BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 508—513 (1971)

Stoichiometric Carbonylation of Aryl Halide with Nickel Tetracarbonyl in the Presence of Potassium Acetate

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(Received July 30, 1970)

In the stoichiometric reaction of aryl halide with $Ni(CO)_4$ in methanol to form the corresponding ester, it has been found that the carbonylation is effectively promoted by adding potassium acetate to the starting materials, and that four moles of the ester are obtained from one mole of $Ni(CO)_4$ without any appreciable side reactions. From the inhibition by gaseous carbon monoxide and the IR measurements during the carbonylation, it has been concluded that nickel tricarbonyl, $Ni(CO)_3$, is the initiator of the carbonylation and that its regeneration is the rate-determining step. The present results provide a basis on which the course of the carbonylation of aryl halide with carbon monoxide catalyzed by $Ni(CO)_4$ under high temperatures and pressures may be reasonable explained.

Nickel tetracarbonyl is highly reactive in the carbonylation of organic halide, especially for aryl[1,2] and allyl halide.[3] They give the corresponding esters in a methanol solution. The yield of the ester is highly increased by adding an acceptor of hydrohalogenic acid formed during the carbonylation, though the role of the acceptor is not yet understood well.

In our previous paper dealing with the carbonylation of aryl bromide catalyzed by nickel carbonyl under high temperatures and pressures, it was reported that the carbonylation is promoted by adding a sufficient amount of carboxylic salt; this yields a quantitative amount of the corresponding carboxylic acid[4] as follows:

$$C_6H_5Br + CO + H_2O + AcOK \xrightarrow{Ni(CO)_4} C_6H_5COOH + AcOH + KBr \qquad (1)$$

The role of the added carboxylic salt has been considered to reduce the concentration of hydrobromic acid, which inhibits the regeneration of nickel carbonyl. A similar effect was also observed in the stoichiometric reaction of aryl iodide with $Ni(CO)_4$ in methanol at a low temperature. That is, the carbonylation rate is effectively increased by adding carboxylic salt. It is to be noticed in this reaction that about four moles of the carboxylic ester are obtained from one mole of $Ni(CO)_4$, without any appreciable side reaction; this novel result is similar to that claimed by Reppe in the stoichiometric carbonylation of acetylene with $Ni(CO)_4$,[5] $Ni(CO)_4 + 4CH{\equiv}CH + 4ROH + 2HX \rightarrow 4CH_2{=}CHCOOR + NiX_2 + H_2$ ($R = CH_3$, C_2H_5, *etc.*; $X = Cl$, Br, CH_3CO_2, *etc.*). During the course of this study, it was reported by Corey and Hegedus[6] that the treatment of organic halide, RX, with several equivalents of nickel carbonyl in an alcoholic medium (R′OH) containing 2—3 equivalents of the corresponding sodium or potassium alkoxide (strongly basic medium) also results in the formation of the RCOOR′ ester, while the reaction path of the coordinated carbon monoxide is still obscure.

The present study has been undertaken in order to investigate the reaction path of coordinated carbon monoxide in the stoichiometric reactions of aryl iodides with nickel tetracarbonyl in a methanol solution. On the basis of the results of this study, the course of catalytic carbonylation with nickel carbonyl has been discussed.

Results

The results of the stoichiometric reaction of iodobenzene with nickel tetracarbonyl in methanol under a nitrogen atmosphere at 50°C are summarized in Table 1. Iodobenzene, which has been known to react with nickel tetracarbonyl in methanol at re-

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[1] N. L. Bauld, *Tetrahedron Lett.*, **1963**, 1841.

[2] E. Yoshisato, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **34**, 1500 (1969).

[3] F. Guerrieri and G. P. Chiusoli, *J. Organometal. Chem.*, **15**, 209 (1968).

[4] M. Nakayama and T. Mizoroki, This Bulletin, **42**, 1124 (1969).

[5] J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York (1949), p. 246.

[6] E. J. Corey and L. S. Hegedus, *J. Amer. Chem. Soc.*, **91**, 1233 (1969).

