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Vapor Phase Carbonylation of Organic Halo Compounds

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Synopsis. RCH_2X, *s*-C_4H_9X, and C_6H_5X were methoxycarbonylated with carbon monoxide and methanol into methyl carboxylates in the presence of rhodium trichloride/potassium iodide supported on activated charcoal. The reactivity decreased in the order: X=I>Br>Cl.

The carbonylation of organic halides under various conditions has been discussed in recent reviews.[1,2] The usual catalysts are based on Ni, Co, Fe, Rh, and Pd carbonyls. The reaction system is kept at elevated pressure to supply a sufficient amount of carbon monoxide in liquid phase. However, little is known about vapor phase carbonylation of organic halides, except for the carbonylation of methyl chloride.[3]

The methoxycarbonylation of methyl chloroacetate (MCA) with carbon monoxide in the presence of methanol has been performed industrially in the liquid phase. In the course of this reaction,[4-10] alkaline reagents are required for the neutralization of hydrogen chloride liberated. This procedure could be eliminated in vapor phase. The vapor phase methoxycarbonylation of MCA with carbon monoxide in the presence of methanol was performed under various reaction conditions to obtain dimethyl malonate (DMM) by use of rhodium trichloride ($RhCl_3$) supported on activated charcoal.[11] At an optimum temperature of 175 °C, DMM was obtained in good yield after a long period of the reaction. The formation rate of DMM well obeyed the first order kinetics.[12] Furthermore, the alkoxycarbonylation proceeded smoothly in the presence of an alkoxide anion donor such as alcohol, ether and ester.[13] Metal iodides enhanced remarkably the reactivity of $RhCl_3$ supported on activated charcoal. In this reaction, rhodium(III) chloride iodide might be formed by replacing the chlorine of $RhCl_3$ with iodine partly and thereby might promote the carbonylation of MCA into DMM.[14]

The present work was done to examine the effect of the structure of substrate molecules on the methoxycarbonylation of organic halo compounds.

Results and Discussion

Carbonylation of RCH_2X. As alkyl chloroacetates were alkoxycarbonylated with carbon monoxide smoothly into dialkyl malonates in the presence of an alcohol,[11] mono-substituted methyl halides (RCH_2X) were chosen as the substrate. While RCH_2X was converted into methyl carboxylate in the presence of methanol by reacting RCH_2X with carbon monoxide, the halogen atom of RCH_2X reacted partly with methanol or water to form an ether or alcohol derivative.

$$RCH_2X + CO + CH_3OH = RCH_2COOCH_3 + HX \tag{1}$$

$$RCH_2X + CH_3OH = RCH_2OCH_3 + HX \tag{2}$$

$$RCH_2X + H_2O = RCH_2OH + HX \tag{3}$$

On the other hand, RCH_2X was transformed into a carboxylic acid in the presence of water with carbon monoxide. Since a carboxylic acid is thermally unstable, it may be pyrolyzed into a methyl derivative (RCH_3) and carbon dioxide according to Eqs. 4 and 5.

$$RCH_2X + CO + H_2O = [RCH_2COOH] + HX \tag{4}$$

$$[RCH_2COOH] = RCH_3 + CO_2 \tag{5}$$

The product distribution by the methoxycarbonylation of RCH_2X in the presence of methanol at 150 °C is given in Table 1. The consumption rate of RCH_2X was increased by introducing an electron-releasing substituent. However, the relationship between the methoxy-

Table 1. Product Distribution by the Carbonylation of RCH_2X at 150 °C

Substrate	σ^*	Product[a)]/mol%				
		RCH_2OCH_3	RCH_2X	RCH_2OH	RCH_2COOCH_3	RCH_3
$NCCH_2Cl$	3.64	0.6	97.2	—	1.1	1.1
CH_3OCOCH_2Cl	2.00	0.1	88.5	0.1	10.4	0.9
CH_3OCOCH_2Br	—	0.7	25.8	0.1	58.1	15.3
CH_3COCH_2Cl	1.65	1.3	74.7	—	1.8	22.2
$C_6H_5CH_2Cl$	0.60	22.0	53.4	—	24.6	—
$C_6H_5CH_2Br$	—	23.2	50.2	10.6	16.0	—
m-$CH_3C_6H_4CH_2Cl$	—	26.6	52.4	—	19.1	1.9
p-$CH_3C_6H_4CH_2Cl$	—	56.3	34.9	—	7.7	1.1
p-$ClC_6H_4CH_2Cl$	—	62.9	32.3	—	4.8	—
$CH_2{:}CHCH_2Cl$	—	48.3	51.7	—	Trace	—
$CH_3CH{:}CHCH_2Cl$	0.36	43.9	32.4	4.1	7.9	11.7

a) Sample was taken from the condensate of effluent at 3—4 h after the start of reaction. σ^* is Taft's substituent constant; Ref. 12, p. 619.

