

## NICKEL-CATALYZED CARBONYLATION OF AROMATIC HALIDES AT ATMOSPHERIC PRESSURE OF CARBON MONOXIDE

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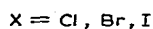
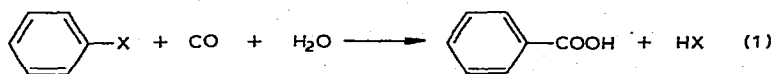
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### SUMMARY

The nickel-catalysed carbonylation of aromatic halides in dipolar aprotic solvents under one atmosphere of carbon monoxide is reported. Aromatic acids are obtained in high yield. The influence of substituents on the aromatic nucleus and of the halide as leaving group on the rate of carbonylation is studied. A possible mechanism for the carbonylation process is discussed. Chloride and bromide ions play an important role in the formation of the catalytic species, which are probably anionic nickel carbonyl complexes.

### INTRODUCTION

The synthesis of aromatic acid derivatives via carbonylation of aromatic halides catalyzed by transition metal compounds has been known<sup>1</sup> since 1927.



Nickel complexes have been shown<sup>2,3</sup> to be the most effective catalysts, although extreme conditions of reaction temperature (200–350°) and pressure (100–300 atm) are required. Only for aromatic iodides does the reaction occur under mild conditions<sup>4</sup>.

In general the carbonylation of aromatic halides occurs<sup>5</sup> more readily in the presence of a base, and it has been suggested<sup>6</sup> that the function of the base is to neutralize the hydrogen halide produced in the reaction. Recently Corey and Hegedus<sup>7</sup> have indicated that the carbonylation of vinyl halides<sup>8</sup> and aromatic iodides is facilitated by the presence of sodium methoxide or potassium tert-butoxide, and have suggested that nickel carbonyl electropositive anionic species are responsible for this carbonylation.

We have found that it is possible to carbonylate aromatic halides at atmospheric pressure of carbon monoxide. In this paper we report an extensive study of this reaction, and describe the most favourable conditions for the formation of the active nickel-containing species which catalyze the carbonylation of aromatic halides.

## RESULTS

The present investigation has shown that in polar aprotic solvents such as dimethylsulphoxide, *N*-dimethylformamide, hexamethylphosphoric triamide, *N*-methylpyrrolidone, and *N*-methylformamide, and in the presence of a base such as calcium hydroxide, the carbonylation of aromatic halides occurs at atmospheric pressure of carbon monoxide and at temperatures as low as 100°. For example 1-chloronaphthalene is transformed into the calcium salt of naphthoic acid [eqn. (2)].

Small quantities of naphthalene (< 5%), derived from reduction of the carbon-halogen bond are also formed [eqn. (3)].

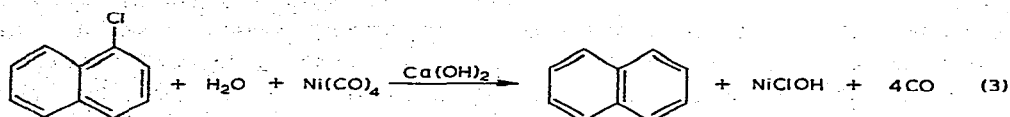
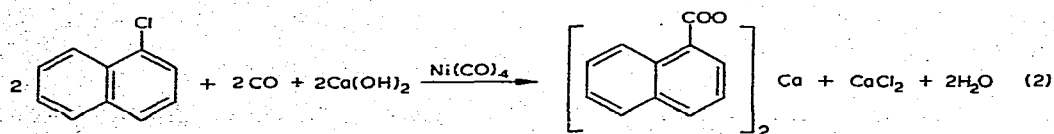


TABLE 1

CARBOXYLATION OF 1-CHLORONAPHTHALENE TO THE CALCIUM SALT OF 1-NAPHTHOIC ACID<sup>a</sup>

Solvent	Temp. (°C)	Time (h)	Naphthoic acid calcium salt Yield <sup>b</sup> (%)
Dimethylsulphoxide	110-112	8	90
<i>N,N</i> -dimethylformamide	110-112	6	95
<i>N</i> -methylformamide	110-112	8	12 <sup>c</sup>
Formamide	110-112	6	<sup>d</sup>
<i>N,N</i> -dimethylacetamide	110-112	8	90
<i>N</i> -Methylpyrrolidone	110-112	6	90
Hexamethylphosphoramide	110-112	8	71
Propylene carbonate	110-112	6	<sup>d</sup>

<sup>a</sup> Solvent, 40 ml; Ca(OH)<sub>2</sub>, 3.0 g; Ni(CO)<sub>4</sub>, 1.5 ml; 1-chloronaphthalene, 7.5 g (see Experimental section).

<sup>b</sup> Yields are based upon the halide used and are of isolated naphthoic acid. <sup>c</sup> 31% of naphthoic acid *N*-methylamide was also formed. <sup>d</sup> Tetracarbonyl nickel decomposed.

