3082 © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 3082—3086 (1985) [Vol. 58, No. 11

Vapor Phase Carbonylation of Alkyl Chloroacetates

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(Received April 19, 1985)

The vapor-phase carbonylation of alkyl chloroacetates with rhodium trichloride supported on active carbon was carried out under various conditions. The reaction equation for the preparation of dialkyl malonate from alkyl chloroacetate in the presence of alcohol with carbon monoxide is given as:

$$CH_2ClCOOR + ROH + CO = CH_2(COOR)_2 + HCl$$

The carbonylation proceeded smoothly at 175 °C with an inert solvent as well as with an alkoxide anion donor, such as alcohol, ether, and an ester. The mechanism of the rhodium trichloride-catalyzed carbonylation is probably similar to that of methanol to acetic acid.

The carbonylations of alkyl chloroacetate with carbon monoxide in the presence of alcohol, catalyzed by cobalt carbonyl, have been known for a number of years.[1–7] At present, though, little is known about the vapor-phase carbonylation, since the volatility of metal carbonyl is unavoidable at high temperatures. Consequently, the reaction system has been held under elevated pressure to keep sufficient carbon monoxide in the liquid phase by the use of an autoclave.

Furthermore, alkaline reagents, such as amine,[1,2] sodium alkoxide,[3] alkali metal hydroxide,[4] sodium carbonate[5,6] and alkaline earth metal hydroxide[7], are necessary to remove hydrogen chloride from the reaction field in a large quantity in order to promote the carbonylation. It is said that the effect of the pH of a reaction system on the yield of dialkyl malonate is sensitive and that the exact control of reaction conditions is extremely important.

The present investigation was undertaken in order to examine the vapor-phase carbonylation of alkyl chloroacetate into dialkyl malonate under atmospheric pressure. In accordance with the above views, several searches were made for an effective catalyst and carrier for the carbonylation. Rhodium trichloride was more active when supported on a carrier of a relatively low activity, such as active carbon. Dimethyl malonate was obtained in a good yield in the vapor-phase carbonylation of methyl chloroacetate with rhodium trichloride supported on active carbon.[8] In particular, the present paper is concerned with several alkyl chloroacetates and with several different solvents such as the alkoxide-anion donor at the vapor-phase carbonylation catalyzed by rhodium trichloride supported on active carbon.

Experimental

Materials. The methyl chloroacetate, ethyl chloroacetate, and isopropyl chloroacetate (Tokyo Kasei Kogyo, K.K.) were of a reagent grade and were used without further purification. The active carbon, rhodium trichloride trihydrate, alcohols, ethers, esters, formaldehyde dimethyl acetal, acetic acid, and dichloromethane were purchased from the Wako Pure Chemicals Co. The active carbon was cylindrical in form, 7 mm in length and 4 mm in diameter.

Preparation of Catalyst. The solution was prepared by dissolving 1 g of rhodium trichloride trihydrate in 100 ml of alcohol or water. 10 g of active carbon was impregnated with this solution, and the solution was evaporated to dryness with the oven in the air.

Apparatus. A flow-type system was used.[9] 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.

General Procedure for the Carbonylation of Alkyl Chloroacetates. 11 g of the catalyst (1 g of rhodium trichloride trihydrate supported on 10 g of active carbon) was placed in the middle of the reactor, the bed being supported by necking the reactor tube. While the reaction temperature was regulated, carbon monoxide gas was passed over the catalyst. A mixture of alkyl chloroacetate and the solvent was prepared with the volume ratio of 1:5. Carbon monoxide gas was fed in at the rate of 0.25 mol/h, as measured with a flow meter. The mixture was then fed into the evaporator with a microfeeder at the rate of 20 ml/h in liquid and preheated to 150 °C, the vapor being passed to the reactor. Therefore, carbon monoxide gas was mixed with the vapor of alkyl chloroacetate and the solvent in the evaporator. The product gas stream entered a cooler and was condensed in a water–ice trap. The reaction products were analyzed by means of gas chromatography (PEG 6000, Porapak).