carbonylation rate of RCH_2X and the nature of substituent was obscure in the experimental results. According to Suzuki and co-workers,[5] the formation of an alkyl ester by cobalt-catalyzed alkoxycarbonylation of RCH_2Cl in the liquid phase decreased in the order: $NCCH_2Cl > CH_3OCOCH_2Cl > C_6H_5CH_2Cl$. Thus, the liquid phase alkoxycarbonylation of RCH_2Cl with carbon monoxide and an alcohol in the presence of $Co_2(CO)_8$ was accelerated by an electron-withdrawing substituent R in the substrate. Since there were many compounds unreactive to carbon monoxide under identical reaction conditions, the nature of alkoxycarbonylation cannot be fully elucidated.

Carbonylation of C_6H_5X. In general, benzoic acid is formed by oxidation of toluene in the presence of a catalyst. The alkoxycarbonylation of halobenzenes (C_6H_5X) with carbon monoxide is of significance from the viewpoint of C_1 chemistry. For this reason, vapor phase methoxycarbonylation of C_6H_5X was performed in the presence of methanol at 200 °C. The experimental results are given in Table 2. Bromobenzene and iodobenzene were converted into methyl benzoate accompanied by the formation of benzene. Probably because of the large dissociation energy, chlorobenzene was less active than other derivatives.

Carbonylation of C_4H_9X. Carbonylation of the three isomeric halides was attempted to examine the effect of the nature of halide on the reaction with carbon monoxide in the presence of methanol. *t*-Butyl halides were not carbonylated, but was dehydrohalogenated into olefins. Table 3 shows the product distribution by the carbonylation of butyl halides (C_4H_9X) over $RhCl_3/KI$ supported on activated charcoal. The reactivity is in the order: $X = I > Br > Cl$.

Metal carbonyls are generally used as catalysts for the carbonylation of organic compounds. Since the volatility of metal carbonyl causes a trouble at high temperatures, the reaction is performed in liquid phase by use of an autoclave. Further, alkaline reagents should be added to remove hydrogen chloride generated in the course of alkoxycarbonylation of organic chlorocompounds. Consequently, it is important to carry out the reaction in the solid liquid phase and to control the reaction conditions exactly. The gas phase carbonylation has several advantages over the liquid phase one. The reaction can be carried out with a continuous flow system. The catalysts supported on activated charcoal are metal halides which are less volatile than metal carbonyls. Hydrogen chloride is liberated in the free state and is reusable for other chemical processes. In addition, the alkoxy carbonylation in the presence of rhodium trichloride supported on activated charcoal with carbon monoxide is applicable to a variety of organic halo compounds.

Table 2. Product Distribution by the Carbonylation of C_6H_5X at 200 °C

Substrate	Product[a)]/mol%		
	C_6H_6	C_6H_5X	$C_6H_5COOCH_3$
C_6H_5Cl	—	99.6	0.4
C_6H_5Br	1.3	89.6	9.1
C_6H_5I	4.9	89.9	5.2

a) Sample was taken from the condensate of effluent at 3—4 h after the start of reaction.

Probably RCH_2X, *s*-C_4H_9X, and C_6H_5X are methoxycarbonylated predominantly into methyl carboxylate according to a mechanism in which rhodium trihalide acts as a catalyst precursor. In the light of previous investigations, the rhodium complex[13] may play an important role in the formation step of an acid halide. In the catalytic synthesis of acid halides, this scheme would consist of the following steps: (A) oxidative addition, (B) carbon monoxide insertion, and (C) reductive elimination.

$$[Rh(CO)_2X_2]^- + RCH_2X = [RCH_2Rh(CO)_2X_3]^- \tag{6}$$

$$[RCH_2Rh(CO)_2X_3]^- = [Rh(CO)(COCH_2R)X_3]^- \tag{7}$$

$$[Rh(CO)(COCH_2R)X_3]^- + CO = [Rh(CO)_2(COCH_2R)X_3]^- \tag{8}$$

$$[Rh(CO)_2(COCH_2R)X_3]^- = [Rh(CO)_2X_2]^- + RCH_2COX \tag{9}$$

The acid halide is immediately converted into methyl ester by reaction with methanol.

$$RCH_2COX + MeOH = RCH_2COOMe + HX \tag{10}$$

Since the bond energy of C–Br is less than that of C–Cl, the bond dissociation of C–Br proceeds more easily than that of C–Cl in the course of oxidative addition. Presumably because of this, bromoderivatives were converted into the corresponding esters in good yield.