The results of carbonylation of 1-chloronaphthalene to the calcium salt of naphthoic acid in various solvents are shown in Table 1. The carbonylation product is obtained in high yield, as shown in Table 2.

We have also examined the effect of substituents in the aromatic nucleus on the rate of carbonylation. The rates relative to bromobenzene are compared in Table 3.

TABLE 2

CARBONYLATION OF AROMATIC HALIDES IN DIMETHYLFORMAMIDE<sup>a</sup>

Aromatic halide	Temp. (°C)	Time (h)	Product yield <sup>b</sup> (%)
1-Chloronaphthalene	110-112	6	1-Naphthoic acid 95 <sup>c</sup>
2-Chloronaphthalene	110-112	8	2-Naphthoic acid 97 <sup>d</sup>
Bromobenzene	100-102	8	Benzoic acid 88
<i>o</i> -Bromotoluene	100-102	8	<i>o</i> -Toluic acid 94
<i>p</i> -Bromotoluene	100-102	14	<i>p</i> -Toluic acid 97
<i>o</i> -Bromoanisole	100-102	8	<i>o</i> -Anisic acid 80
<i>m</i> -Bromoanisole	100-102	8	<i>m</i> -Anisic acid 83
<i>p</i> -Bromoanisole	100-102	13	<i>p</i> -Anisic acid 85
<i>p</i> -Bromobenzonitrile	100-102	3	<i>p</i> -Cyanobenzoic acid 80 <sup>e</sup>
<i>o</i> -Chlorobromobenzene	100-102	8	<i>o</i> -Chlorobenzoic acid 87 <sup>f</sup>
<i>m</i> -Chlorobromobenzene	100-102	5	<i>m</i> -Chlorobenzoic acid 88
<i>p</i> -Chlorobromobenzene	100-102	5	<i>p</i> -Chlorobenzoic acid 85

<sup>a</sup> DMF 40 ml; Ca(OH)<sub>2</sub> 3.0 g; Ni(CO)<sub>4</sub> 1.5 ml; Ratio Ni(CO)<sub>4</sub>/halide 1/4 (see experimental section).

<sup>b</sup> Yields are based upon the halide used, and are of isolated products. <sup>c</sup> Naphthalene 5%. <sup>d</sup> Naphthalene 3%. <sup>e</sup> Benzonitrile 16%. <sup>f</sup> Chlorobenzene 10%. <sup>g</sup> Yields determined by gas chromatography.

The rates were measured with dimethylsulphoxide as solvent, under the conditions shown in Table 3. Equimolar quantities of the reference halide (*e.g.* bromobenzene) and the halide whose reactivity was to be established were mixed and carbonylated. This is the simplest way to determine the difference of carbonylation rate of the two halides<sup>9</sup>, all the other conditions being common to the two halides. The reaction was stopped at a low degree of conversion, and the resulting aromatic acids were esterified with diazomethane and analyzed by GC. It is necessary to stop the reaction at a low degree of conversion to avoid a change in the concentration of the two halides, especially when the difference in reactivity between the two halides is large.

Under the conditions used to determine the relative rates, the reactions are first order in the aromatic halide, as shown by the data in Table 4. Moreover, it is evident that the carbonylation is a substitutive one, the carboxy group being always found on the carbon originally bound to the halogen. The relative rates obtained for the various *para* and *meta* substituents correlate with the  $\sigma$  of Hammett (Fig. 1). The  $\rho$  value (2.7) is large and positive.

Following the carbonylation of a single halide one can observe that the reaction exhibits autocatalytic behaviour, as clearly illustrated by the rate plots for acid forma-

TABLE 3

RELATIVE RATES OF CARBONYLATION OF AROMATIC HALIDES IN DIMETHYLSULPHOXIDE AT 105°<sup>a</sup>

R	X	Relative Rate $v_{(ArX)}/v_{(C_6H_5Br)}$
H	Br	1
<i>p</i> -OCH <sub>3</sub>	Br	0.4
<i>p</i> -NHCOCH <sub>3</sub>	Br	0.4
<i>p</i> -CH <sub>3</sub>	Br	0.5
<i>p</i> -CH=CH <sub>2</sub>	Br	1.5
<i>p</i> -Cl	Br	3.4
<i>p</i> -COCH <sub>3</sub>	Br	35.0
<i>p</i> -CN	Br	108.0
<i>m</i> -CH=CH <sub>2</sub>	Br	0.9
<i>m</i> -CH <sub>3</sub>	Br	0.9
<i>m</i> -Cl	Br	5.3
<i>m</i> -CN	Br	30.0
<i>o</i> -OCH <sub>3</sub>	Br	0.8
<i>o</i> -CH <sub>3</sub>	Br	1.3
<i>o</i> -(CH) <sub>4</sub>	Br	21.0
<i>o</i> -Cl	Br	1.2
<i>o</i> -NHCOCH <sub>3</sub>	Br	5.3
2,4,6-CH <sub>3</sub>	Br	0.03
H	Cl	0.002
<i>p</i> -CN	Cl	0.3
<i>o</i> -(CH) <sub>4</sub>	Cl	0.054
H	F	0.0001
H	I	650.0

<sup>a</sup> Reaction conditions are reported in the experimental section.