Carbonylation of Methyl Chloroacetate. Methyl chloroacetate was fed into the reactor at the rate of 0.038 mol/h, together with the solvent, and was carbonylated with carbon monoxide over the catalyst. The feed mole ratio of the solvent to methyl chloroacetate was made to vary with the changes in the molecular weight and density of the solvents, because the volume ratio of the solvent to methyl chloroacetate was kept constant. These values are given in Tables 1 and 2. The main reaction products were methyl acetate and dimethyl malonate. The side reaction products were the methyl methoxyacetate and methyl glycolate formed by the direct reaction of methyl chloroacetate with methanol and water. On the other hand, methanol, formaldehyde dimethyl acetal, and methyl acetate reacted with methyl chloroacetate in an atmosphere of carbon monoxide to form dimethyl malonate and were converted at the same time into hydrogen chloride, chloromethyl ether, and acetyl chloride respectively. Since hydrogen chloride was not detected in the waste gas, the chloride ion in the liquid product was determined by the Volhard method. This was confirmed by titration with a standard solution of a base. Moreover, the effect of water on the product composition was investigated by varying the amount of water added to the methanol.

Carbonylation of Ethyl Chloroacetate. A mixture of ethyl chloroacetate and a solvent was fed into the reactor at the rate of 20 ml/h. Therefore, the feed rate of ethyl chloroacetate was 0.032 mol/h. Ethyl chloroacetate was carbonylated with carbon monoxide in the presence of ethanol, diethyl ether, or ethyl acetate into diethyl malonate. While diethyl ether was transformed into ethyl chloride, ethyl acetate was converted into acetyl chloride.

Carbonylation of Isopropyl Chloroacetate. The feed rate of isopropyl chloroacetate was 0.027 mol/h. The isopropyl chloroacetate was carbonylated in the presence of diisopropyl ether with carbon monoxide into diisopropyl malonate in a good yield, and diisopropyl ether was transformed into isopropyl chloride. Isopropyl chloroacetate reacted with isopropyl acetate to give diisopropyl malonate and acetyl chloride.

Results and Discussion

Carbonylation of Alkyl Chloroacetate in the Presence of Alcohol. Dialkyl malonates are important chemical intermediates for the fine chemicals and are manufactured in the form of various alkyl types.

Hence, the relation of the alkyl group to the reactivity was investigated at 150—175 °C. The product compositions for the carbonylation of methyl chloroacetate in the presence of methanol at 175 °C are given in Table 1. The chlorine liberated from methyl chloroacetate during carbonylation was recovered as hydrogen chloride. Several times as much hydrogen chloride was formed in the steady state as at the initial step of the reaction. It might be assumed that the desorption rate of hydrogen chloride from the surface of active carbon was faster than that of dimethyl malonate. The recovery of hydrogen chloride in the free form was 50—70%. It seemed that hydrogen chloride reacted partly with methanol on the surface of the catalyst at the reaction temperature, as methyl chloride was found in the effluent gas.

The reaction equation for the preparation of dimethyl malonate from methyl chloroacetate in the presence of methanol with carbon monoxide is given as:

$$CH_2ClCOOCH_3 + CH_3OH + CO = CH_2(COOCH_3)_2 + HCl \quad (1)$$

Figure 1 shows the effect of the water content in methanol upon the conversion of methyl chloroacetate into methyl acetate. The formation of methyl acetate increased with an increase in the water content. Methyl chloroacetate may be carbonylated, in the presence of water with carbon monoxide, into methyl hydrogen malonate. However, there was no detectable amount of methyl hydrogen malonate. It has been well-known that malonic acid and methyl hydrogen malonate are thermally unstable compounds. Therefore, methyl acetate might be formed by the thermal decomposition of methyl hydrogen malonate. The carbonylation of methyl chloroacetate catalyzed by rhodium trichloride supported on active carbon is a fairly selective reaction.

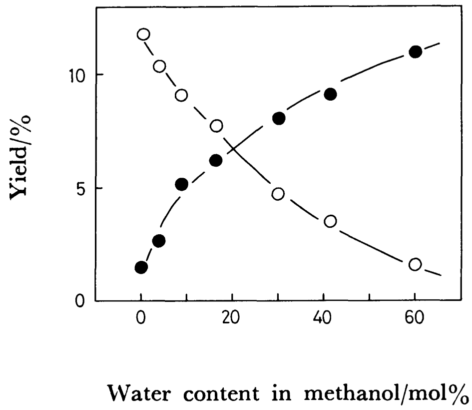


Fig. 1. Effect of the water content in methanol on the formation of methyl acetate at 175°C.
●: CH_3COOCH_3, ○: $CH_2(COOCH_3)_2$