Table 1. Mass balance of the carbonylation of iodobenzene with $Ni(CO)_4$

(mol ratio)			Ni^0 b) (mmol)	Ni^{2+} (mmol)	total Ni (mmol)	I^-		$C_6H_5COOCH_3$	
$Ni(CO)_4$ a)	C_6H_5I	AcOK				(mmol)	(%) c)	(mmol)	(%) c)
1	4	0	0	0.8	0.8	0.3	0	0	0
1	4	2	2.84	8.2	11.0	33.7	306	23.6	214
1	4	4	3.98	5.98	9.97	40.6	407	32.1	321
1	4	6	3.42	6.72	10.1	38.6	382	31.0	307
1	6	6	0.50	10.9	11.4	49.7	436	41.0	367

a) $Ni(CO)_4$, 11.6 mmol; CH_3OH, 2.0 mol
b) Metallic nickel isolated.
c) Based on the amount of total nickel.

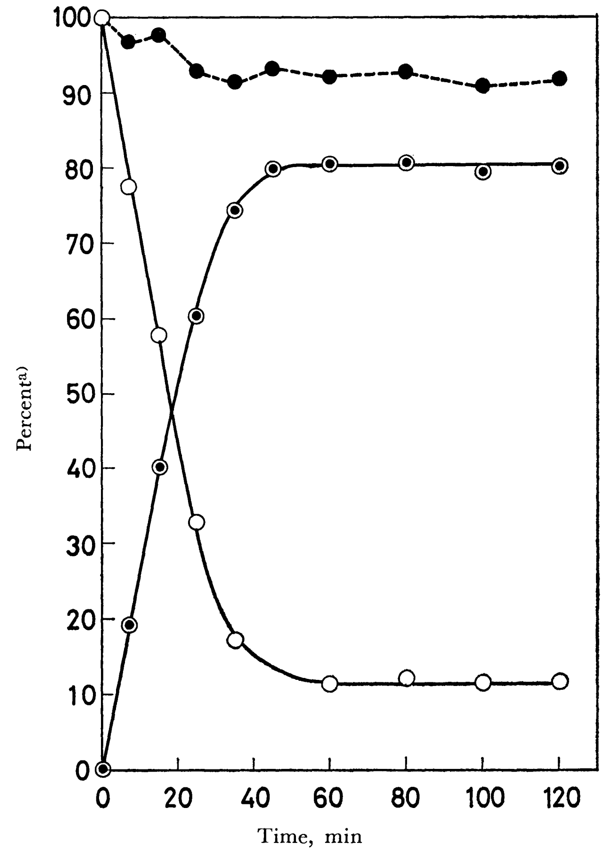

Fig. 1. Reaction rate of iodobenzene with nickel tetracarbonyl at 50°C under nitrogen. The rates illustrated are for iodobenzene, ○, methyl benzoate, ⊙, and mass balance of iodobenzene, ●.

C_6H_5I, 0.046 mol; $Ni(CO)_4$, 0.012 mol; AcOK, 0.046 mol; CH_3OH, 2.0 mol

a) The percentage was based on the amount of iodobenzene used.

flux to form methyl benzoate, was unchanged in the absence of potassium acetate under the conditions specified in Table 1, while it was vigorously changed by the addition of potassium acetate. It is highly soluble in methanol (more than 33 g/100 g methanol at 25°C). This is why potassium acetate and methanol were used preferably in this study. As soon as the temperature of the solution reached 50°C, its color changed from almost colorless to a reddish brown; this change was followed by the deposition of a black precipitate within half an hour. In the final stage, the solution turned green because of the Ni(II) ion.

