SHORT COMMUNICATIONS

The Synthesis of Carboxylic Acid from the Reaction of a Stoichiometric Mixture of a Carboxylic Salt and an Arylhalide with Carbon Monoxide Catalyzed by a Nickel Carbonyl

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The reaction of arylhalide with carbon monoxide and water in the presence of a nickel salt as the catalyst results in the formation of carboxylic acid, as has been reported in several papers.[1-4] The yields of carboxylic acids described in those papers, however, depend to a considerable extent on the catalysts and solvents used.

From our study, it has been found that the yield of benzoic acid from the reaction with bromobenzene sharply increases when a stoichiometrical amount of a carboxylic salt, such as potassium acetate or sodium benzoate, is added to starting materials containing a catalytic amount of nickel(II) acetate as the catalyst. Nickel(II) acetate and nickel(II) iodide were used as the catalyst, no measurable difference was found in their catalytic activities. In the product, hydrobromic acid formed from the reaction was present in its salt form, and the carboxylic salt added was in its acid form, through the reaction of $RCOOK + HBr \rightarrow KBr + RCOOH$ ($R = CH_3$ or C_6H_5); most of the nickel(II) acetate added was in the form of nickel tetracarbonyl when the amount of potassium acetate added was more than that of the bromobenzene used. The reaction can be represented as follows:

$$C_6H_5Br + CO + H_2O + RCOOK \rightarrow$$

$$C_6H_5COOH + RCOOH + KBr$$

In the reaction with *p*-dibromobenzene or α-naphthylbromide, practically no carboxylic acid was formed when no potassium acetate was added under the same conditions.

In these reactions, hydrohalogenic acid would disturb the carbonylation reaction of arylhalide. The addition of carboxylic salt would effectively decrease the amount of hydrohalogenic acid formed during the reaction, because the reaction rate of carboxylic salt with hydrohalogenic acid is usually quite fast.

The reactions were carried out using a titanium-manganese alloy autoclave (200 m*l* in vol). An arylbromide (0.2—0.3 mol), water (3.0 mol), carboxylic salt (0.1—0.3 mol), and nickel(II) acetate (0.004 or 0.008 mol) were placed in the autoclave.

The autoclave had been heated up to 250—260°C by a shaking-type electric furnace before carbon monoxide (its purity was more than 98%) was introduced (up to 200—300 kg/cm²). The pressure was kept constant during the reaction by suppling carbon monoxide from a pressure accumulator. The reaction time was 90 min, most of carbon monoxide being absorbed within 40 min. The experimental results are represented in the table.

TABLE 1

Bromide	mol	Ni(AcO[c])$_2$4H$_2$O, mol	Salt	mol	Press. kg/cm^2	Acid formed	mol	(%)
C_6H_5Br	0.20	0.008	AcOK	0.00	300	C_6H_5COOH	0.051	(25)
C_6H_5Br	0.20	0.008	AcOK	0.10	300	C_6H_5COOH	0.148	(74)
C_6H_5Br	0.20	0.008	AcOK	0.20	300	C_6H_5COOH	0.162	(81)
C_6H_5Br	0.20	0.008	AcOK	0.30	300	C_6H_5COOH	0.168	(84)
C_6H_5Br	0.20	0.008	C_6H_5COONa	0.20	300	C_6H_5COOH	0.389	(94)[a]
C_6H_5Br	0.30	0.004	AcOK	0.30	200	C_6H_5COOH	0.279	(93)
p-$C_6H_5Br_2$	0.15	0.004	AcOK	0.30	200	*p*-$C_6H_4(COOH)_2$	0.109	(73)[b]
α-$C_{10}H_7Br$	0.30	0.004	AcOK	0.30	200	α-$C_{10}H_7COOH$	0.249	(83)

a) Benzoic acid 0.20 mol was subtracted from the total one, because no sodium benzoate was detected in the product.
b) Small amounts of benzoic acid and *p*-bromobenzoic acid were contained.
c) $AcO = CH_3COO$

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