TABLE 4

RELATIVE RATES OF CARBONYLATION OF AROMATIC HALIDES; INFLUENCE OF THE CONCENTRATION OF THE AROMATIC HALIDE<sup>a</sup>

Bromobenzene (moles/l) C <sub>6</sub> H <sub>5</sub> Br	Aromatic halide (moles/l) ArX	Relative Rate $v_{(ArX)}/v_{(C_6H_5Br)}$
0.2	<i>p</i> -Bromoanisole 0.2	0.4
0.2	<i>p</i> -Bromoanisole 0.4	0.9
0.2	<i>p</i> -Bromoanisole 0.8	1.8
0.2	<i>p</i> -Bromoanisole 1.6	3.5
0.2	<i>p</i> -Bromoacetophenone 0.2	35.0
0.4	<i>p</i> -Bromoacetophenone 0.2	18.0
0.8	<i>p</i> -Bromoacetophenone 0.2	9.0

<sup>a</sup> Reaction conditions are reported in the experimental section.

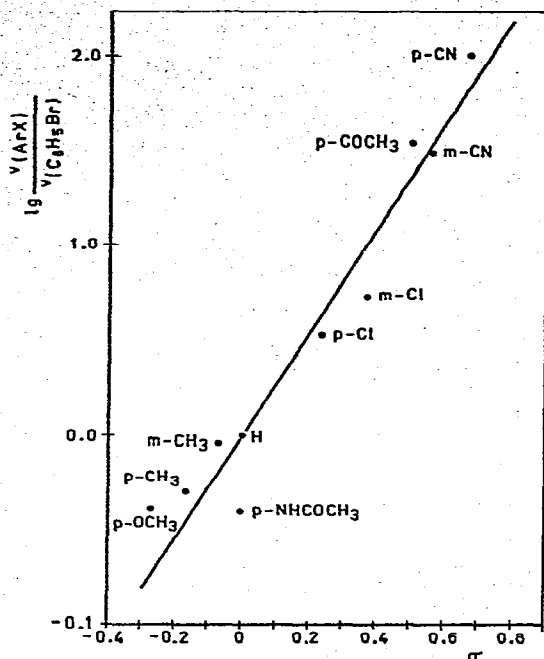


Fig. 1. Correlation of relative rates of carbonylation of substituted aromatic halides with  $\sigma$  constants<sup>27</sup>  $\rho = 2.7$  ( $r = 0.968$ ).

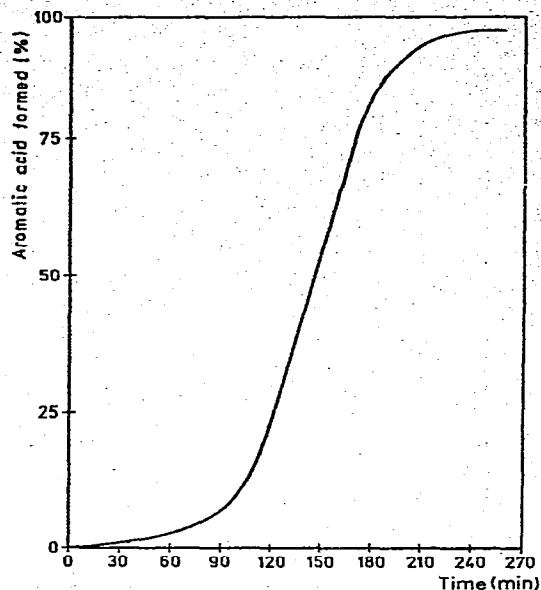


Fig. 2. Carbonylation of bromobenzene in DMSO; temp.  $105^\circ$ ;  $\text{Ni}(\text{CO})_4$  0.17 moles/l; bromobenzene 0.3 moles/l;  $\text{Ca}(\text{OH})_2$  0.4 moles/l; CO 1 atm.

tion from bromobenzene and 1-chloronaphthalene in Figs. 2 and 3.

To establish whether some of the products formed during the carbonylation were responsible for the autocatalytic behaviour, we examined the effect of adding the calcium salt of the aromatic acid as well as other inorganic salts. The results of these studies are depicted in Fig. 4. The presence of iodide ions has a deactivating effect, whereas chloride and bromide ions have a strong activating effect ( $\text{Cl}^- > \text{Br}^-$ ). The nature of the cation does not influence the reaction, identical results being obtained using salts of a given anion with different cations. A salt effect is excluded by the observation that benzoate, perchlorate and fluoride have very little effect on the rate.

In the presence of added chloride ion, the carbonylation of bromobenzene shows pseudo-first order kinetic behaviour with respect to the aromatic halide; the induction period is completely removed, as shown in Fig. 5 and Table 5. The rate of carbonylation increases with increasing the concentration of chloride ions and tetracarbonylnickel (Table 6).

