SELECTIVE CLEAVAGE OF C-O BONDS IN ESTERS THROUGH OXIDATIVE ADDITION TO NICKEL(0) COMPLEXES

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Zero-valent nickel complexes, especially bis(1,5-cyclooctadiene)nickel Ni(cod)$_2$ in the presence of various tertiary phosphines, promote cleavage of C-O bonds in phenyl carboxylates and alkenyl acetates to give nickel complexes such as nickel carbonyls and nickel phenoxide and other gaseous and liquid products. The position of cleavage of the ester and consequently the products of the reaction depend on the ester, nickel complex employed and the ligand added to the reaction mixture.

Oxidative addition of alkyl(aryl) halides and acyl halides to transition metal involving the cleavage of carbon-halogen bond is well known, but very few studies have been made concerning the oxidative addition of esters to transition metal complexes.[1-3] We report here the selective cleavage of C-O bonds in esters proceeding through the oxidative addition of esters to zero-valent nickel complexes and the effect of the kinds of the esters, the nickel complexes and the ligands on the position of cleavage of the C-O bonds in esters.

Interaction of the esters with nickel complexes leads to cleavage of the esters at two positions as shown below and the results are summarized in Table 1. The occurrence of the Type A or B reaction was deduced on the basis of the product analysis.
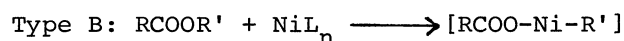
Type A: RCOOR' + NiL$_n$ ⟶ [RCO-Ni-OR']

Type B: RCOOR' + NiL$_n$ ⟶ [RCOO-Ni-R']
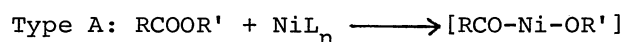
Table 1.   Mode of Cleavage of C-O Bonds in Phenyl Carboxylate and Alkenyl Acetate by the Reactions with Ni(cod)$_2$ in the Presence of Ligands[a]

Ester \ Ligand[b]	None	PPh$_3$	PCy$_3$	PEt$_3$	bpy	Ni(PPh$_3$)$_4$[c]
Phenyl carboxylate	-	A	A	A + B	A	A + B
Alkenyl acetate	B	B	A + B	-	B	-

a. Symbols A and B denote Type A and Type B reactions, respectively.

b. PPh$_3$ = triphenylphosphine, PCy$_3$ = tricyclohexylphosphine
   PEt$_3$ = triethylphosphine, bpy = 2,2'-bipyridine

c. Ni(PPh$_3$)$_4$ was employed in the place of Ni(cod)$_2$ and a ligand.

Detailed examinations were made regarding the reactions of Ni(cod)$_2$ with phenyl carboxylates in the presence of triphenylphosphine (PPh$_3$) as summarized in Table 2.

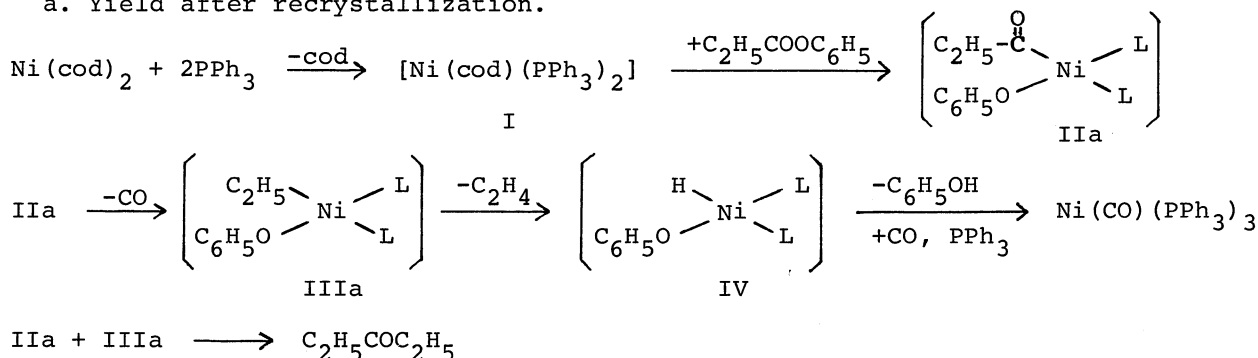The reaction of Ni(cod)$_2$ with phenyl propionate in the presence of PPh$_3$ gave ethylene, tris(triphenylphosphine)carbonylnickel(0),[4] phenol and diethyl ketone. The results may be accounted for by assuming formation of propionyl, ethyl and hydrido intermediate, IIa, IIIa, and IV:

