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Short Communication

AN EFFECTIVE RHODIUM CATALYST SYSTEM ON THE SYNTHESIS OF ACETIC ACID FROM METHYL FORMATE

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Abstract—Rh/LiI/SnR_4 is an effective catalyst system for the conversion of methyl formate to acetic acid under carbon monoxide pressure. The effects of solvent and initial CO partial pressure on the turnover rate of the reaction were investigated. The possibility of replacing some of the iodide promoters by tin compounds has been probed.

Key words: Rhodium, Methyl Formate, Acetic Acid, Iodide, Tin Compound

In the last few decades the potential of methyl formate as a building block in the production of large variety of useful organic derivatives has stirred up considerable interest [Ikarashi, 1980; Röper, 1984; Lee et al., 1990]. Because of its unique position in C_1 chemistry, it is quite conceivable to envision a chemical industry complex based on methyl formate.

Among the processes studied so far with this compound, its transition metal catalyzed isomerization to more valuable acetic acid has been under thorough investigation.

$$HCOOMe \xrightarrow{cat.} AcOH \qquad (1)$$

The reaction can be an economically viable process when methyl formate is obtained as an undesirable byproduct, e.g., in butane oxidation, or if it can be made cheaply. In the latter case, it is conceivable that in certain parts of the world carbonylation of methanol using impure carbon monoxide to methyl formate, followed by isomerization to acetic acid, can compete favorably with direct methanol carbonylation using pure carbon monoxide to acetic acid.

Satisfactory yields have been obtained employing transition metal complex catalysts from Rh [Antoniades, 1980; Hoeg and Bub, 1984; Schreck et al., 1988], Ir [Pruett and Kacmarcik, 1982], Co [Isogai, 1974; Jenner, 1990; Jenner and Nahmed, 1991], Ni [Isogai, 1974; Isshiki et al., 1981a; Rizkalla, 1986; Cheong et al., 1990; Cheong et al., 1991], Ru [Isshiki et al., 1981b; Röper et al., 1985], or Pd [Jenner, 1990; Isshiki et al., 1981b; Röper et al., 1985], and an iodide promoter. Rhodium and iridium are the most active and selective catalysts. The activities and selectivities depend not only on the nature of the iodide used as a promoter [Schreck et al., 1988] but also on the solvent [Pruett and Kacmarcik, 1982; Jenner, 1990; Cheong et al., 1991] and the carbon monoxide pressure which is necessary to stabilize the catalytic species. The selectivities into acetic acid and methyl acetate are generally good, formic acid being the major by-product observed with several catalysts.

Recently we reported that a catalyst system, involving nickel as a catalyst and a trialkylamine, a tetraalkyltin and hydrogen as promoters, shows high activities and selectivities in the isomerization of methyl formate to acetic acid in the temperature range 140-220℃, initial partial pressure range 10-50 atm of carbon monoxide, and 1.4-10 atm of hydrogen [Cheong et al., 1990]. An interesting feature of this system is the presence of little or no water, which could provide considerable savings in capital and operating costs involved in the prevention of the corrosion of the reactor and the separation of acetic acid from appreciable quantities of water (4-10 M) in commercial processes. In this paper, we describe our results dealing with Rh/LiI/$SnBu_4$ catalyst system, the effect of solvent, and the possibility of replacing some of the iodide promoters by tin compounds in the synthesis of acetic acid from methyl formate. Reaction can be carried out efficiently by adding a catalytic amount of $RhCl_3$, LiI, and various amounts of promoter to methyl formate (340 mmol) into a glass liner in a Parr 125 ml autoclave equipped with a temperature controller. After being purged with CO several times, the reactor was pressured with CO and heated to the desired temperature with stirring. After the required time, the liquid phase was cooled, sampled, and analyzed by a Varian gas chromatograph with a flame ionization detector and a thermal conductivity detector using dimethylformamide as an internal standard. Since methyl formate can produce gas products, such as CH_4, CO_2, and CO, catalysts which promote these reactions must be avoided. By comparing methyl and acetyl portions of the reactants with those of products, it was evident that methyl formate does not decompose to methane, carbon dioxide or carbon monoxide in appreciable quantities under experimental conditions.

The selectivity data for the Rh-catalyzed isomerization of methyl formate should be used with caution as a catalyst performance criteria, since the facile transesterification reaction of the unreacted methyl formate with the product acetic acid produces formic acid and methyl acetate.

$$HCOOMe + AcOH \rightleftharpoons HCOOH + AcOMe \qquad (2)$$

A selectivity of nearly 100% can be reached at sufficiently long reaction time, methyl acetate and formic acid being eventually converted to acetic acid during the reaction under experimental conditions.