In all of the reactions described so far calcium hydroxide was present as the base component. Calcium hydroxide is not completely soluble in the reaction mixture, and we have noted that an excess of calcium hydroxide does not influence the rate of the reaction. Moreover the rate of disappearance of the organic halides is not influenced by calcium hydroxide when chloride ions are added (Table 6). This means that the

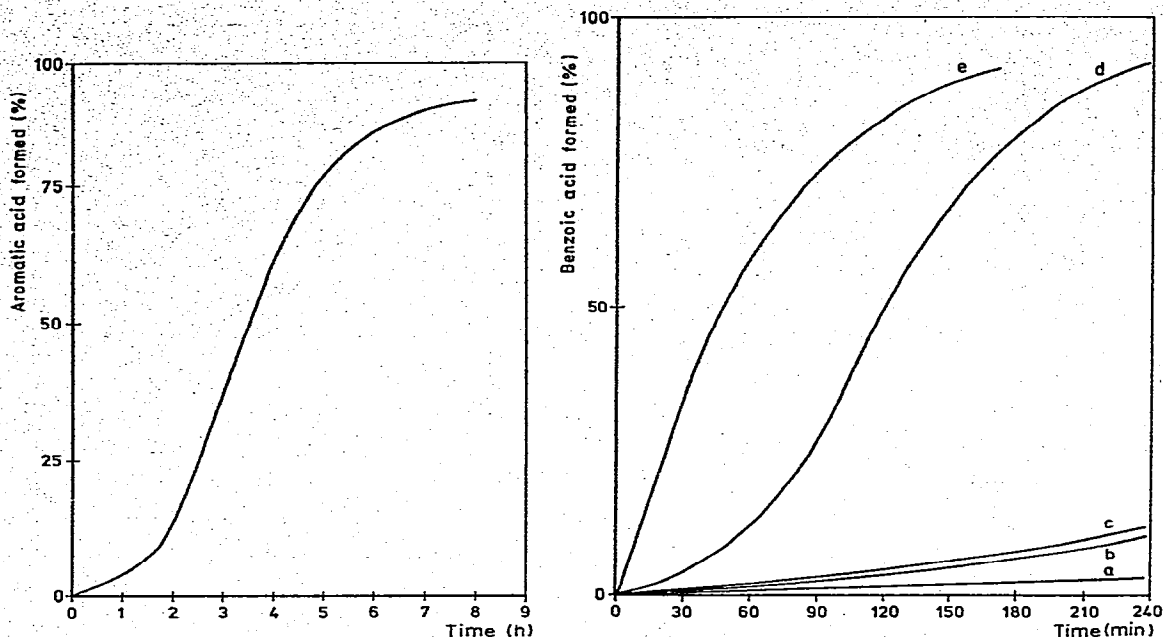


Fig. 3. Carbonylation of 1-chloronaphthalene in DMSO; temp.  $110^{\circ}$ ;  $\text{Ni}(\text{CO})_4$  0.25 moles/l; 1-chloronaphthalene 1.0 moles/l;  $\text{Ca}(\text{OH})_2$  1.0 moles/l; CO 1 atm.

Fig. 4. Carbonylation of bromobenzene in the presence of salts. Solvent = DMSO/ $\text{H}_2\text{O}$  (95/5); temp.  $96^{\circ}$ ;  $\text{Ni}(\text{CO})_4$  0.17 moles/l;  $\text{Ca}(\text{OH})_2$  0.20 moles/l; bromobenzene 0.20 moles/l; a)  $\text{N}(\text{C}_4\text{H}_9)_4\text{I}$  or  $\text{NaI}$ : 0.23 moles/l; b) no salt or  $\text{LiF}$ : 0.23 moles/l; c)  $(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$  or  $\text{Ca}(\text{ClO}_4)_2$ : 0.11 moles/l;  $\text{N}(\text{C}_4\text{H}_9)_4\text{ClO}_4$ : 0.23 moles/l; d)  $\text{N}(\text{C}_4\text{H}_9)_4\text{Br}$ ; 0.23 moles/l; e)  $\text{N}(\text{C}_4\text{H}_9)_4\text{Cl}$  or  $[(\text{CH}_3)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{N}]\text{Cl}$ : 0.23 moles/l; CO 1 atm.

