2.8	168–174	10	10.1	11.0	6.8	8.3 (42.3)	7.1 (36.3)	53.8
17	X=Br 2.8	168–172	10	10.5	9.0	25.4	5.4 (32.9)	5.3 (32.2)	50.6
18	X=Cl 2.8	168–173	10	10.8	8.0	49.6	4.7 (41.3)	4.8 (42.0)	49.6
19	X=I 1.9	168–173	7.5	8.0	9.5	9.7	3.7 (24.5)	3.4 (22.3)	52.3
20	X=Br 1.9	170–172	7.5	8.9	6.5	33.3	3.2 (25.8)	3.3 (26.7)	49.1
21	X=Cl 1.9	169–170	7.5	8.1	10.0	43.2	2.8 (29.1)	2.8 (29.1)	49.8

isobutyric acid in two isomeric butyric acids in the case of dibromobis(triphenylphosphine)nickel catalyst was constantly about 50%. Nickel carbonyl gave an extremely high selectivity of the isobutyric acid (72.5–77.5%). Dibromobis(triphenylphosphine)-nickel catalyst gave a little high proportion of isobutyric acid compared with the catalyst system composed of 1 molar equivalent of nickel carbonyl and 2 molar equivalents of triphenylphosphine (shown in the parentheses): 51.6% (45.6%) for 170°C and 4 atm of carbon monoxide pressure, 53.8% (50.8%) for 170°C and 15 atm, 50.0% (46.9%) for 170°C and 7.5 atm, and 56.5% (50.0%) for 160°C and 8 atm. Moreover, among the three dihalobis(triphenylphosphine)nickels the order of the proportion of isobutyric acid was as follows; $I > Br \geq Cl$. These results suggest that the more bulky and less electronegative anion gave *iso*-isomer favorably. In the previous paper, the increase in *n*-isomer in the presence of triphenylphosphine was explained by the two factors, sterical bulkiness and electron donor character of triphenylphosphine compared with carbon monoxide. The results on halogens are not explained by these factors.

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