Table 1. Product compositions for the carbonylation of methyl chloroacetate at 175 °C[a)]

Reaction time/h	Product composition/mol × 10^{-3}/h					
	CH_3COOCH_3	$CH_2(OCH_3)COOCH_3$	$CH_2ClCOOCH_3$	$CH_2(OH)COOCH_3$	$CH_2(COOCH_3)_2$	HCl
1	1.20	—	36.17	—	0.52	6.31
3	1.07	0.02	31.71	—	5.09	4.26
6	1.15	0.04	30.98	—	5.72	3.26
11	1.03	0.05	31.26	—	5.55	3.45
16	0.98	0.04	31.34	0.04	5.49	3.35
20	0.89	0.04	31.34	0.03	5.59	3.46

a) The feed mole ratio ($CH_3OH/CH_2ClCOOCH_3$) was 10.9.

Ethyl chloroacetate was carbonylated into diethyl malonate in the presence of ethanol with carbon monoxide on the rhodium trichloride catalyst, while diisopropyl malonate was formed from isopropyl chloroacetate and 2-propanol.

Figure 2 shows the effect of the reaction time on the conversion of alkyl chloroacetates into dialkyl malonates at 150 °C. All curves have a tendency to increase the conversion at the initial reaction step because of the adsorption of dialkyl malonate on active carbon. It has been reported that the elongation of the reaction time led to a decrease in the yield of dimethyl malonate at higher temperatures.[8] However, no indications of the deactivation of the catalyst were recognized at this temperature. It could be anticipated that the durability of catalytic activity was continued for a considerably long time at a moderate temperature. The yield of dialkyl malonate decreased with an increase in the bulkiness of the alkyl group. The carbonylation of alkyl chloroacetate with carbon monoxide in the presence of alcohol is a nucleophilic reaction. The nucleophilicity of higher alcohol is increased by the inductive effect of the alkyl group. The steric hindrance and inductive effect of the alkyl group compensated for each other. Consequently, it was thought that the conversion of ethyl chloroacetate into diethyl malonate was approximately equal to that of isopropyl chloroacetate.

Carbonylation of Alkyl Chloroacetate in the Presence of the Alkoxide Anion Donor. Alkyl chloroacetate was diluted with an inert solvent such as dichloromethane as well as with an ether and an ester as an alkoxide-anion donor. In addition, we tried to carbonylate methyl chloroacetate into dimethyl malonate when such diluents were not used. The method of carbonylation was identical to that described

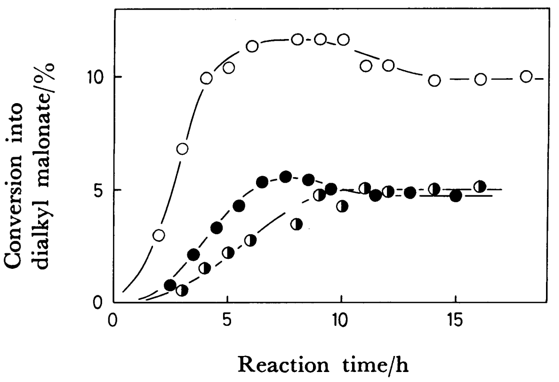


Fig. 2. Variation of catalytic activity with reaction time at 150 °C.
○: $CH_2(COOCH_3)_2$, ◑: $CH_2(COOC_2H_5)_2$,
●: $CH_2[COOCH(CH_3)_2]_2$
Mole ratio: $CH_3OH/CH_2ClCOOCH_3=10.9$,
$C_2H_5OH/CH_2ClCOOC_2H_5=9.1$,
$(CH_3)_2CHOH/CH_2ClCOOCH(CH_3)_2=8.2$