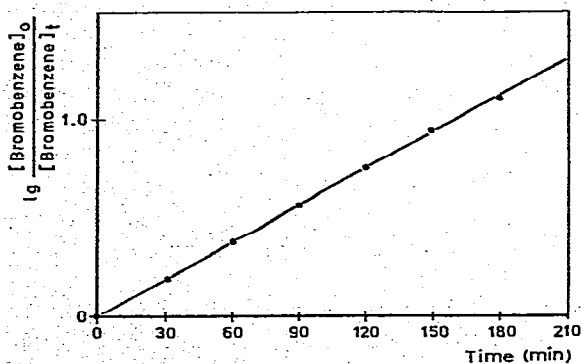


Fig. 5. Carbonylation of bromobenzene in the presence of chloride ions; temp.  $96^{\circ}$ ;  $[(\text{CH}_3)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{N}]\text{Cl}$  0.23 moles/l;  $\text{Ni}(\text{CO})_4$  0.17 moles/l; bromobenzene 0.20 moles/l;  $\text{Ca}(\text{OH})_2$  0.4 moles/l; CO 1 atm. Solvent: DMSO/ $\text{H}_2\text{O}$  (95/5).

reaction can be carried out even in the absence of calcium hydroxide. In this case, however, a mixture of aromatic acid and aromatic hydrocarbon results (benzoic acid/benzene 40/60). In the absence of both base and added halide ions no reaction is observed under the same conditions. The use of strong bases such as sodium or

TABLE 5

CARBONYLATION OF BROMOBENZENE IN THE PRESENCE OF CHLORIDE ION<sup>a</sup>

Bromobenzene (moles/l)	$K_{\text{obs.}} (\text{sec}^{-1})$
0.05	$2.3 \times 10^{-4}$
0.11	$2.1 \times 10^{-4}$
0.16	$2.1 \times 10^{-4}$
0.20	$2.1 \times 10^{-4}$

<sup>a</sup> Temp. 96°;  $[(\text{CH}_3)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{N}]\text{Cl}$ , 0.23 moles/l;  $\text{Ni}(\text{CO})_4$ , 0.17 moles/l; Solvent: DMSO/ $\text{H}_2\text{O}$  95/5;  $\text{Ca}(\text{OH})_2$ , 0.4 moles/l;  $\text{CO}$ , 1 atm; see Experimental section.

TABLE 6

REACTIONS OF BROMOBENZENE<sup>a</sup> WITH  $\text{Ni}(\text{CO})_4$  IN THE PRESENCE OF BASES AND CHLORIDE ION UNDER ONE ATMOSPHERE OF CO

$[\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}]\text{Cl}$ (moles/l)	Base (moles/l)	$\text{Ni}(\text{CO})_4$ (moles/l)	Temp. (°C)	$K_{\text{obs.}} (\text{sec}^{-1})$ ( $\times 10^4$ )
0.1	$\text{Ca}(\text{OH})_2$ 0.3	0.17	104.5	3.7
0.15	$\text{Ca}(\text{OH})_2$ 0.3	0.17	104.5	10
0.20	$\text{Ca}(\text{OH})_2$ 0.3	0.17	104.5	23
0.40	$\text{Ca}(\text{OH})_2$ 0.3	0.17	104.5	28
0.80	$\text{Ca}(\text{OH})_2$ 0.3	0.17	104.5	30
0.15		0.17	104.5	9 <sup>b</sup>
0.23	$\text{Ca}(\text{OH})_2$ 0.3	0.085	104.5	3.8
0.23	$\text{Ca}(\text{OH})_2$ 0.3	0.250	104.5	28
	$\text{NaOH}$ 0.3	0.17	104.5	21 <sup>c</sup>
0.20	$\text{NaOH}$ 0.3	0.17	104.5	20 <sup>c</sup>

<sup>a</sup> The concentration of bromobenzene is 0.05 mole/l. <sup>b</sup> Benzene 60% and benzoic acid 40% are formed.

<sup>c</sup> Benzene (>95%) is obtained.  $\text{HCOONa}$  is slowly formed. Solvent: DMSO/ $\text{H}_2\text{O}$  95/5.

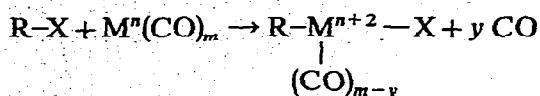
potassium hydroxide causes a change in the reaction products, leading to preferential formation of hydrocarbons. Under these conditions the addition of halide ions has no effect on the reaction rate (Table 6).

From the preparative point of view it is important to mention that in the carbonylation of bromobenzene to benzoic acid we have obtained about 15 moles of acid per mole of tetracarbonylnickel introduced. It is relevant to note that tetracarbonylnickel can be prepared *in situ* by reducing<sup>10</sup>  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with a manganese/iron alloy in the presence of a small quantity of  $\text{Na}_2\text{S}$ .

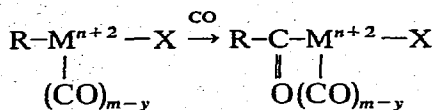
## DISCUSSION

The probable mechanistic scheme for carbonylation of aromatic halides (as well as of organic halides in general), involves several processes which are well established in organometallic chemistry.

