

Formic Acid Promotion of Transition-metal Catalysed Isomerization of Methyl Formate

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MeI-HCO₂H is an extremely effective promoter/solvent combination for the transition-metal catalysed conversion of methyl formate to acetic acid in the absence of initial carbon monoxide pressure.

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 role as a precursor to C-C bond formation in C₂₊ 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 isomerization [eqn. (1)] to the more valuable acetic acid has been investigated thoroughly.



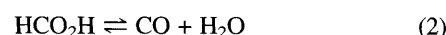
Satisfactory yields have been obtained employing transition-metal (Rh,⁴⁻⁶ Ir,⁷ Co,⁸⁻¹⁰ Ni,^{8,11-13} Ru,^{14,15} or Pd^{9,14,15}) complex catalysts and an iodide promoter under CO pressure in a liquid phase. Rhodium and iridium are the most active and selective catalysts. The activities and selectivities depend not only on the nature of the iodide used as a promoter⁶ but also on the solvent^{7,9,13} and the pressure of carbon monoxide employed which is necessary to stabilize the catalytic species. Selectivity into acetic acid and methyl acetate are generally good, formic acid being the major by-product observed with several catalysts.

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. In this paper, we describe our results that the addition of formic acid to transition-metal catalysts gives highly productive catalyst systems without the need for added carbon monoxide and we propose the possible role of the acid in the reaction. Reactions can be carried out efficiently by adding a catalyst and MeI in formic acid to methyl formate (200 mmol) in a glass liner in a Parr 100 ml autoclave equipped with a PID temperature controller. After being purged with CO several times, 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 CH₄, CO₂ and CO, by

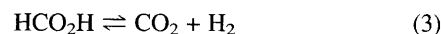
comparing methyl and acetyl portions of the reactants with those of products, we can discern whether or not methyl formate decomposes to methane and carbon dioxide in appreciable quantities under the experimental conditions.

Table 1 reveals that MeI-HCO₂H is an extremely effective promoter/solvent combination for the transition-metal catalysed conversion of methyl formate to acetic acid in the absence of carbon monoxide. Although *isomerization* of methyl formate does not consume CO stoichiometrically, it is usually carried out under CO, iridium being the only catalyst for which reaction proceeds without the need of an initial CO pressure, in the presence of propionic acid as a solvent.⁷ Therefore, the fact that not only iridium but also rhodium can catalyse the transformation of methyl formate to acetic acid without initial CO pressure is of interest. Also the initial turnover rate observed for rhodium or iridium catalysts is considerably higher than previously reported values (200-400 h⁻¹) though this is not the case for ruthenium or palladium catalysts (Table 1).

Since strong acids can decompose formic acid to carbon monoxide and water [eqn. (2)],¹⁶ this aspect was investigated in the present systems.



For iridium catalysts, the pressure in the autoclave rose to 130-140 atm after 2 h at 190 °C. The gaseous product was analyzed to be 75% carbon monoxide, 12% carbon dioxide, 12% hydrogen and < 1% methane by GC/MS (using molecular sieve 5 Å and Poraplot Q columns). Therefore, the highly effective catalytic activity of iridium might arise from its ability to efficiently decompose formic acid. To investigate the role of formic acid as a supplier of carbon monoxide *via* eqn. (2), the effect of initial carbon monoxide pressure on the activity of the Ir-MeI catalyst system in acetic acid was studied. As shown in Table 2 consideration of CO pressure alone is not sufficient to explain the exceptionally high turnover rate. Since formic acid can also be decomposed to hydrogen and carbon dioxide [eqn. (3)],¹⁷ we also studied the effect of hydrogen partial pressure on the activity in Ir-catalysed isomerization of methyl formate in acetic acid.



As shown in Table 2, the H₂ partial pressure appears to have no distinct effect on the reaction rate. Other decomposition

Table 1 Isomerization of methyl formate catalysed by various transition-metal catalyst systems in the absence of initial carbon monoxide pressure^a

Catalyst	HCO ₂ Me converted (%)	Selectivity ^b (%)		Initial turnover rate/h ⁻¹
		MeCO ₂ Me	MeCO ₂ H	
[Ir(cod)Cl] ₂ ^{c,d}	92	3	96	1670
IrCl ₄ ·H ₂ O	90	4	94	1650
[RhCl(C ₇ H ₈)] ₂ ^c	43	17	63	640
RhCl ₃ ·3H ₂ O	36	17	64	560
RuCl ₃ ·3H ₂ O	0	—	—	0
Pd(O ₂ CMe) ₂	16	0	28	79

^a Methyl formate (200 mmol), catalyst (0.054 mmol), MeI (17 mmol), HCO₂H solvent (18 ml), *t* = 2.0 h after increasing temperature to 190 °C. Turnover rate is given in terms of moles of acetic acid and methyl acetate produced per h and per mol of transition metal catalyst. ^b Selectivity is given in terms of mol.% and is based on HCO₂Me converted. ^c 0.027 mmol. ^d Cod = cycloocta-1,5-diene.

Table 2 Effect of initial CO-H₂ partial pressure on the isomerization of methyl formate catalyzed by the Ir-MeI system in acetic acid solvent at 190 °C^a

Initial CO-H ₂ partial pressure (bar)	HCO ₂ Me converted (%)	Selectivity (%)		Initial turnover rate/h ⁻¹
		MeCO ₂ Me	MeCO ₂ H	
40/0	66	35	29	800
80/0	78	31	37	990
120/0	75	31	39	960
80/10	77	27	46	1020
80/20	73	27	48	980

^a Methyl formate (200 mmol), [Ir(cod)Cl]₂ (0.027 mmol), MeI (17 mmol), acetic acid solvent (18 ml), *t* = 2.0 h after increasing temperature to 190 °C.

products of formic acid such as water^{7,13} or carbon dioxide¹⁸ seem to be detrimental to activity. Therefore, the high efficiency of formic acid as a solvent is not as a result of its gaseous decomposition products but possibly because of its acidity. Comparison of the results in Tables 1 and 2 shows that the mole percent of methyl acetate is considerably lower in the presence of formic acid. Since methyl acetate is hydrolysed to methanol and acetic acid, this reaction might be catalysed by formic acid.

Iridium catalyst systems are considerably more complicated than other Group 8 metal catalyst systems and little is known with respect to the kinetic effects of reaction parameter variations and there are apparently complex interactions among solvent, water, iodide form, and initial CO pressure.

Other roles of formic acid need to be studied further, but these results are quite promising for its use as a solvent in catalyst systems for the isomerization of methyl formate to acetic acid without the need for an initial CO pressure, showing a very high turnover rate significantly improved over usual values obtained with other catalysts in the presence of CO.

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