TABLE 2. PRODUCT COMPOSITIONS FOR THE CARBONYLATION OF ALKYL CHLOROACETATES WITH VARIOUS SOLVENTS AT 175 °C

Starting material	Mole ratio (Solvent/$CH_2ClCOOR$)	Product composition/mol %			By-product/mol %
$CH_2ClCOOCH_3$[a]	—	1.5 CH_3COOCH_3,	90.5 $CH_2ClCOOCH_3$,	5.3 $CH_2(COOCH_3)_2$	2.7 $CH_2ClCOCl$
$CH_2ClCOOCH_3$-CH_2Cl_2	6.87	1.5 CH_3COOCH_3,	92.9 $CH_2ClCOOCH_3$,	3.4 $CH_2(COOCH_3)_2$	2.2 $CH_2ClCOCl$
$CH_2ClCOOCH_3$-$CH_2(OCH_3)_2$	4.97		97.4 $CH_2ClCOOCH_3$,	2.6 $CH_2(COOCH_3)_2$	5.3 CH_2ClOCH_3 + CH_3COOCH_3
$CH_2ClCOOCH_3$-CH_3COOCH_3	5.54		93.7 $CH_2ClCOOCH_3$,	6.3 $CH_2(COOCH_3)_2$	6.7 CH_3COCl
$CH_2ClCOOCH_3$-CH_3COOH	7.69	9.5 CH_3COOCH_3,	90.3 $CH_2ClCOOCH_3$,	0.2 $CH_2(COOCH_3)_2$	CH_3COCl
$CH_2ClCOOC_2H_5$-$C_2H_5OC_2H_5$	5.09	2.2 $CH_3COOC_2H_5$,	89.6 $CH_2ClCOOC_2H_5$,	8.2 $CH_2(COOC_2H_5)_2$	2.5 C_2H_5Cl
$CH_2ClCOOC_2H_5$-$CH_3COOC_2H_5$	5.40		94.2 $CH_2ClCOOC_2H_5$,	5.8 $CH_2(COOC_2H_5)_2$	8.2 CH_3COCl
$CH_2ClCOOCH(CH_3)_2$-$(CH_3)_2CHOCH(CH_3)_2$	4.45	0.4 $CH_3COOCH(CH_3)_2$,	87.3 $CH_2ClCOOCH(CH_3)_2$,	12.3 $CH_2[COOCH(CH_3)_2]_2$	4.3 $(CH_3)_2CHCl$
$CH_2ClCOOCH(CH_3)_2$-$CH_3COOCH(CH_3)_2$	5.35		94.6 $CH_2ClCOOCH(CH_3)_2$,	5.4 $CH_2[COOCH(CH_3)_2]_2$	2.0 CH_3COCl

a) The feed rate of $CH_2ClCOOCH_3$ was 0.057 mol/h.

previously in the case of alcohol. The experimental results obtained by the vapor-phase carbonylation of alkyl chloroacetate in the presence of various solvents at 175 °C are given in Table 2.

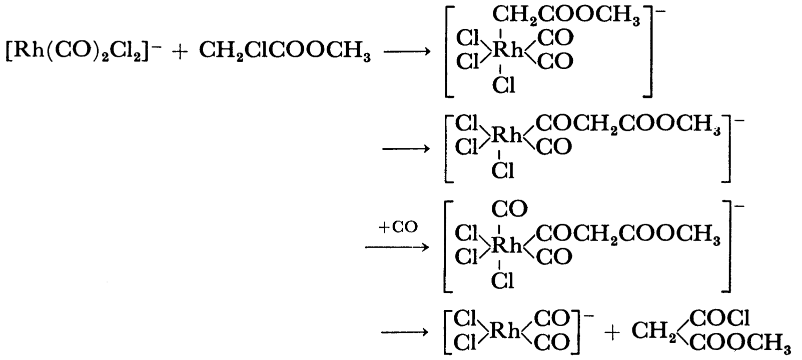
These results are particularly surprising in view of the fact that dimethyl malonate was formed with dichloromethane, which is an inert solvent, and in the absence of a solvent in the vapor-phase carbonylation. It was found that the reaction product contained a small quantity of dimethyl malonate, even when acetic acid was used. On the other hand, dimethyl malonate was obtained in a good yield by the use of methyl acetate instead of dichloromethane. When considered in connection with these experimental results, ester might act as the alkoxide-anion donor. The reason why the formation of dimethyl malonate in the absence of a solvent or in the presence of an inert solvent was found is as follows. Methyl chloroacetate itself has been shown to act as an anion donor. These reactions proceeded according to the following equation:

$$\begin{aligned}&2\mathrm{CH_2ClCOOCH_3} + \mathrm{CO}\\ &\quad = \mathrm{CH_2(COOCH_3)_2} + \mathrm{CH_2ClCOCl} \qquad (2)\end{aligned}$$

