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Kinetics of the Reaction of α-Bromonaphthalene with Carbon Monoxide Catalyzed by Nickel Carbonyl

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In a previous paper,[1)] it has been reported that the reaction rate of an aryl halide with carbon monoxide catalyzed by nickel tetracarbonyl to form the corresponding aromatic carboxylic acid is much increased by adding a sufficient amount of potassium acetate; its kinetics showed that the course of the reaction could be represented by the scheme similar to that of an oxo reaction when nickel tetracarbonyl was regenerated rapidly under high temperatures and pressures. On the other hand, nickel carbonyl complexes are more reactive than cobalt carbonyl complexes, and their stoichiometrical reactions with aryl iodides take place under a *ca.* 1 atmosphere of nitrogen and at low temperatures (<100°C), resulting in the formation of aromatic carboxylic compounds.[2)] Accordingly, their catalytic carbonylation reactions must take place under milder reaction conditions as long as nickel carbonyls are regenerated smoothly from carbon monoxide. This work was undertaken in order to study the carbonylation reaction of α-bromonaphthalene under milder conditions and to discuss its kinetics.

Experimental

α-Bromonaphthalene obtained from commercial sources was purified by distillation under a vacuum. The other materials used were the same as those in the previous work.[1)] The reaction was carried out under a constant temperature and at a constant pressure for a given period by using the same apparatus as that described in the previous paper.[1)] The absorption rate of carbon monoxide was also determined. The autoclave used was made of titanium-molybdenum alloy (300 m*l* in vol).

The products were taken out of the autoclave by using sufficient amounts of diethyl ether and water. An aqueous sodium bicarbonate solution was added to the ether phase to separate α-naphthoic acid form α-naphthol and the other organic compunds. α-Naphthoic acid was then precipitated again by adding

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1) M. Nakayama and T. Mizoroki, This Bulletin, **42**, 1124 (1969).

2) N. L. Bauld, *Tetrahedron Lett.*, **1963**, 1840.

a sufficient amount of an aqueous hydrochloric acid solution to the sodium α-naphthoate solution. The α-naphthoic acid had been washed well with cold water before its amount was determined by titration with an aqueous potassium hydroxide solution. The amounts of nickel(II) ion and bromide ion were determined according to the EDTA method and the Volhard method respectively.

Results

The absorption rate of carbon monoxide in the reaction of α-bromonaphthalene (0.30—0.55 mol) with carbon monoxide in the presence of water (1.60—4.00 mol), potassium acetate (0.75 mol), and nickel(II) acetate (0.0040 mol) under 100 kg/cm^2 at 200°C is plotted in Fig. 1. The figure shows that the absorption rate depends neither on the amount of α-bromonaphthalene nor on that of water. The effects of the amounts of nickel(II) acetate and potassium acetate on the absorption rate are shown in Figs. 2 and 3. The rate increases nearly proportionally with the increase in the amount of nickel(II) acetate, which is converted almost quantitatively into nickel tetracarbonyl under these reaction conditions, and also with the increase in potassium acetate. The effect of the

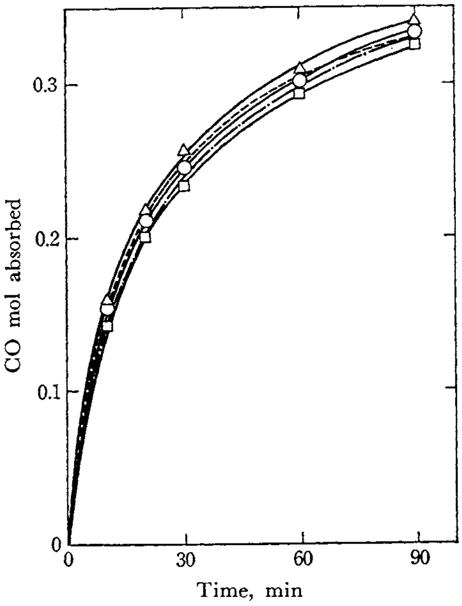

Fig. 1. Effect of the amounts of α-bromonaphthalene and water on absorption rate of carbon monoxide.
Reaction conditions: Temperature 200°C, Pressure 100 kg/cm^2, $Ni(AcO)_2\cdot 4H_2O$ 0.004 mol, AcOK 0.75 mol.