In the absence of aryl halide, no reaction of nickel tetracarbonyl with potassium acetate was observed. The variations in the amounts of iodobenzene and methyl benzoate during the reaction were followed by gas chromatography; the results are shown in Fig. 1. The reaction was practically finished within 1 hr. The black precipitation did not show any absorption in the NaCl region of the IR spectrum, and it was easily dissolved in a dilute aqueous nitric acid solution, while some gas was evolved. The precipitate was found, by elementary analysis, to be metallic nickel, which has been partially oxidized by air during the separation. As is shown in Table 1, the mole ratio of the iodide ion to the total nickel[7] in the product ($[I^-]/[\text{Total Ni}]$), and that of methyl benzoate to the total nickel in the product ($[C_6H_5COOCH_3]/[\text{Total Ni}]$), are both approximately four. Practically no carbon monoxide was evolved during the carbonylation. From these results, we may conclude that all the carbon monoxide involved in nickel tetracarbonyl is consumed in the carbonylation of iodobenzene, as is represented by Eq. (2):

$$Ni(CO)_4 + 4C_6H_5I + 4CH_3OH + 4AcOK \longrightarrow Ni + 4C_6H_5COOCH_3 + 4AcOH + 4KI \qquad (2)$$

That the $[C_6H_5COOCH_3]/[\text{Total Ni}]$ ratio was smaller than 4 seems to be caused by the formation of smaller amounts of benzene and anisole. Neither free benzoic acid nor phenyl acetate could be detected.

Under a nitrogen atmosphere the carbonylation of iodobenzene took place smoothly, as has been described above; no carbonylation was, however, observed at all under a carbon monoxide atmosphere, and the solution remained colorless for at least 3 hr at 50°C, despite our expectation that the carbonylation might take place catalytically even under these mild conditions. This means that the reaction was completely inhibited by an atmospheric pressure of carbon monoxide. It was found that the carbonylation really started, even at room temperature (20°C), when a trace amount of carbon monoxide in the gas phase was removed by means of a nitrogen gas stream.

The IR absorption during the reaction with iodobenzene and with α-iodonaphthalene is shown in Figs. 2 and 3. As soon as the solution turned a reddish brown, four new bands are observed, at 1993, 1963,

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[7] "Total nickel" means the sum of the Ni^{2+} and the metallic nickl formed.

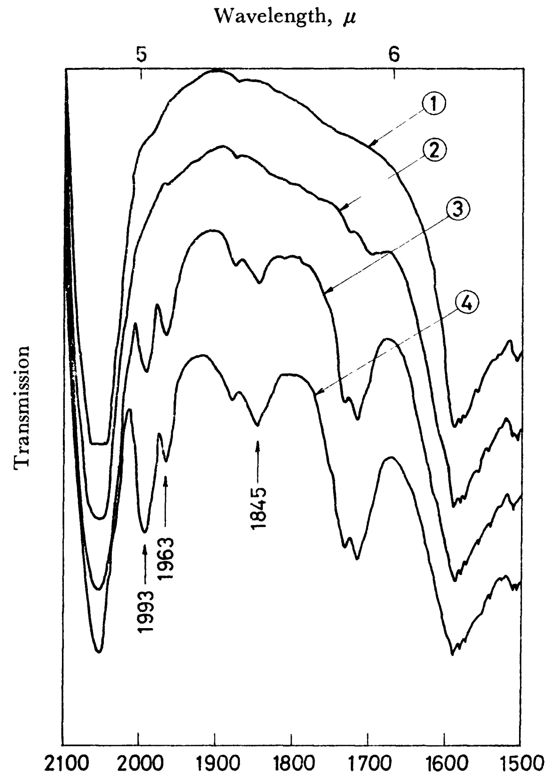

Fig. 2. IR absorption during the reaction of iodobenzene with nickel tetracarbonyl in methanol at 30—40°C under nitrogen.
① starting solution
②—④ during the reaction