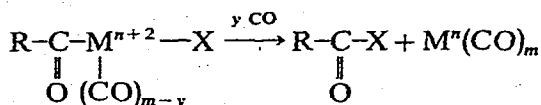
(1). *Oxidative addition*<sup>11</sup>:



(2). *Carbon monoxide insertion*<sup>12</sup>:



(3). *Reductive elimination*<sup>13</sup>:



For the catalytic carbonylation of organic halides using tetracarbonylnickel, it is likely that, in general, the difficult step is the oxidative addition, since alkyl or aryl nickel complexes are very reactive<sup>8,14</sup>, and undergo insertion, coupling and hydrogen substitution.

The data in Table 3 permit comparison of the effect of different halides as leaving groups on the reaction rate. The reactivity decreases in the following order: I > Br > Cl > F. This order correlates qualitatively with the carbon-halogen bond energies, suggesting that the dissociation of this bond is involved in the rate determining step. These differences of reactivity of various halides are characteristic of oxidative-addition reactions of organic halides with transition metal complexes such as those of Co<sup>115</sup>, Co<sup>116</sup>. These considerations strongly indicate that the oxidative addition is the rate determining step of the carbonylation. Moreover the reported effect of the substituents in the aromatic ring on the reaction rate (Fig. 1) suggests that the nickel species which gives the oxidative addition, has a nucleophilic character<sup>17</sup>. A qualitatively similar order of reactivity has been found for the oxidative addition of aromatic halides to Pd[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub><sup>18</sup> and to Ni[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>C<sub>2</sub>H<sub>4</sub><sup>19</sup>, both with respect to the substituents and to the halide as leaving group. The oxidative addition could probably occur by a two-step mechanism, analogous to the aromatic S<sub>N</sub>2 mechanism, involving a metastable intermediate. However we cannot exclude other mechanisms such as a one step mechanism<sup>20</sup>, an halogen abstraction mechanism<sup>16</sup>, or an electron transfer mechanism<sup>21</sup>.

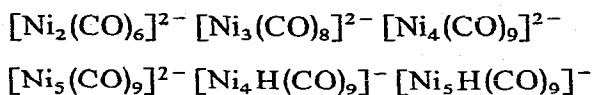
The enhancing effect of chloride and bromide ions explains the autocatalytic behaviour, these ions being formed during the carbonylation process. Moreover the fact that the reaction shows to depend on the first power of the concentration of the aromatic halide (Tables 3 and 4), while the kinetic profile of the reaction is autocatalytic, reveals that the effect of the halide ions operates in the formation of the active nickel species.

As to the action of the base present in the reaction medium one effect is to neutralize the acidity formed during the carbonylation. The formation of a mixture of the aromatic hydrocarbon and of the aromatic acid, when the carbonylation is carried out only in the presence of chloride ions, can be attributed to cleavage of the

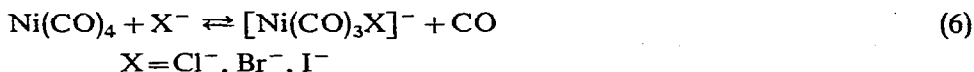


intermediate aryl-nickel complex by the halogenhydride acid formed during the carbonylation reaction. However, the neutralization is not the only function of the base, which is also able to induce the carbonylation reaction [ $\text{Ca}(\text{OH})_2$ ] or the hydrogenation to aromatic hydrocarbon ( $\text{NaOH}$ ).

It is known that tetracarbonylnickel, in the presence of bases, is transformed into anionic complexes (nickelates)<sup>22</sup>, and that different species are obtained depending on the basicity of the system:



However, the chemistry of these anionic complexes is not well characterized and is complicated by equilibria between the different species. Moreover very few spectroscopic data for the isolated nickelates are available. As to the effect of halide ions it is known that  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  react with tetracarbonylnickel to give halogenotricarbonylnickel anions<sup>23</sup> [eqn. (6)].



We can exclude the possibility that these anions are the effective catalysts because iodide ion, which reacts with  $\text{Ni}(\text{CO})_4$  more readily<sup>23</sup> than bromide and chloride, has a deactivating effect on the carbonylation. Furthermore it has been observed that halogenotricarbonylnickel anions are unstable, and can give anionic complexes such as nickelates among their decomposition products. The stability of  $[\text{Ni}(\text{CO})_3\text{X}]^-$  increases in the following order:  $\text{X} = \text{Cl} < \text{Br} < \text{I}$ , however, and it is this which gives rise to the different behaviour of the halides in the carbonylation. To support our hypothesis that anionic nickel complexes are the active species, we prepared a nickelate  $[\text{Ni}_3(\text{CO})_8]^{2-}$  by the method of Sternberg and coworkers and isolated it as tetrabutylammonium salt<sup>24</sup> [ $\text{IR C}=\text{O}$ : 1970 vs, 1915 s, 1780 s  $\text{cm}^{-1}$ ]. In the absence of base and of added halide ions, but otherwise under the same conditions as those previously described, this complex carbonylates bromobenzene to benzoic acid. During the carbonylation the solution containing the nickelate changes from red to colourless, indicating that the nickelate has completely reacted.