	α-$C_{10}H_7Br$	H_2O	Exp. No.
—□—	0.55 mol	2.40 mol	22
—○—	0.40	2.40	7
—△—	0.30	2.40	23
- - -○- - -	0.40	4.00	9
—·—○—·—	0.40	1.60	10

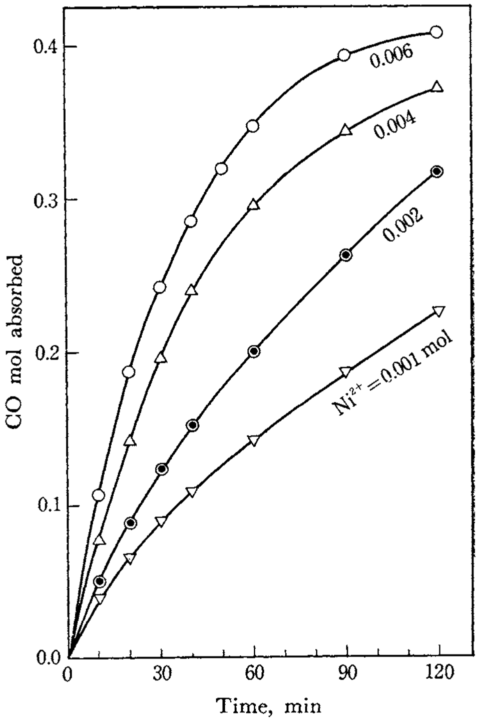

Fig. 2. Effect of the amount of nickel(II) acetate on absorption rate of carbon monoxide.
Reaction conditions: Temperature 200°C, Pressure 100 kg/cm^2, α-$C_{10}H_7Br$ 0.40 mol, H_2O 2.40 mol, AcOK 0.75 mol

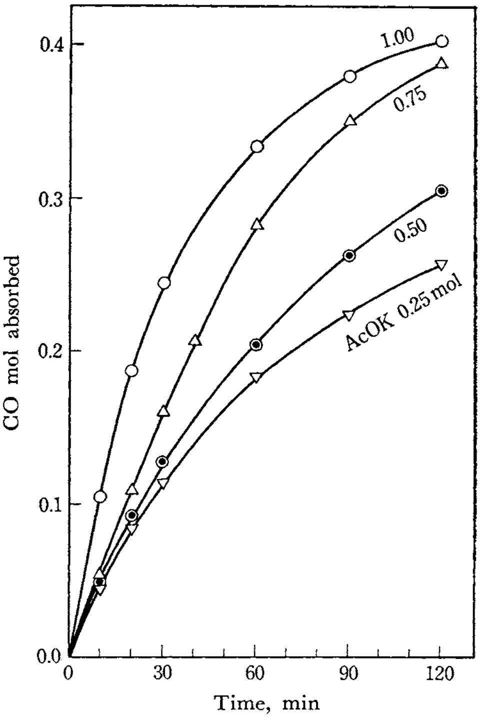

Fig. 3. Effect of the amount of potassium acetate on absorption rate of carbon monoxide.
Reaction conditions: Temperature 200°C, Pressure 100 kg/cm^2, α-$C_{10}H_7Br$ 0.40 mol, H_2O 2.40 mol, $Ni(AcO)_2\cdot 4H_2O$ 0.004 mol

Table 1. Experimental results under various conditions
(Standard reaction conditions: α-$C_{10}H_7Br$ 0.40 mol, H_2O 2.40 mol, Ni^{2+} 0.004 mol, AcOK 0.75 mol; temp. 200°C, press. 100 kg/cm^2, time 90 min)