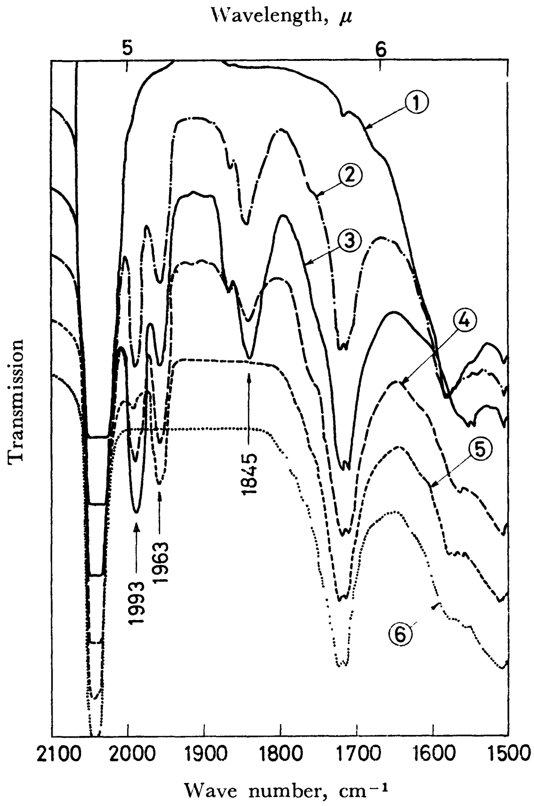

Fig. 3. IR absorption during the reaction of α-iodonaphthalene with nickel tetracarbonyl in methanol at 20—25°C under nitrogen.
① starting solution
②—⑤ during the reaction
⑥ after the reaction finished

1845, and about 1720 cm^{-1}, in the range of the CO stretching vibration. The last one consisted of two absorptions due to the methyl esters formed and acetic acid; these absorptions were checked by authentic samples. Figure 3 shows that the intensities of the former three absorptions gradually decrease with the consumption of α-iodonaphthalene in the carbonylation, and that they disappear when the reaction is almost finished. In fact, α-iodonaphthalene is more reactive than iodobenzene, resulting in an almost quantitative formation of α-methyl naphthoate under the reaction conditions cited in Fig. 3. It should be noticed here that the absorptions at 1993 and 1845 cm^{-1} disappear more rapidly than that at 1963 cm^{-1}.

Aryl bromides, such as bromobenzene, α-bromonaphthalene or *p*-bromoanisole, did not undergo carbonylation under even more forced conditions than those cited in Table 1, while both α- and ω-bromostyrene were much more reactive than aryl iodides; in the cases of α- and ω-bromostyrene, methyl α-phenyl acrylate, and methyl cinnamate were selectively formed respectively.[8] Most of the carbon monoxide involved in nickel tetracarbonyl was found to be also consumed in their carbonylations. These carbonylations too rapidly, even at room temperature, and they were accompanied by the formation of much potassium bromide precipitation; this prevented the taking of the IR absorption spectrum during their reactions. Such alkyl halides as ethyl-, *t*-butyl-, *n*-amyl-, *t*-amyl, and cyclohexyl halides, including iodides, were treated with $Ni(CO)_4$ by the same procedure; however, no carbonylation was observed, only dehalogenation products as the corresponding alcohols and methyl ethers from ethyl-, *t*-butyl-, *n*-amyl-, or *t*-amyl halides and cyclohexene from cyclohexyl halide. On the other hand, allyl halide reacted vigorously with $Ni(CO)_4$ in methanol, even at 0°C, to form methyl 3-butenoate, plus considerable amounts of such by-products as 1,5-hexadiene, methyl allyl ether, and diallyl ether. The amount of methyl 3-butenoate was also increased by adding potassium acetate, whereas only half the amount of the carbon monoxide involved in $Ni(CO)_4$ could be used for the carbonylation of allyl halide, where no inhibition by gaseous carbon monoxide was observed. In this respect, the carbonylation of aryl halide was quite different from that of allyl halide, which has been studied in detail by Guerrieri and Chiusoli.[3]

Discussion

It is known that nickel tetracarbonyl forms unstable substitution products with such relatively weak bases as pyridine in a methanol solution and that they are

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[8] α-Phenylacrylic acid and cinnamic acid, besides their esters, were isolated from the respective products.

present in solution in equilibrium[9] with such polynuclear carbonyl anion as $[Ni_2(CO)_6]^{2-}$, $[Ni_3(CO)_8]^{2-}$, *etc.*[10,11] In a strong basic solution, as in potassium hydroxide solution, $[Ni_2(CO)_6]^{2-}$ or $[Ni_3(CO)_8]^{2-}$ is preferably formed. If these nickel carbonyl anions were reactive species in the carbonylation of aryl halide, a stronger basic solution would be more favorable for the carbonylation. However, carbonylation takes place more readily in a weak basic solution, as in the presence of potassium acetate, than in a strong basic solution, though no interaction between $Ni(CO)_4$ and potassium acetate is observed in the absence of aryl iodide.