When MCA was methoxycarbonylated with carbon monoxide into DMM in the presence of methanol, the yield of DMM decreased and that of methyl acetate increased with an increase in the water content in methanol.[14] As water was formed from methanol on

Table 3. Product Distribution by the Carbonylation of C_4H_9X at 200 °C

Substrate	Product[a)]/mol%				
	$CH_2{:}CHCH_2CH_3$	*t*-$CH_3CH{:}CHCH_3$	*c*-$CH_3CH{:}CHCH_3$	C_4H_9X	$C_4H_9COOCH_3$
n-C_4H_9I	1.5	4.1	10.5	83.9	0.03
s-C_4H_9Cl	13.5	4.0	33.5	48.3	0.7
s-C_4H_9Br	4.1	0.1	17.6	72.1	6.1
s-C_4H_9I	0.3	15.4	23.0	50.5	10.8

a) Sample was taken from the condensate of effluent at 3—4 h after the start of reaction.

the catalyst, RCH_3, C_6H_6, and s-C_4H_{10} may be produced in the same way from RCH_2X, C_6H_5X, and s-C_4H_9X, respectively.[14]

$$RCH_2COX + H_2O = [RCH_2COOH] + HX \qquad (11)$$

$$[RCH_2COOH] = RCH_3 + CO_2 \qquad (5)$$

On the other hand, the ratio of methyl carboxylate to ether and alcohol in the product varied in a broad range depending on the nature of R in the methoxycarbonylation of RCH_2X. In particular, the methoxylation and hydroxylation of benzyl chlorides and allyl chlorides were faster than those of other compounds. From these observations it is assumed that RCH_2X dissociates partially into carbonium and halide ions on the acid site of the catalyst. The ether and alcohol derivatives may be formed by reaction of the carbonium ion with methanol or water, namely, according to the S_N1 mechanism.

$$RCH_2X \rightleftarrows RCH_2^+ + X^- \qquad (12)$$

$$RCH_2^+ + MeOH = RCH_2OMe + H^+ \qquad (13)$$

$$RCH_2^+ + H_2O = RCH_2OH + H^+ \qquad (14)$$

Experimental

Materials. Organic reagents were purchased from Tokyo Kasei Kogyo Co. and used without further purification. Activated charcoal, rhodium trichloride trihydrate, and potassium iodide were from Wako Pure Chemical Industries. The activated charcoal was cylindrical in form, 7 mm in length and 4 mm in diameter, with a surface area of 1340 $m^2 g^{-1}$.

Preparation of Catalyst. Rhodium trichloride trihydrate 1 g and potassium iodide 0.63 g (molar ratio 1:1) were dissolved in 100 ml of water. Ten grams of activated charcoal was impregnated with this solution and the solution was evaporated to dryness in an oven in the air. Hence the weight proportion among rhodium, potassium, and carbon was 0.039, 0.015, and 1.0.

General Procedures for the Carbonylation. A flow-type system was used. A Pyrex reaction vessel, with a tube 40 cm in length and 2.6 cm in diameter, was heated in a vertical electric furnace. The evaporator, a glass tube, was placed in an electrically wound vertical furnace. The reaction temperature was measured with a Chromel–Alumel thermocouple in a thermowell placed in the catalyst bed. The catalyst (1 g of rhodium trichloride trihydrate and 0.63 g of potassium iodide supported on 10 g of activated charcoal) was placed in the reactor, which was heated in an electric furnace. A mixture of a substrate and methanol was prepared with a molar ratio of 1:10. Carbon monoxide was fed into the reactor at a rate of 0.25 mol h^{-1}, as measured with a flowmeter. The mixture was then fed into the evaporator with a microfeeder at a rate of 10 ml h^{-1} in liquid and preheated to 150 °C, the vapor being passed to the reactor. The reaction temperature was kept constant by means of a temperature controlling device. The product gas stream entered into a cooler and was condensed in a water-ice trap. The products were analyzed by gas chromatography (Shimadzu GC-8A, PEG 6000).

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