Exp. No.	Variable		Initial absorp. rate of CO mol/hr	Conversion[a] %	Selectivity %	$Ni(CO)_4$[b] %
22	α-$C_{10}H_7Br$	0.55 mol	0.29	73.3	93.6	16.7
7		0.40	0.31	89.8	98.8	63.2
23		0.30	0.30	84.8	97.9	77.6
9	H_2O	4.00	0.29	82.8	96.0	21.2
7		2.40	0.31	89.8	98.8	63.2
10		1.60	0.29	81.4	97.6	50.7
11	Ni^{2+}	0.006	0.35	103	100	81.7
7		0.004	0.31	89.8	98.8	63.2
12		0.002	0.20	69.5	99.2	56.3
13		0.001	0.14	42.8	97.0	85.6
8	AcOK	1.00	0.33	92.0	98.3	80.8
7		0.75	0.31	89.8	98.8	63.2
5		0.50	0.21	76.0	98.1	45.1
6		0.25	0.18	61.0	98.4	23.5
14	p_{CO}	60 kg/cm^2	0.26	65.7	98.8	7.6
15		80	0.31	98.8	99.3	26.3
7		100	0.31	89.8	98.8	63.2
16		120	0.34	95.3	99.2	67.2
17		140	0.31	82.8	98.0	87.1
18		160	0.25	88.9	99.2	82.5
19		200	0.22	56.0	89.5	95.6

a) Obtained from the amount of Br^- formed.
b) Obtained from the amount of Ni(II) ion present in the product.

pressure of carbon monoxide is represented in Table 1, where the other results already shown in Figs. 1, 2, and 3 are also summarized. The absorption rate is almost independent of the pressure of carbon monoxide over the range from 80 to 150 kg/cm^2. Its decrease under pressures lower than 60 kg/cm^2 is caused by the fact that these pressures are not high enough to convert nickel(II) acetate into nickel tetracarbonyl quantitatively; the decrease under pressures higher than 200 kg/cm^2 is probably because these high pressures of carbon monoxide prevent α-bromonaphthalene from coordination to nickel tetracarbonyl, as was discussed in the previous paper.

In summary, the reaction rate of α-bromonaphthalene with carbon monoxide to form α-naphthoic acid increases with an increase in the amounts of nickel tetracarbonyl or potassium acetate, while it depends on neither the amount of α-bromonaphthalene nor on that of water, nor on the partial pressure of carbon monoxide.

Discussion

The course of the reaction with α-bromonaphthalene can be explained by the scheme proposed for the reaction with bromobenzene:[1)]

$$\text{Ary-Br} + Ni(CO)_4 \rightleftarrows (\text{Ary-Br})Ni(CO)_3 + CO \quad (1)$$

$$(\text{Ary-Br})Ni(CO)_3 + H_2O \rightarrow \text{Ary-COOH} + (HBr)Ni(CO)_2 \quad (2)$$

$$(HBr)Ni(CO)_2 + \text{AcOK} \rightarrow Ni(CO)_2 + \text{AcOH} + KBr \quad (3)$$

$$Ni(CO)_2 + 2CO \rightarrow Ni(CO)_4 \quad (4)$$

(Ary-Br=aryl bromide)

Under pressures of carbon monoxide high enough to regenerate nickel tetracarbonyl quickly, Eq. (2) became the rate-determining step of the carbonylation of bromobenzene and its kinetics could be expressed by Eq. (5), where k and K are the rate constant of Eq. (2) and the equilibrium constant of Eq. (1) respectively. Preliminary experiments showed that the carbonylation rate of α-bromonaphthalene could also be expressed by the same equation under pressures higher than 200 kg/cm^2, while its kinetics under lower pressures of cabon monoxide is very different from Eq. (5) and is, rather, given by Eq. (6):

$$r = \frac{d[C_6H_5COOH]}{dt} = k \cdot K \frac{[Ni(CO)_4][C_6H_5Br][H_2O]}{p_{CO}} \quad (5)$$

$$r = d[\alpha\text{-}C_{10}H_7COOH]/dt \propto [Ni(CO)_4][AcOK] \quad (6)$$

This finding can, however, be understood on the basis of the scheme described above. Lower pressures of carbon monoxide should be favorable for the equilibrium of Eq. (1) to incline much toward the right, and the rate of Eq. (2) must be large enough because α-bromonaphthalene is usually more reactive than bromobenzene, as has been reported in the cases of other organic reactions. The rate of the carbonylation is, accordingly, determined by that of regeneration of nickel tetracarbonyl by Eqs. (3) and (4); we thus find that the rate of the carbonylation is independent of the amounts of α-bromonaphthalene and water. The fact that the rate of carbonylation is also independent of the partial pressure of carbon monoxide, as described in Table 1, suggests that the rate of Eq. (4) is much faster than Eq. (3) and that the true nickel catalyst is nickel tricarbonyl rather than nickel tetracarbonyl.