

NOTE

RODIUM-CATALYZED CARBONYLATION OF METHYL GLYCOLATE AND GLYCOLIC ACID

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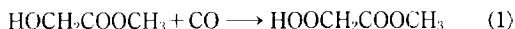
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Abstract—Catalytic carbonylation of methyl glycolate in the presence of a homogeneous Rh complex and an iodide promoter yields acetoxy methyl acetate and acetic acid. Carbonylation of glycolic acid under the same conditions gives acetic acid and CO₂, probably from decomposition of the malonic acid intermediate.

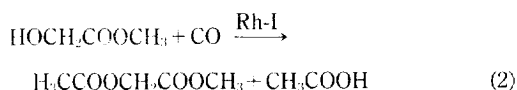
INTRODUCTION

Esters of malonic acid are important intermediates in fine chemical industry. Currently the most advanced commercial technology of the manufacture of malonic acid esters is based on the carbonylation of alkyl chloroacetates in the presence of an alcohol catalyzed by cobalt carbonyl [1]. The process yields HCl as a coproduct which gives many operational problems. Recently, some efforts have been made to develop a heterogeneous catalytic processes based on supported Rh to reduce those problems [2-4].

Carbonylation of methyl glycolate (reaction 1) was proposed as a potential synthetic route to monomethyl malonate [5, 6].

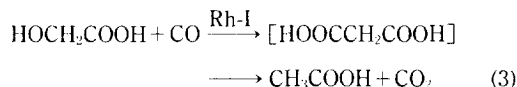


No experimental results, however, have been reported. The reaction, if proceeds well as written, would give a chlorine-free route to the malonic acid ester. We have screened group 8 metal complexes and halogen promoters as catalysts for the carbonylation of methyl glycolate or glycolic acid. In the presence of well known carbonylation catalysts of a homogeneous Rh complex and an iodide promoter, the reaction was found to yield acetoxy methyl acetate (AMA) and acetic acid instead of expected monomethyl malonate.



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When glycolic acid is employed as a starting material, acetic acid and CO₂ was formed probably through malonic acid as an intermediate.



This communication reports typical results of these reactions.

EXPERIMENTAL PROCEDURE

A 300 cm³ high pressure stirred autoclave with Hastelloy-C wall was charged with 100 cm³ of solution containing methyl glycolate(MG) or glycolic acid, catalyst and diethyl ether. While stirring, the gas phase in the vessel was flushed three times with CO before the reactor was pressurized to a desired pressure with CO. The reactor content was then heated to a reaction temperature. After 6h of the reaction, the reactor was cooled down and the liquid phase in the vessel was analyzed by a gas chromatography equipped with a thermal conductivity detector and a 0.32 mm O.D. and 20 m long Carbowax 20 M capillary column. The formation of AMA was confirmed by a GC/MS and an NMR.

RESULTS AND DISCUSSION

The scope of screening experiments is summarized in Table 1 for catalyst components and reaction conditions. Total ca. 70 batches of experiments were run.

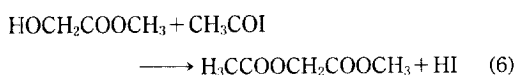
Table 1. The scope of screening experiments

Catalyst	Metal: Rh, Co, Ni, Ru, Pd, Ir Promoter: HX, KX, CH ₃ I, NEt ₄ X (X=I, Cl, Br)
Pressure	50-100 bar
Temperature	50-200°C
Solvents	Ethers, alcohols, water, nonpolar hydrocarbons

As the metallic component of catalyst, complexes of Rh, Co, Ni, Ru, Pd, or Ir were tested. As the halide promoter, salts of I, Cl, or Br were employed. The CO pressure and reaction temperature were varied 50-100 bar and 50-200°C, respectively. Ethers, alcohols, water, and some nonpolar organic solvents were tested. The reaction proceeded smoothly only with Rh and iodide promoters. Other catalysts showed little or no activity under the above reaction conditions. Diethyl ether gave the best results among the solvents tested. The major product AMA was confirmed by GC-MS(*m/e* = 43, 73, 90, 102, and 132) and H-NMR analyses of isolated products.

Representative results of Rh-catalyzed carbonylation of MG are summarized in Table 2. In the most favorable case with RhCl₃-KI catalyst, an AMA yield of 70% (or a selectivity of 93%) was obtained. Other iodide promoters were less effective in both conversion of MG and selectivity to AMA. However, compounds of chlorine or bromine were totally ineffective. The kind of Rh complex appears to affect the reaction yield only slightly. The system showed measureable activity only above 120°C. When glycolic acid was employed as the reactant instead of MG under otherwise identical reaction conditions, only acetic acid was detected in liquid phase. Gas phase was not analyzed quantitatively. But the presence of CO₂ was confirmed by a GC analysis.

In order for the proposed reaction 1 to take place, the hydroxyl part of MG must be first activated by iodide as in the case of methanol carbonylation to acetic acid with the similar catalyst system [7]. However, the present reaction appears to proceed through the following reaction steps, for example, in the case of HI as a promoter.

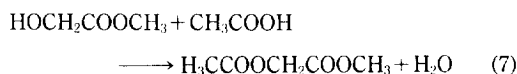
**Table 2. Carbonylation of methyl glycolate in the presence of Rh-I catalysts^a**

Catalyst		Reaction yield ^b , %	
Rh	I	AMA	Acetic acid
RhCl ₃	KI	70.0	5.2
RhCl ₃	HI	9.9	16.6
RhCl ₃	CH ₃ I	9.9	16.6
Rh ₆ (CO) ₁₆	HI	17.4	18.3
Rh ₄ (CO) ₁₂	HI	32.0	32.5
[Rh(CO) ₂ Cl] ₁₂	HI	26.3	31.5

^aFollowing reaction conditions were employed: initial CO pressure, 70 bar, temperature, 150°C; concentration of catalysts, 3 wt% for Rh compounds and 10 wt% for iodides; reaction time, 6 h; solvent, diethyl ether.

^bRemaining mass balance was unreacted methyl glycolate.

Note that initial activation of MG by HI take place on the methyl group. Acetic acid could be formed by hydrolysis of CH₃COI [8]. Formed acetic acid could also react with MG to form AMA directly.



Glycolic acid formed in reaction 4 can further react in several ways as proposed previously [8]. For example, it could be carbonylated to form malonic acid CH₂(CO₂H)₂, which, then, decomposes to acetic acid and CO₂. This decomposition is known to occur above 70°C [9]. This seems to be the case when glycolic acid was employed as a reactant instead of MG. In this case of the carbonylation of glycolic acid, the iodide promoter appears to have activated the hydroxyl group of glycolic acid.

In conclusion, carbonylation of MG in the presence of Rh-I catalysts yields AMA instead of the methyl ester of malonic acid envisioned previously. This is due to higher reactivity of the methyl part of MG than the hydroxyl part toward the iodide promoters. Hence, the proposition that the reaction 1 could be a feasible route to malonic acid esters is not substantiated at least with common transition metal complex-halide promoter catalysts. When glycolic acid is carbonylated, absence of the methyl part drives the reaction to the hydroxyl part, and indeed malonic acid might have formed. However, at the reaction temperatures that allows the measurable rates, malonic acid is unstable and decomposes to acetic acid and CO₂. Hence, if malonic acid is desired, research in the future should be directed towards the development of a more active catalyst system that would promote the reaction below the temperature of the product decomposition.

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