From the following considerations, it has been concluded that nickel tricarbonyl is an active species in the carbonylation.

The Inhibition by Carbon Monoxide. The fact that iodobenzene does not undergo carbonylation at all under an atmospheric pressure of carbon monoxide, as has been described in the preceding section, can be understood on the basis of the following scheme:

$$Ni(CO)_4 \underset{k_2}{\overset{k_1}{\rightleftarrows}} Ni(CO)_3 + CO \quad (k_1 \ll k_2) \tag{3}$$

$$Ni(CO)_3 + C_6H_5I \xrightarrow{k_3} (C_6H_5I)Ni(CO)_3 \quad (k_3 \ll k_2) \tag{4}$$

It is well known that the exchange reaction between $Ni(CO)_4$ and ^{14}CO proceeds *via* S_N1 $(k_2 \gg k_1)$ and that its rate is very large under a normal temperature and pressure (the half-value period of ^{14}CO radioactivity in the gas phase is less than 4 min in a toluene solution[9]). Accordingly, the coordination of iodobenzene to nickel tricarbonyl is in competition with the rapid recombination of carbon monoxide, where k_3 must be much smaller than k_2. The carbonylation starts practically when the former rate becomes larger than the latter. Accordingly, the lower the pressure of carbon monoxide, the more favorable for the coordination of iodobenzene to nickel tricarbonyl. It can be understood why no carbonylation is observed when $Ni(CO)_3(PPh_3)$ or $Ni(CO)_2(PPh_3)_2$ $(Ph=C_6H_5)$ is used instead of $Ni(CO)_4$, since the dissociation rates of carbon monoxide from these carbonyls are extremely small.[12]

IR Absorption Spectrum During the Course of Reaction. Figures 2 and 3 show that the IR absorptions at 1845, 1963, and 1993 cm^{-1} during the carbonylation of iodobenzene are identical with those observed during the reaction of α-iodonaphthalene. These absorptions can not be regarded as due to some acyl complex such as RCO-$Ni(CO)_nI$, nor due to some σ-complex such as R-$Ni(CO)_nI$ $(R=C_6H_5$ or α-$C_{10}H_7)$, because absorptions of acyl metal carbonyls are usually observed in the range between 1700—1750 cm^{-1}. If they correspond to aryl σ-complexes, the IR absorption of the phenyl σ-complex will probably be different from that of the naphthyl complex.

As was pointed out in the preceding section, the absorptions at 1993 and 1845 cm^{-1} disappear more quickly than that at 1963 cm^{-1}. This suggests that there are two kinds of intermediates present during the carbonylation. One has two absorptions, at 1993 and 1845 cm^{-1}, while the other has only one, at 1963 cm^{-1}. In the neutral binary carbonyls, the higher frequencies (2050—1900 cm^{-1}) are regarded as being due to terminal carbonyl groups, and the lower frequencies (1900—1800 cm^{-1}), as due to the bridging carbonyl groups, whose molar extinction coefficients are smaller than those of terminal carbonyls.[13] Accordingly, one of the intermediates can be ascribed to a binuclear nickel complex[14] with both bridging and terminal carbonyls, and the other, to a mononuclear nickel complex with only terminal carbonyls.