Starting with a Rh/LiI system we studied the effect of solvent on the turnover rate. Jenner [1990] reported that Pd-catalyzed isomerization of methyl formate could be achieved at high rates and selectivities in N-methylpyrrolidone (NMP). Table 1 indicates

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Table 1. Effect of solvent on the isomerization of methyl formate catalyzed by the Rh/LiI system at 180°C and 400 psi of initial carbon monoxide pressure[a]

Solvent	No SnR_4			SnR_4 added		
	Conv.	Selec.	Turnover rate (h^{-1})	Conv.	Selec.	Turnover rate (h^{-1})
Methyl formate	16	76	140	7	53	42
Acetic acid	48	35	190	56	53	350
NMP	10	49	60	6	49	37

[a]Methyl formate (340 mmol), $RhCl_3$ (0.20 mmol), LiI (13 mmol), $SnBu_4$ (6.5 mmol, if added), solvent (20 ml), t = 1.5 hr after increasing temperature to 180°C. Conversion and selectivity are given in terms of mol-% and turnover rate is given by the moles of acetic acid and methyl acetate produced per hr and per mol of Rh.

Table 2. Effect of initial CO partial pressure on the isomerization of methyl formate catalyzed by the Rh/LiI/$SnBu_4$ System at 180 °C[a]

Initial CO partial pressure (psi)	Conv. (%)	Selec. (%)	Turnover rate (h^{-1})
200	55	48	310
500	64	60	440
800	65	62	460
1200	66	62	470

[a]Methyl formate (340 mmol), $RhCl_3$ (0.20 mmol), LiI (13 mmol), $SnBu_4$ (6.5 mmol), acetic acid solvent (20 ml), t = 1.5 hr after increasing temperature to 180°C.

that, when the experiments are performed with reactant methyl formate or product acetic acid as a solvent, similar turnover rate is observed. However, with NMP as a solvent turnover rate is considerably lower as observed by Jenner [1990] for Rh/LiI catalyst system.

Introduction of $SnBu_4$ to the system modifies the reactivity of the catalyst showing considerably enhanced activity in acetic acid solvent, while rather decreased activity in methyl formate and NMP solvent. Best way in engineer's point of view is not to use solvent if possible or is to use the product as the solvent, because use of an expensive solvent increases requirement for separation capital, replenishment, pollution abatement, and reworking. Therefore, Rh/LiI/$SnBu_4$ system with acetic acid as a solvent can be quite promising in that respect.

The activity of Rh/LiI/$SnBu_4$ catalyst system is affected by initial carbon monoxide partial pressure, total pressure of the system being kept constant at 1200 psi by applying argon gas in order to keep the distribution of very volatile methyl formate and methyl iodide between the liquid and the gas phases unchanged (Table 2). The activity of the catalyst improves with increasing initial carbon monoxide partial pressure up to ca. 500 psi, above which the reaction is independent of initial carbon monoxide pressure. The influence of CO pressure on the catalytic process may be due to difficulty of transfering CO from the gas phase to the liquid phase.

Table 3 indicates that we can substitute tetrabutyltin for the same moles of iodide without influencing the turnover rate for the Rh catalyst system. Since the reaction solution of Rh and iodide are highly corrosive, in commercial process the reactors, separators, and recycle loops must be constructed of expensive corrosion-resistant materials. The process could be improved if an iodide promoter could be reduced in quantity still having an activity analogous to that of unreduced system with less corrosive alternative promoter added. Replacing iodide by bromide or organic pseudohalide such as pentachlorobenzenethiol resulted in slower reaction rate than in the iodide system by one or two orders of magnitude [Webber et al., 1977]. Therefore, it might be intriguing if we could replace some part of iodide by tin compounds without affecting reaction rate. The role of tin compounds needs to be studied further, but these results are quite promising for the use of tetrabutyltin as an alternative. Also with acetic acid as a solvent this catalyst system shows a very high turnover rate significantly improved over usual values obtained with Rh catalyst (200-400 h^{-1}).

Table 3. Effect of tin compound and iodide concentration on the isomerization of methyl formate catalyzed by the Rh system at 190°C and 600 psi of initial carbon monoxide pressure[a]

LiI (mmol)	$SnBu_4$ (mmol)	Conv. (%)	Selec. (%)	Turnover rate (h^{-1})
0.0	6.5	37	24	100
6.5	0.0	35	33	130
13.0	0.0	52	55	330
19.5	0.0	80	63	570
13.0	6.5	74	67	560

[a]Methyl formate (340 mmol), $RhCl_3$ (0.20 mmol), acetic acid solvent (20 ml), t = 1.5 hr after increasing temperature to 190°C.

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