A comparison between the relative rates of carbonylation of some aromatic halides using the nickelate and the  $\text{Ni}(\text{CO})_4/\text{Ca}(\text{OH})_2$  mixture is reported in Table 7. The excellent correlation between the two systems supports the suggestion that nickelates are involved in the catalytic carbonylation of aromatic halides. As to the substitutive hydrogenation observed in the presence of strong bases ( $\text{NaOH}$ ) we suggest that under these conditions the active species is a nickelate able to give the oxidative addition but not the carbon monoxide insertion. In this case, then, the intermediate  $\sigma$  nickel-aryl bond is preferentially hydrogenolysed. The enhancement of reactivity by polar aprotic solvents<sup>25</sup> can also be accounted for if anionic species are postulated as the catalysts, since these may be weakly coordinated in these solvents. However it is possible that the solvent also has other effects, such as facilitating the interaction between halide ions and tetracarbonylnickel and stabilizing the reactive anionic species.

TABLE 7

RELATIVE RATES OF CARBONYLATION OF AROMATIC HALIDES IN DIMETHYL-SULPHOXIDE AT 105°<sup>a</sup>

Aromatic halide	$v_{ArX}/v_{C_6H_5Br}$	
	$(Ni(CO)_4/Ca(OH)_2)$	$[Ni_3(CO)_8]^{2-}$
<i>p</i> -Bromoanisole	0.4	0.4
<i>p</i> -Bromotoluene	0.5	0.5
Bromobenzene	1.0	1.0
<i>p</i> -Bromochlorobenzene	3.4	3.2
<i>o</i> -Bromoanisole	0.75	0.65

<sup>a</sup> Reaction conditions are described in the experimental section.

## EXPERIMENTAL

*Materials*

All reagents were commercially available and used without further purification. Ni(CO)<sub>4</sub> was prepared by the procedure of Chiusoli and Mondelli<sup>26</sup>.

*Gas chromatography*

Samples were analyzed on a 3 m diethylenglycol succinate on Chromosorb column. Known samples of the products were commercially available.

*General procedure for carbonylation of aromatic halides (Tables 1 and 2)*

Solvent 40 ml, Ca(OH)<sub>2</sub> 3.0 g, Ni(CO)<sub>4</sub> 1.5 ml and the organic halide 47 mmol were placed in a 100 ml round bottomed flask equipped with mechanical stirrer. A water cooled condenser was attached to the flask, and the condenser connected to a buret containing the carbon monoxide. The mixture was stirred at the temperature reported in Tables 1 and 2 for the required length of time, and then cooled, and the Ni(CO)<sub>4</sub> was eliminated by passing a stream of nitrogen. The mixture was then poured in 200 ml of water containing 10 ml of conc. HCl. The organic products were extracted with diethyl ether (3 × 50 ml) and the ether solution extracted with an aqueous solution of sodium bicarbonate. The alkaline extract was then acidified and the aromatic acid extracted with diethyl ether (or CHCl<sub>3</sub>). The ether extract, dried with Na<sub>2</sub>SO<sub>4</sub>, was evaporated under reduced pressure to give the pure aromatic acid.

*General procedure for the determination of the relative rates of carbonylation (Tables 3 and 4)*

Dimethylsulphoxide 25 ml, Ni(CO)<sub>4</sub> 1.0 ml, Ca(OH)<sub>2</sub> 1.5 g and 5 mmol each of two aromatic halides were placed in a 50 ml round bottomed flask containing a magnetic stirring bar. A water cooled condenser was attached to the flask and the condenser connected to a buret containing the carbon monoxide. The mixture was warmed at 105° for about 15 min. (A shorter time was used for the more reactive halide). The mixture was then partitioned between 1 N hydrochloric acid solution and ether, and the aqueous solution extracted with ether (3 × 20 ml). The ether was

extracted with an aqueous solution of  $\text{NaHCO}_3$ . The alkaline solution was acidified with aqueous  $\text{HCl}$  and extracted with diethyl ether ( $3 \times 25$  ml). The organic extract was dried, concentrated, treated with diazomethane, and analysed by gaschromatography.

The following couples were tested:

Bromobenzene/ <i>p</i> -bromoanisole	Bromobenzene/ <i>o</i> -bromoanisole
Bromobenzene/ <i>p</i> -bromoacetanilide	Bromobenzene/ <i>o</i> -bromotoluene
Bromobenzene/ <i>p</i> -bromotoluene	Bromobenzene/1-bromonaphthalene
Bromobenzene/ <i>p</i> -bromostyrene	Bromobenzene/ <i>o</i> -bromoacetanilide
Bromobenzene/ <i>p</i> -bromochlorobenzene	Bromobenzene/2,4,6-trimethylbromobenzene
Bromobenzene/ <i>p</i> -bromoacetophenone	Bromotoluene/chlorobenzene
Bromobenzene/ <i>p</i> -bromobenzonitrile	Bromobenzene/ <i>p</i> -chlorobenzonitrile
Bromobenzene/ <i>m</i> -bromostyrene	Bromobenzene/1-chloronaphthalene
Bromobenzene/ <i>m</i> -bromotoluene	1-chloronaphthalene/fluorobenzene
Bromobenzene/ <i>m</i> -bromochlorobenzene	<i>p</i> -bromoacetophenone/iodobenzene
Bromobenzene/ <i>m</i> -bromobenzonitrile	