That is to say, the ester was transformed into acid chloride, which was then converted into acid with water and ester with alcohol. Similarly, ether, as the alkoxide-anion donor, reacted with alkyl chloroacetate and carbon monoxide to form alkyl chloride. When acetic acid was used as the starting material, methyl acetate was produced in a significant amount because of the decomposition of methyl hydrogen malonate. Many reports have been published on the mechanism of a rhodium complex-catalyzed carbonylation of methanol to acetic acid.[10-14] Rhodium compounds, in conjunction with various forms of iodide, can be used for the carbonylation of methanol to acetic acid, whereas no direct evidence has been provided as to the chloride forms with a variety of catalysts.

However, it can be assumed that rhodium trichloride acts as a catalyst or catalyst precursor, because the reaction system does not contain any type of iodide.

Taking these previous papers into account, the present reaction scheme may be illustrated as below:



$$[\mathrm{Rh(CO)_2Cl_2}]^- + \mathrm{CH_2ClCOOCH_3} \longrightarrow \left[\begin{array}{c}\mathrm{CH_2COOCH_3}\\ {}^{\mathrm{Cl}}_{\mathrm{Cl}}{>}\mathrm{Rh}{<}^{\mathrm{CO}}_{\mathrm{CO}}\\ \mathrm{Cl}\end{array}\right]^- \qquad (3)$$

$$\longrightarrow \left[\begin{array}{c}{}^{\mathrm{Cl}}_{\mathrm{Cl}}{>}\mathrm{Rh}{<}^{\mathrm{COCH_2COOCH_3}}_{\mathrm{CO}}\\ \mathrm{Cl}\end{array}\right]^- \qquad (4)$$

$$\xrightarrow{+\mathrm{CO}} \left[\begin{array}{c}\mathrm{CO}\\ {}^{\mathrm{Cl}}_{\mathrm{Cl}}{>}\mathrm{Rh}{<}^{\mathrm{COCH_2COOCH_3}}_{\mathrm{CO}}\\ \mathrm{Cl}\end{array}\right]^- \qquad (5)$$

$$\longrightarrow \left[{}^{\mathrm{Cl}}_{\mathrm{Cl}}{>}\mathrm{Rh}{<}^{\mathrm{CO}}_{\mathrm{CO}}\right]^- + \mathrm{CH_2}{<}^{\mathrm{COCl}}_{\mathrm{COOCH_3}} \qquad (6)$$

Since the amount of dialkyl malonate remained unchanged upon the addition of water or alcohol, intermediary acid chloride probably plays an important role in the postulated step. On the basis of the experimental results, the pathways for the formation of dialkyl malonates can be given by the following equations:

$$\begin{aligned}\mathrm{ClCOCH_2COOR} &+ \mathrm{ROH} = \mathrm{CH_2(COOR)_2} + \mathrm{HCl} && (7)\\ &+ \mathrm{ROR} = \mathrm{CH_2(COOR)_2} + \mathrm{RCl} && (8)\\ &+ \mathrm{CH_2(OR)_2} = \mathrm{CH_2(COOR)_2}\\ &\quad + \mathrm{CH_2ClOR} && (9)\\ &+ \mathrm{CH_3COOR} = \mathrm{CH_2(COOR)_2}\\ &\quad + \mathrm{CH_3COCl} && (10)\\ &+ \mathrm{CH_2ClCOOR} = \mathrm{CH_2(COOR)_2}\\ &\quad + \mathrm{CH_2ClCOCl} && (11)\\ &+ \mathrm{CH_3COOH} = [\mathrm{HOOCCH_2COOR}]\\ &\quad + \mathrm{CH_3COCl} && (12)\\ &+ \mathrm{H_2O} = [\mathrm{HOOCCH_2COOR}]\\ &\quad + \mathrm{HCl} && (13)\end{aligned}$$

Methyl hydrogen malonate is unstable and may be decomposed into methyl acetate and carbon dioxide according to Eq. 14:

$$[\mathrm{HOOCCH_2COOR}] = \mathrm{CH_3COOR} + \mathrm{CO_2} \qquad (14)$$

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