Reaction Path. From the considerations described above and the fact that all the carbon monoxide in $Ni(CO)_4$ are used for the carbonylation of aryl iodide, the reaction path can be represented as follows:

$$Ni(CO)_4 \rightleftarrows Ni(CO)_3 + CO \tag{3}$$

$$Ni(CO)_3 + RI \longrightarrow (RI)Ni(CO)_3 \tag{4}$$

$$(RI)Ni(CO)_3 + CH_3OH \longrightarrow (HI)Ni(CO)_2 + RCOOCH_3 \tag{5}$$

$$(HI)Ni(CO)_2 + AcOK \longrightarrow Ni(CO)_2 + AcOH + KI \tag{6}$$

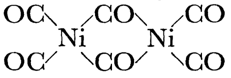
$$Ni(CO)_2 + Ni(CO)_4 \rightleftarrows Ni_2(CO)_6 \tag{7}$$

$$3Ni(CO)_2 \rightleftarrows Ni + Ni_2(CO)_6 \tag{7'}$$

$$Ni_2(CO)_6 \longrightarrow 2Ni(CO)_3 \tag{8}$$

$$(R=C_6H_5 \text{ or } \alpha\text{-}C_{10}H_7)$$

The reaction (5) proceeds rapidly, probably through steps analogous to those reported in the carbonylation using *cis*-$Rh(PPh_3)_2(CO)Cl$,[16] namely: $(C_6H_5I)Ni(CO)_3 \rightarrow C_6H_5\text{-}Ni(CO)_3I \rightarrow C_6H_5CO\text{-}Ni(CO)_2I \xrightarrow{+CH_3OH} (HI)Ni(CO)_2 + C_6H_5COOCH_3$. The reaction (6) means that the acetate anion effectively takes proton from $(HI)Ni(CO)_2$. In the absence of potassium acetate, $(HI)Ni(CO)_2$ will be rapidly decomposed and $Ni(CO)_3$ will not be supplied smoothly, with the result that practically no carbonylation is observed. The two intermediates expected from the IR absorptions observed during the carbonylation can be regarded as:



$(Ni_2(CO)_6)$ and $Ni(CO)_2$.[17] These

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[9] Namely: $3Ni(CO)_3Py + 3Py \rightleftarrows [NiPy_6][Ni_2(CO)_6] + 3CO$
$3Ni(CO)_2Py_2 \rightleftarrows [NiPy_6][Ni_2(CO)_6]$
$[NiPy_6][Ni_2(CO)_6] + Ni(CO)_3Py \rightleftarrows [NiPy_6][Ni_3(CO)_8] + Py + CO$

[10] F. Calderazzo, R. Ercoli, and G. Natta, "Organic Syntheses *via* Metal Carbonyls," Vol 1, ed. by I. Wender and P. Pino, Interscience Publishers, New York (1968), p. 67.

[11] W. Hieber, J. Ellermann, and E. Zahn, *Z. Naturforsch.*, *B*, **18**,. 589 (1963).

[12] F. Basolo and A. Wojcicki, *J. Amer. Chem. Soc.*, **83**, 520 (1961).

[13] E. W. Abel, *Quart. Rev.* (London), **17**, 133 (1963).

[14] The hexacarbonyldinickelate anion, $[Ni_2(CO)_6]^{2-}$, has four absorptions, at 1978, 1968, 1927, and 1870 cm^{-1}, in a potassium hydroxide methanol solution; these are all different from the absorptions observed during the carbonylation. This anion was prepared according to the method described in Ref. 15.

[15] W. Hieber, W. Kroder, and E. Zahn, *Z. Naturforsch.*, **B**, **15**, 325 (1960).

[16] J. Tsuji and K. Ohno, *Tetrahedron Lett.*, **1966**, 4713.

[17] The solvent molecule or iodide ion probably coordinates to these intermediates.

intermediates can be accumulated sufficiently to be observed by IR absorption when the reaction (8) (the regeneration of $Ni(CO)_3$) is rate-determining. The formation of a considerable amount of metallic nickel[18] can also be explained by the reaction (7′). The stoichiometric equation (2), showing that all the carbon monoxide involved in $Ni(CO)_4$ is used for the carbonylation of aryl iodide, can be derived by combining the reaction path described above.