Table 2.   Reactions of Ni(cod)$_2$ with Phenyl Carboxylate RCOOC$_6$H$_5$ in the Presence of PPh$_3$

RCOOC$_6$H$_5$ (mmol)	Ni(cod)$_2$ (mmol)	$\dfrac{PPh_3}{Ni}$	Temp. (°C)	Time (hr)	Gas	Products (mmol)	
						Liquid	Solid
R=C$_2$H$_5$ 10	0.71	1.0	54	12	C$_2$H$_4$(0.31)	C$_6$H$_5$OH(tr) C$_2$H$_5$COC$_2$H$_5$(tr)	Ni(CO)(PPh$_3$)$_3$ (tr)[a]
R=C$_2$H$_5$ 6	0.40	2.0	54	12	C$_2$H$_4$(0.24)	C$_6$H$_5$OH(0.16) C$_2$H$_5$COC$_2$H$_5$(tr)	Ni(CO)(PPh$_3$)$_3$ (0.13)[a]
R=C$_2$H$_5$ 7	0.47	3.0	54	20	C$_2$H$_4$(0.42)	C$_6$H$_5$OH(0.45) C$_2$H$_5$COC$_2$H$_5$(tr)	Ni(CO)(PPh$_3$)$_3$ (0.27)[a]
R=C$_2$H$_5$ 8	0.55	4.0	54	20	C$_2$H$_4$(0.52)	C$_6$H$_5$OH(0.55) C$_2$H$_5$COC$_2$H$_5$(tr)	Ni(CO)(PPh$_3$)$_3$ (0.35)[a]
R=CH$_3$ 63	4.7	1.5	50-55	30	CH$_4$(0.63) C$_2$H$_6$(0.09)	anisol(tr)	Ni(CO)(PPh$_3$)$_3$ (0.80)[a] Ni(OC$_6$H$_5$)$_2$

a. Yield after recrystallization.

$$Ni(cod)_2 + 2PPh_3 \xrightarrow{-cod} [Ni(cod)(PPh_3)_2] \xrightarrow{+C_2H_5COOC_6H_5} \left[\begin{array}{c} C_2H_5 - \overset{O}{\overset{\|}{C}} \diagdown \\ C_6H_5O \diagup \end{array} Ni \diagup^{L}_{\diagdown L} \right]$$
$$\text{I} \qquad\qquad\qquad\qquad \text{IIa}$$

$$\text{IIa} \xrightarrow{-CO} \left[\begin{array}{c} C_2H_5 \diagdown \\ C_6H_5O \diagup \end{array} Ni \diagup^{L}_{\diagdown L} \right] \xrightarrow{-C_2H_4} \left[\begin{array}{c} H \diagdown \\ C_6H_5O \diagup \end{array} Ni \diagup^{L}_{\diagdown L} \right] \xrightarrow[+CO,\ PPh_3]{-C_6H_5OH} Ni(CO)(PPh_3)_3$$
$$\text{IIIa} \qquad\qquad\qquad \text{IV}$$

IIa + IIIa $\longrightarrow$ C$_2$H$_5$COC$_2$H$_5$

where L represents PPh$_3$ or cod ligand.

It has been reported that the reaction of Ni(cod)$_2$ with PPh$_3$ gives the complex I.[5] The formation of diethyl ketone, ethylene and phenol supports the intermediacy of the propionylnickel, ethylnickel and hydridonickel complexes.

