

# Phosphorus pentoxide promotion of iridium-catalysed rearrangement of methyl formate in the absence of initial CO pressure

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Received 26 January 1996; accepted 27 May 1996

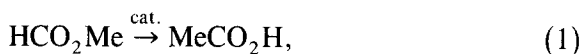
## Abstract

The possible roles of formic acid as an effective solvent for the iridium-catalysed conversion of methyl formate to acetic acid in the absence of initial carbon monoxide pressure are elucidated. Based on the finding, a strong acid anhydride, such as phosphorus pentoxide, which can maintain the concentration of methyl formate as high as possible compared to that of methyl acetate, is proposed as and proved to be a highly effective promoter for the reaction.

**Keywords:** Methyl formate; Acetic acid; Phosphorus pentoxide; Iridium catalyst

## 1. Introduction

In the last few decades the potential of methyl formate as a building block in the production of a large variety of useful organic derivatives has aroused considerable interest [1–3]. Because of its unique position in C<sub>1</sub> 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 catalysed rearrangement reaction,



to the more valuable acetic acid has been under thorough investigation.

Satisfactory yields have been obtained employing transition metal (Rh [4–8], Ir [8,9], Co [10–12], Ni [10,13–15], Ru [16,17], or Pd [11,16,17]) complex catalysts and an iodide promoter in a liquid phase. Rhodium and iridium are the most active and selective catalysts with which the reaction can proceed even in the *absence* of initial CO pressure [8]. The activities and selectivities depend not only on the nature of the iodide used as promoter [6] but also on the solvent [9,11,15] and the initial pressure of carbon monoxide employed. Selectivity into acetic acid and methyl acetate is generally good, formic acid being the major by-product observed with several catalysts. The reaction can be an economically viable process when methyl formate is obtained as an undesirable byproduct,

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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 such as Korea carbonylation of methanol using *impure* carbon monoxide such as steel-mill off-gases to methyl formate, followed by rearrangement to acetic acid, can compete favorably with direct methanol carbonylation using *pure* carbon monoxide to acetic acid. This system needs 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 methanol carbonylation processes.

The most thermodynamically favoured reaction from methyl formate is the formation of methane and carbon dioxide. Catalysts or reaction conditions which promote this reaction must be avoided if other more valuable products are desired.

Recently we have observed [8] that MeI–HCO<sub>2</sub>H is an effective promoter/solvent combination for the transition-metal catalysed conversion of methyl formate to acetic acid in the absence of initial carbon monoxide pressure. Although iridium has been known to catalyse the reaction without the need of an initial CO pressure in the presence of propionic acid, an

interesting feature of our catalyst system is that not only iridium but also rhodium can catalyse the transformation of methyl formate to acetic acid without initial CO pressure. Also, the turnover frequency observed for rhodium or iridium catalysts is considerably higher than previously reported values. The present work is undertaken to elucidate the possible roles of formic acid and to find a catalyst system superior to our previous ones.

## 2. Results and discussion

### 2.1. Effect of solvent

Starting with a Ir/MeI system we studied the effect of solvent on the turnover frequency. Table 1 indicates that, when the experiments are performed with reactant methyl formate, methyl acetate, or NMP as a solvent, essentially no reaction occurs even at 190°C. This results are quite contrary to previous studies of rearrangement reactions with other groups 9 and 10 metals in the *presence* of initial carbon monoxide pressure [4,10,11,15]. With carboxylic acids, such as propionic acid, acetic acid, or formic acid, as a solvent turnover frequency becomes considerably higher. Strong acids can decom-

Table 1

Effect of solvent on the isomerization of methyl formate catalysed by the Ir/CH<sub>3</sub>I system at 190°C in the absence of initial carbon monoxide pressure<sup>a</sup>

Solvent	HCO <sub>2</sub> Me converted (%)	Selectivity (%)			Turnover frequency (h <sup>-1</sup> )
		MeCO <sub>2</sub> Me	MeCO <sub>2</sub> H	RCO <sub>2</sub> Me <sup>b</sup>	
Methyl formate	0	0	0	—	0
Methyl acetate	16	0	0	—	0
NMP	38	0	0	—	0
Propionic acid	74	8	45	39	700
Acetic acid	82	45	10	na <sup>c</sup>	840
Formic acid	92	3	96	na <sup>c</sup>	1670
Trifluoroacetic acid	51 <sup>d</sup>	8	13	64	200

<sup>a</sup> Methyl formate (200 mmol), [Ir(cod)Cl]<sub>2</sub> (0.027 mmol), MeI (17 mmol), solvent (18 ml), *t* = 2.0 h after increasing temperature to 190°C. Conversion and selectivity based on HCO<sub>2</sub>Me converted are given in terms of mol% change of compounds and turnover frequency is given in terms of the moles of acetic acid and methyl acetate produced per h and per mol of Ir. Cod = cycloocta-1,5-diene.

<sup>b</sup> Methyl ester of corresponding organic acid solvent.