The catalytic carbonylation of aryl bromide under high temperatures and pressures can be reasonably explained by this reaction path, with Br and H_2O replacing I and CH_3OH respectively. The catalytic carbonylation of α-bromonaphthalene with carbon monoxide and water in the presence of $Ni(CO)_4$ is highly promoted by adding a sufficient amount of potassium acetate, resulting in the quantitative formation of α-naphthoic acid, as has been reported in the preceding paper.[19] That is, its rate increasing with an increase in the amount of $Ni(CO)_4$ and also with that of potassium acetate, while it depends on neither the amounts of α-bromonaphthalene and water, nor on the pressure of carbon monoxide under 60—150 kg/cm^2 at 200°C, though the rate decreases with an increase in the pressure to more than 200 kg/cm^2. Lower pressures should favor the equilibria of the reactions (3) and (4) inclining much toward the right, and the rate of the reaction (5) must be sufficiently large at this temperature. Accordingly, the rate of carbonylation will be determined by either the reaction (6) or the regeneration of nickel tricarbonyl. In this catalytic reaction, nickel tricarbonyl must be regenerated, preferably by the coordination of carbon monoxide to the $Ni(CO)_2$ formed by the reaction (6) instead of that formed by the reactions (7) and (8). Since the carbonylation rate of α-bromonaphthalene under lower pressures is independent of the pressure of carbon monoxide, the reaction (6) must be rate-determining.

On the other hand, a different kinetics has been observed for the carbonylation of bromobenzene under pressures of more than 150 kg/cm^2 at 250°C, where the rate is proportional to the amounts of $Ni(CO)_4$, bromobenzene, water, and the reciprocal of the pressure of carbon monoxide, and is independent of the amount of potassium acetate when its amount is more than that of the bromobenzene used, as has been reported in a previous paper.[4] In this case, bromobenzene is less reactive than α-bromonaphthalene and the catalyst must be present predominantly in the form of $Ni(CO)_4$ because of the high pressures of carbon monoxide. The carbonylation rate of bromobenzene can, accordingly, be explained by the same reaction path, assuming that the reactions (3) and (4) are in equilibrium and that (5) is rate-determining.

From the above discussion, it can be concluded that nickel tricarbonyl is the active species in the carbonylation of aryl halide with nickel tetracarbonyl in the presence of potassium acetate in methanol, and that the course of its catalytic reaction can reasonably be explained by the reaction path derived from the stoichiometric reaction.

Experimental

Materials. The iodobenzene and *trans*-ω-bromostyrene were commercial products. They were distilled before use. Iodobenzene especially was carefully purified by fractional distillation (Podbielniak 4500; glass concentric-tube column), because a trace amount of nitrobenzene strongly inhibited the carbonylation of iodobenzene. The *trans*-ω-bromostyrene might contain a small amount of *cis*-ω-bromostyrene, which was difficult to separate by distillation. The α-iodonaphthalene was freshly prepared by the iodination of naphthalene using $AgClO_4$, according to the method described in the literature.[20] The α-bromostyrene was prepared by drawing out hydrobromic acid with a potassium hydroxide ethanol solution from the α,ω-dibromoethylbenzene obtained by the bromination of styrene.[21] All these substances were purified by distillation under a vacuum. The nickel tetracarbonyl, potassium acetate, and other compounds employed in this study were obtained from commercial sources.

Carbonylation of Iodobenzene. A methanol solution of iodobenzene and potasssium acetate was placed in a two-necked flask (100 m*l* in vol.) equipped with a reflux condenser. A given amount of distilled nickel tetracarbonyl was condensed into the flask, which had been cooled by immersing it in solid carbon dioxide - methanol; then the flask was warmed up to 50°C while being vigorously stirred under an atmospheric pressure of nitrogen, with the temperature being kept constant. After 2 hr, the residual nickel tetracarbonyl was completely evacuated; then the solution was filtered to separate a black precipitate (metallic nickel). Sufficient amounts of ether and water were added to the filtrate to extract and separate organic compounds from the Ni^{2+} and I^- formed. The amounts of methyl benzoate and iodobenzene in the ether solution were determined by gas chromatography. The black precipitate was dissolved in aqueous nitric acid; its quantity was determined by the ordinary EDTA method. These results are summarized in Table 1.