The reactivities of the intermediate IIa may be compared with those of an isolated propionylnickel complex Ni(COC$_2$H$_5$)(acac)(PPh$_3$) (acac = acetylacetonato)[6] which has almost the same structure as IIa except for the difference in the anionic ligands(OC$_6$H$_5$ and acac). 1,5-Cyclooctadiene liberated from Ni(cod)$_2$ was isomerized during the reaction of Ni(cod)$_2$ with C$_2$H$_5$COOC$_6$H$_5$ in the presence of PPh$_3$ to give a mixture of cod, 1,3-cyclooctadiene, 1,4-cyclooctadiene, bicyclooctene-1 and

bicyclooctene-2. This fact affords additional evidence for the intermediacy of the hydridonickel complex.[7]

The yields of products per $Ni(cod)_2$ increased with increase in the amount of PPh_3 added. However, the initial rate of the reaction became maximum at $PPh_3/Ni(cod)_2 = 2$ and further increase in the amount of PPh_3 decreased the rate. These observations imply that coordination of PPh_3 with nickel is essential for the reaction to proceed but presence of excess PPh_3 prevents the coordination of $C_2H_5COOC_6H_5$ and thus retards the reaction.

In contrast to the reaction of phenyl propionate with $Ni(cod)_2$ that of phenyl acetate takes a somewhat different course evolving methane and ethane. From the reaction mixture $Ni(CO)(PPh_3)_3$ and $Ni(OC_6H_5)_2$ were isolated, the latter compound being identified by IR spectroscopy (3068, 1582, 1485, 1250 cm^{-1} (ν_{C-O})) and chemical reactivities of the compound. Reactions of $Ni(OC_6H_5)_2$ with H_2SO_4 and CH_3I gave phenol and anisol, respectively, and two moles of phenyl propionate per nickel was formed by the reaction of $Ni(OC_6H_5)_2$ with propionic anhydride. Those results of the reaction of $Ni(cod)_2$ with phenyl acetate in the presence of PPh_3 may be accounted for by assuming acetyl and methyl intermediates, IIb and IIIb:

$$\left[\begin{array}{c} CH_3-\overset{O}{\overset{\|}{C}}\diagdown \\ \diagup Ni \diagup L \\ C_6H_5O \diagup \diagdown L \end{array} \right] \xrightarrow{-CO} \left[\begin{array}{c} CH_3 \diagdown \\ Ni \diagup L \\ C_6H_5O \diagup \diagdown L \end{array} \right] \xrightarrow{+CO} Ni(CO)(PPh_3)_3 + Ni(OC_6H_5)_2 + \text{"}CH_3\text{"}$$

$$\qquad\qquad IIb \qquad\qquad\qquad\qquad IIIb \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad [CH_4 + C_2H_6]$$

Formation of anisol in the reaction is consistent with the formation of the intermediate IIIb. In contrast to the reaction of $Ni(cod)_2$ with phenyl propionate, cod liberated from $Ni(cod)_2$ was not isomerized during the reaction of $Ni(cod)_2$ with phenyl acetate. The yields of the products in the reaction of phenyl acetate with $Ni(cod)_2$ in the presence of PPh_3 were lower than those of the products in the reaction of phenyl propionate indicating that the oxidative addition of phenyl acetate to nickel is more difficult than that of phenyl propionate. The yields of the products of the reaction of phenyl acetate, however, may be increased by increasing the reaction time or raising the reaction temperature.

The reaction of $Ni(cod)_2$ with phenyl carboxylates in the presence of tricyclohexylphosphine or 2,2'-bipyridine caused the same type of cleavage (Type A reaction) of phenyl carboxylates to give analogous products. However, the reaction of $Ni(cod)_2$ with phenyl acetate in the presence of triethylphosphine and the reaction of tetrakis(triphenylphosphine)nickel with phenyl acetate caused both types of cleavage of phenyl acetate to give $Ni(CH_3CO_2)_2$ and nickel carbonyls (Table 1).