<sup>c</sup> Not applicable.

<sup>d</sup> By-product is MeOH.

Table 2

Effect of various carboxylic acid solvent on the transesterification of methyl formate or methyl acetate in the presence of Ir at 190°C<sup>a</sup>

Solvent	With methyl formate		Gaseous products				With methyl acetate	
	HCO <sub>2</sub> Me	RCO <sub>2</sub> Me <sup>b</sup>	H <sub>2</sub>	CO	CO <sub>2</sub>	press. (atm) <sup>c</sup>	MeCO <sub>2</sub> Me	RCO <sub>2</sub> Me <sup>b</sup>
Propionic acid	77	23	12	76	12	5	86	13
Acetic acid	67	27	10	80	10	7	94	na <sup>d</sup>
Formic acid	100	na <sup>d</sup>	6	87	7	40	46	53
Trifluoroacetic acid	63	37	8	83	9	29	43	57

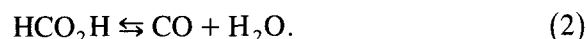
<sup>a</sup> Methyl formate or methyl acetate (200 mmol), [Ir(cod)Cl]<sub>2</sub> (0.027 mmol) or IrCl<sub>4</sub> · H<sub>2</sub>O (0.054 mmol), solvent (18 ml), *t* = 1.0 h after increasing temperature to 190°C. Product composition is given in terms of mol%.

<sup>b</sup> Methyl ester of corresponding organic acid solvent.

<sup>c</sup> Reactor pressure at ambient temperature after the reaction.

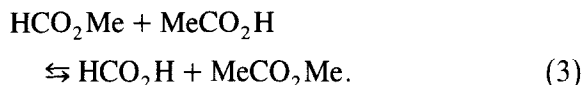
<sup>d</sup> Not applicable.

pose formic acid to carbon monoxide and water [18],



In formic acid solvent, the pressure in the autoclave rose to 130–140 atm during the reaction and the gaseous product was analyzed to be 75% carbon monoxide, 12% carbon dioxide, 12% hydrogen and < 1% methane by GC/MS (using molecular sieve 5A and Poraplot Q columns). However, in trifluoroacetic acid solvent, rather low conversion and turnover frequency were observed. In the previous communication [8], we proposed the high efficiency of formic acid as a solvent is partly because of its acidity to catalyse the hydrolysis of methyl acetate which is formed by the facile transesteri-

fication reaction of the unreacted methyl formate with the product acetic acid,



Considering the acidity alone, trifluoroacetic acid should give turnover frequencies superior to any other carboxylic acid. However, another transesterification product should be considered when an organic acid solvent other than acetic acid or formic acid is used,

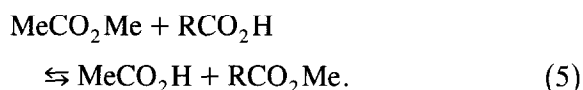
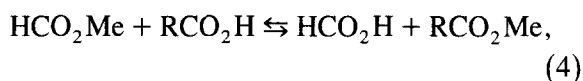


Table 3

Comparison of turnover frequency for the carbonylation of methyl ester of various organic acid catalysed by the Ir/MeI system at 190°C in the absence of initial carbon monoxide pressure<sup>a</sup>

Reactant	Methyl ester converted (%)	Selectivity (%)			Turnover frequency (h <sup>-1</sup> )
		MeCO <sub>2</sub> H	MeCO <sub>2</sub> Me	HCO <sub>2</sub> Me	
Methyl alcohol	100	9 <sup>b</sup>	—	16	170
Methyl formate	90	94	4	na <sup>c</sup>	1650
Methyl acetate	86	70	na <sup>c</sup>	13	1130
Methyl propionate	80	20	—	42	300
Methyl trifluoroacetate	85	51	11	28	970

<sup>a</sup> Methyl ester (200 mmol), IrCl<sub>4</sub> · H<sub>2</sub>O (0.054 mmol), MeI (17 mmol), formic acid solvent (18 ml), *t* = 2.0 h after increasing temperature to 190°C. Conversion and selectivity based on methyl ester converted are given in terms of mol% change of compounds and turnover frequency is given in terms of the moles of acetic acid and methyl acetate produced per h and per mol of Ir.

<sup>b</sup> From methyl iodide added.

<sup>c</sup> Not applicable.

Therefore, we analyzed the reaction medium without added iodide promoter. Table 2 shows that transesterification in the presence of iridium, presumably the first reaction occurring during the rearrangement reaction of methyl formate in a carboxylic acid solvent, gives the highest amount of methyl formate in formic acid as expected and the lowest in trifluoroacetic acid. However, transesterification of methyl acetate in various organic acid solvents gives the lowest amount of methyl acetate in formic acid and in trifluoroacetic acid. In other words, the stronger acid solvent tends to have more of its ester form. This result clearly indicates that the role of formic acid is to maintain most of methyl ester in the form of reactant methyl formate rather than side product methyl acetate.