*General procedure for the determination of the rate of carbonylation of aromatic halides (Tables 5 and 6, Figs. 2-5)*

The solvent (50 ml) and the other reactants, as shown in Tables 5 and 6 and Figs. 2-5, were placed in a 100 ml flask containing a magnetic stirring bar, a thermometer, a water cooled condenser connected with a 1 l buret containing carbon monoxide, and a serum cap. Temperatures were controlled to  $\pm 0.1^\circ$  by means of a constant temperature bath. At appropriate intervals of time samples (1 ml) of the reaction mixture were removed, placed in 20 ml of water acidified with  $\text{HCl}$  and extracted with ether ( $2 \times 5$  ml). The ether extracts were treated with diazomethane, and the products analysed by GC.

*Preparation of  $[\text{N}(\text{C}_4\text{H}_9)_4]_2\text{Ni}_3(\text{CO})_8$  (I).* This nickelate was prepared according to the method described by Sternberg, Markby and Wender<sup>24</sup>, and isolated as tetrabutylammonium salt which is insoluble water. IR (in DMSO): 1970 vs, 1915 s, 1780  $\text{cm}^{-1}$ . This complex was not obtained pure. During its crystallization new carbonyl bands appeared, indicating the formation of other nickelates.

*Carbonylation of bromobenzene with  $[\text{N}(\text{C}_4\text{H}_9)_4]_2\text{Ni}_3(\text{CO})_8$ .* Into a 50 ml flask fitted with a magnetic stirring bar, a thermometer, a water cooled condenser, under a  $\text{CO}$  atmosphere, were introduced 25 ml of dimethylsulphoxide, 0.9 g of (I) and 2.0 g of bromobenzene. The red solution was warmed at  $105^\circ$ , and after one hour the colour disappeared. Benzoic acid 0.24 g was separated as described in the previous experiments.

*General procedure for the determination of the relative rates of carbonylation in the presence of  $[\text{N}(\text{C}_4\text{H}_9)_4]_2\text{Ni}_3(\text{CO})_8$  (I). (Table 7)*

In a 50 ml round bottomed flask fitted with a magnetic stirring bar and provided with an atmosphere of  $\text{CO}$ , was placed 25 ml of dimethylsulphoxide, 1.0 g of (I), and 5 mmol each of two aromatic halides. The mixture was warmed at  $105^\circ$  for about 2 h (the red colour disappeared). The mixture was then partitioned between 1 *M* hydrochloric acid solution and ether, and the aqueous solution extracted with ether ( $3 \times 20$  ml). The ether was extracted with an aqueous solution of  $\text{NaHCO}_3$ , and the

alkaline solution was acidified with aqueous HCl and extracted with diethyl ether (3 × 25 ml). The ether extract was dried, concentrated, and treated with diazomethane, and the products analysed by GC.

The following couples were tested:

Bromobenzene/ <i>p</i> -bromoanisole	Bromobenzene/ <i>p</i> -bromochlorobenzene
Bromobenzene/ <i>p</i> -bromotoluene	Bromobenzene/ <i>o</i> -bromoanisole

#### *Carbonylation of bromobenzene with a catalyst prepared in situ*

A 100 ml round bottomed flask was equipped with a mechanical stirrer, a dropping funnel, a thermometer, and a water cooled condenser connected to a buret containing carbon monoxide. The apparatus was swept out with carbon monoxide, and dimethylsulphoxide (40 ml), NiCl<sub>2</sub>·6H<sub>2</sub>O (1.15 g), powdered iron/manganese alloy (Mn 80%) (1.0 g), Na<sub>2</sub>S (0.100 g) and [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)(CH<sub>3</sub>)<sub>3</sub>N]Cl (1.0 g) were introduced. The well stirred solution at 30° took up 430 ml of carbon monoxide in 5 h. The temperature was slowly raised to 108–110° and dimethylsulphoxide (25 ml) and Ca(OH)<sub>2</sub> (8.0 g) were added. The bromobenzene (12 g) was dropped in 1 h. The absorption of carbon monoxide started immediately, and 1200 ml of CO were taken up in 6 h. The reaction mixture was poured into 200 ml of aqueous 1 N hydrochloric acid, and the organic part was extracted with ether (3 × 50 ml). Benzoic acid was purified by extracting it from the ethereal solution with an aqueous solution of NaHCO<sub>3</sub>. The alkaline solution was acidified with aqueous HCl and extracted with diethyl ether. The ether extract was then dried and evaporated. 7.8 g of pure benzoic acid were obtained. (Yield based on the charged bromobenzene 84%.)

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