Reactions of $Ni(cod)_2$ with alkenyl acetates (vinyl acetate and allyl acetate) proceed smoothly even in the absence of ligand. When the mixture of $Ni(cod)_2$ (2.8 mmol) and allyl acetate (3 mmol) in 3 ml of diethyl ether was allowed to stand for 1 hr at 10°C, the reaction was completed to give $Ni(CH_3CO_2)_2$ and $Ni(\pi-C_3H_5)_2$ quantitatively. $Ni(CH_3CO_2)_2$ was isolated as a pyridine adduct $Ni(CH_3CO_2)_2(py)$ and this was characterized by IR spectroscopy and elemental analysis: Found: C, 42.9; H, 4.35; N, 6.05; Calcd.: C, 42.2; H, 4.34; N, 5.47. $Ni(\pi-C_3H_5)_2$ was collected by

distillation in vacuum and identified by NMR spectroscopy. The products of the reaction clearly indicate that Type B reaction occurred:

$$Ni(cod)_2 + CH_3COOCH_2\text{-}CH=CH_2 \xrightarrow{-2cod} [CH_3COO\text{-}Ni(\pi\text{-}C_3H_5)]$$
$$V$$

$$\longrightarrow Ni(\pi\text{-}C_3H_5)_2 + Ni(CH_3CO_2)_2$$

Teyssié and his coworkers have isolated haloacetate analogs of V from the reaction mixtures of $Ni(cod)_2$ and allyl haloacetates.[1] They claimed that V itself was isolable from the reaction mixture of $Ni(cod)_2$ and allyl acetate. However, we could not obtain V under the same conditions as reported in their paper.

Cleavage of ester bond in vinyl acetate promoted by $Ni(cod)_2$ proceeded more slowly than that of allyl acetate. Evolution of 0.4 mmol of ethylene was observed after heating a mixture of $Ni(cod)_2$ (2.8 mmol) and vinyl acetate (77 mmol) for 4 days at 40°C. The yellow precipitate produced during the reaction was identified as $Ni(CH_3CO_2)_2$ from IR spectroscopy. These results indicate that Type B reaction occurred:

$$Ni(cod)_2 + CH_3COOCH=CH_2 \xrightarrow{-2cod} [CH_3COO\text{-}Ni\text{-}CH=CH_2]$$

$$\longrightarrow Ni(CH_3CO_2)_2 + \text{ethylene}$$
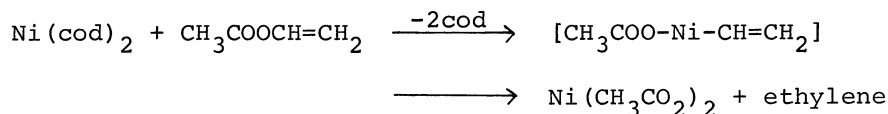
Reactions of $Ni(cod)_2$ with vinyl acetate in the presence of PPh_3 or 2,2'-bipyridine also gave ethylene and $Ni(CH_3CO_2)_2$. However, the reaction with vinyl acetate in the presence of tricyclohexylphosphine (PCy_3) gave not only ethylene and $Ni(CH_3CO_2)_2$ but also a nickel carbonyl complex $Ni(CO)_2(PCy_3)_2$ indicating that both Type A and Type B reactions took place (Table 1).

In contrast to the reactions of $Ni(cod)_2$ with phenyl carboxylates and alkenyl acetates reactions of alkyl methacrylates such as methyl methacrylate and ethyl methacrylate in the presence of PPh_3 did not cause the scission of ester bond but gave π-complexes formulated by $Ni(PPh_3)_2$(alkyl methacrylate).

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    (b) T. Nishiguchi, H. Imai, and K. Fukuzumi, J. Catal., 39, 375 (1975).