Carbonylation of α-Iodonaphthalene. The reaction of α-iodonaphthalene (0.023 mol) with $Ni(CO)_4$ (0.0056 mol) was carried out at 30°C for 6 hr in methanol(2.0 mol) containing potassium acetate (0.023 mol) under an atmospheric pressure of nitrogen. By treating the product according to the same procedure described above, I^- (0.0177 mol) and total nickel (0.0049 mol; metallic nickel 0.0017 mol and Ni^{2+} 0.0032 mol) were separated from the organic compounds, where $[I^-]/[\text{Total Ni}]$ was 3.64. The amount of α-methylnaphthoate could be estimated from the amount of I^- formed, because no other organic compounds, such as naphthalene or ketones, were detected.

Carbonylation of Bromostyrene. Under the same reaction conditions and using the same procedure as those used for iodobenzene, ω-bromostyrene (0.046 mol) reacted with $Ni(CO)_4$ (0.012 mol) in methanol (2.0 mol) containing potassium acetate (0.046 mol) to give methyl cinnamate and cinnamic acid. In this case, the amounts of Br^- and Ni^{2+} were 0.046 mol and 0.0095 mol respectively. From an ethereal

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[18] The Ni^{2+} ion is presumably formed by the reaction of metallic nickel with the acetic acid formed, namely: $Ni + 2\,AcOH \rightarrow Ni(AcO)_2 + H_2\uparrow$.

[19] M. Nakayama and T. Mizoroki, This Bulletin, **43**, 569 (1970).

[20] L. Birckenbach and J. Goubeau, *Ber.*, **65**, 395 (1932).

[21] F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, **1928**, 1801.

solution, free cinnamic acid (0.0054 mol) beside its ester (0.0271 mol) were isolated, though no free carboxylic acid was isolated from the carbonylation product of iodobenzene or α-iodonaphthalene. α-Bromostyrene (0.046 mol) also gave methyl α-phenyl acrylate and α-phenylacrylic acid (atropic acid) (Found: C, 72.6; H, 5.4%. Calcd for $C_9H_8O_2$: C, 73.0; H, 5.4%. mp 108—9°C), and a small amount of styrene (0.0059 mol) was observed on their gas chromatograms. The total amount of α-phenylacrylic acid formed could be estimated from that of Br^- (0.0441 mol).

Analytical Procedure. Most of the organic compounds were quantitatively determined by gas chromatography. A 1.5-m stainless steel column (3 mmϕ) with silicone DC 11 was used at a temperature of 160 or 190°C, with a hydrogen carrier and a gas-flow rate of 40 m*l*/min. In this procedure, naphthalene was used as the internal standard for determining the amounts of iodobenzene and methyl benzoate, and α-bromonaphthalene was used for bromostyrene and their corresponding esters. Free carboxylic acids (cinnamic acid and α-phenylacrylic acid) were precipitated by adding an aqueous hydrochloric acid solution to their potassium salts, and their amounts were titrated with an aqueous potassium hydroxide solution. The compounds were identified by means of the IR absorption spectrum, the melting points, a comparison of their gas chromatograms with those of authentic samples, or the results of elementary analysis, if necessary. The halide ion (Br^- or I^-) and the nickel(II) ion were determined by the Volhard and EDTA methods respectively.

IR Absorption Spectra during the Carbonylation. To record the IR absorption spectrum during the course of the reaction with iodobenzene or α-iodonaphthalene, the carbon monoxide present in the gas phase had been excluded by a nitrogen-gas stream before the reaction was carried out at room temperature. A part of the solution was drawn out from the vessel about once an hour by means of a small cylinder and put into a KRS-5 cell under nitrogen in order to record the variation in the IR absorption spectra during the carbonylation.

The authors wish to acknowledge the enthusiastic assistance of Mr. Masao Ichinose in carrying out this work.