The advantage of keeping methyl ester as methyl formate can be clearly seen by running the carbonylation reaction of various methyl esters or methyl alcohol under the same reaction condition with added iodide promoter (Table 3). It is found that the turnover frequency is considerably higher for methyl formate than any other methyl ester. Another interesting fact is that methyl alcohol is not carbonylated at all under our experimental condition only to give methane, carbon dioxide and some soot. Therefore, without initial carbon monoxide pressure the reaction mechanism must be considerably different

from the one in the presence of initial CO pressure.

## 2.2. Effect of phosphorus pentoxide

From the above findings, any acidic reaction condition that can maintain the concentration of methyl formate high and that of methyl acetate low should be sought for a catalytic system superior to previous ones. Since formic acid can be decomposed to carbon monoxide and water, Eq. (2), and the decomposition product water is detrimental to catalytic activity [9,15], a suitable candidate for an efficient promoter for the reaction might be an acid anhydride.

Phosphorus pentoxide is an anhydrous form of phosphoric acid. Table 4 shows that with only 2 g of phosphorus pentoxide turnover frequency surpasses previously reported values even though the reaction was carried out without initial CO pressure and in the absence of any solvent. Also, the reaction does not proceed without phosphorus pentoxide. Whether the roles of phosphorus pentoxide as a dehydrating agent and as the one we hoped it would play (vide supra) are fully accomplished or not is not clear. However, these results give a vague idea on the mechanism of rearrangement of methyl formate to acetic acid which is different from methanol carbonylation.

Iridium catalyst systems are considerably

Table 4  
Effect of phosphorus pentoxide on the isomerization of methyl formate catalysed by the Ir/MeI system at 190°C in the absence of initial carbon monoxide pressure<sup>a</sup>

P <sub>2</sub> O <sub>5</sub> (g)	HCO <sub>2</sub> Me converted (%)	Selectivity (%)		Turnover frequency (h <sup>-1</sup> )
		MeCO <sub>2</sub> Me	MeCO <sub>2</sub> H	
0.0	0	0	0	0
1.0	44	41	18	1210
2.0	77	36	28	2260
3.0	90	36	30	2760
4.0	96	27	45	3200
5.0	96	22	56	3360

<sup>a</sup> Methyl formate (490 mmol), IrCl<sub>4</sub> · H<sub>2</sub>O (0.054 mmol), MeI (17 mmol), *t* = 2.0 h after increasing temperature to 190°C. Conversion and selectivity based on HCO<sub>2</sub>Me converted are given in terms of mol% change of compounds and turnover frequency is given in terms of the moles of acetic acid and methyl acetate produced per h and per mol of Ir.

more complicated than other groups 9 and 10 metal catalyst systems and there is little agreement among the various investigations with respect to the kinetic effects of reaction parameter variations. There are apparently complex interactions among solvent, water, and iodide form. Therefore, extensive mechanistic studies need to be followed but these results are quite promising for the use of phosphorus pentoxide as an additive in catalyst systems for the rearrangement of methyl formate to acetic acid without the need for an initial CO pressure and in the absence of any solvent.

### 3. Experimental

#### 3.1. Materials

[Ir(cod)Cl]<sub>2</sub> (Strem), IrCl<sub>4</sub> · H<sub>2</sub>O (High Purity), methyl formate (Aldrich), iodomethane (Janssen), methyl acetate (Aldrich), *N*-methylpyrrolidone (Aldrich), propionic acid (Aldrich), acetic acid (Aldrich), formic acid (> 98%, Janssen), trifluoroacetic acid (> 98%, Janssen), methyl alcohol (Aldrich), methyl propionate (Aldrich), methyl trifluoroacetate (Aldrich), phosphorus pentoxide (Junsei), carbon monoxide (> 99.5%) are commercial products and were used without further purification.

#### 3.2. Typical procedure for catalytic rearrangement of methyl formate to acetic acid

All reactions can be carried out efficiently by adding a catalytic amount of IrCl<sub>4</sub> · H<sub>2</sub>O or [IrCl(COD)]<sub>2</sub>, MeI, and methyl formate with various acid solvents or phosphorus pentoxide into a glass liner in a Parr 125 ml autoclave equipped with a PID temperature controller. After being purged several times with CO, the reactor was heated to the desired temperature with stirring. After the required time, the liquid

phase was cooled, sampled, and analyzed by a Hewlett-Packard gas chromatograph with a thermal conductivity detector using *N*-methylpyrrolidone (NMP) as an internal standard. Since methyl formate can produce gaseous products, such as CH<sub>4</sub>, CO<sub>2</sub> and CO, by comparing methyl and acetyl portions of the reactants with those of products, we can discern whether methyl formate decomposes to methane and carbon dioxide in appreciable quantities under the experimental conditions.

### Acknowledgements

This research was supported by Korea Science and Engineering Foundation.

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