Methyl Formate Synthesis by Hydrogenation of Supercritical Carbon Dioxide in the Presence of Methanol

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Addition of methanol in the homogeneous ruthenium-catalysed hydrogenation of supercritical carbon dioxide to formic acid results in thermal esterification, producing methyl formate in higher yields and at lower temperatures than previously reported.

The hydrogenative fixation of CO_2, a process which is appealing for both scientific and environmental reasons, is particularly efficient if the CO_2 is in the supercritical state. This observation has been made recently for syntheses of formic acid[1,2] and *N,N*-dimethylformamide,[3] but may be a more general phenomenon. We have now found that the synthesis of methyl formate from supercritical CO_2 ($scCO_2$), H_2 and methanol can be performed at lower temperatures and with higher yields than previously reported.

As we have described,[1] the hydrogenation of CO_2 in the presence of NEt_3 and catalyst precursors $RuH_2(PMe_3)_4$ **1** or $RuCl_2(PMe_3)_4$ **2** [eqn. (1)] is faster in $scCO_2$ than in liquid

$$CO_2 + H_2 \xrightarrow[NEt_3]{\text{catalyst}} HCO_2H \qquad (1)$$

solvents such as THF. The high rate of reaction is attributed to favourable mass transfer effects, high solubility of H_2 and weak solvation of the catalyst in $scCO_2$ compared to liquid solvents.

In the course of studies of the effect of additives on the rate of the reaction,[4] we have found that the presence of methanol in $scCO_2$ causes thermal esterification of the formic acid to methyl formate [eqn. (2)], as has been found in

$$CO_2 + H_2 + ROH \xrightarrow[NEt_3]{RuCl_2(PMe_3)_4} HCO_2R + H_2O \qquad (2)$$

subcritical systems, typically at 100–170 °C.[5–12] The result in $scCO_2$ at 80 °C is efficient synthesis of methyl formate from CO_2, H_2 and methanol with yields of up to 3 500 TON‡ (mol product per mol catalyst; Table 1, entry 1), two orders of magnitude greater than the only literature result, *ca.* 40 TON[12] at this low temperature and one order of magnitude greater than the most efficient system at any temperature. The high TON values obtained in the supercritical system are indicative of the high activity and long lifetime of the catalyst under these conditions, rather than significantly altered thermodynamics. The lower temperatures required may be partly owing to the high rate[1] of CO_2 hydrogenation in the supercritical state.

The reactions typically were performed in a 50 ml steel reactor at 80 °C with 5.0 mmol NEt_3, 13 mmol MeOH and 3 µmol of **2** dissolved in a supercritical mixture of H_2 (80 atm at reaction temperature) and CO_2 (total pressure 200–210 atm). This mixture of reactants forms a single supercritical phase. The reaction was stopped by cooling the reactor to −78 °C, venting the H_2 and thawing the reactor to release the CO_2. The products were identified and analysed by ^1H NMR spectroscopy in $CDCl_3$.§ The product mixture composition for the reaction at 80 °C is plotted in Fig. 1 as a function of reaction time. Because of an induction period, the yield of formic acid after 1 h is neither large nor reproducible, ranging up to 360 TON. At this time, no methyl formate is observed. During the second hour, the formic acid reaches an equilibrium concentration of 4.0 mmol (0.80 mol per mol of amine), while methyl formate production begins at a TOF‡ (TON per h) of 68. The selectivity for methyl formate increases with reaction time. This is consistent with a two-step process[11,12] of CO_2 hydrogenation [eqn. (1)] followed by thermal esterification [eqn. (3)]:

$$HCO_2H + ROH \rightarrow HCO_2R + H_2O \qquad (3)$$

Esterification under basic conditions is rarely used in organic synthesis; strong acid is usually added as a catalyst. However, in the present case, the solution is basic and the esterification must take place thermally. Amine is an inhibitor of the esterification, but its presence is required for reasonable yields in the

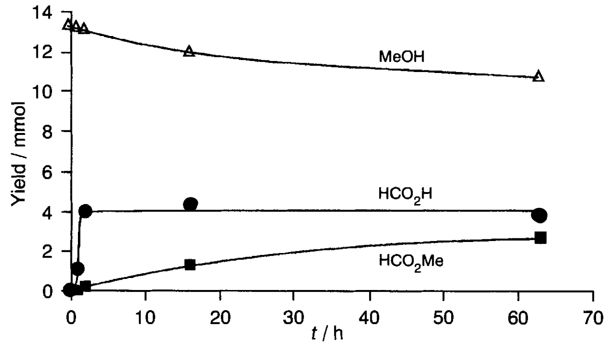

Fig. 1 Time dependence of the product yields after reactions at 80 °C in a 50 ml reactor with 80 atm H_2, 130 atm CO_2, 5.0 mmol NEt_3, 3–4 µmol $RuCl_2(PMe_3)_4$ and 13 mmol MeOH

Table 1 The production of alkyl formates in $scCO_2$[a]

						HCO_2H		HCO_2R		Total[b]	
Entry	Ru/µmol	Amine/mmol	ROH/mmol	*T*/°C	*t*/h	mmol	TON	mmol	TON	TON	Selectivity (%)
1	2.9	30[c]	80[c]	80	64	20	6 800	10.4	3 500	10 000	34
2	3.2	30[c]	80[c]	50	60	21	6 700	0.84	270	7 000	4
3	3.4	5.0	13	100	16	0.85	250	0.51	150	400	37
4	2.7	5.0	13	100[d]	17[d]	1.4	500	1.0	370	870	42
5	4.2	5.0	13	80	16	4.5	1 100	1.4	330	1 400	24
6	2.3	0.72	13	80	16	0.29	130	0.094	41	170	24
7	2.7	0.72[e]	13	80	16	0.23	86	0.084	31	120	26
8	2.5	5.0	14[f]	80	14	3.5	1 400	0.49	190	1 600	12

[a] With $RuCl_2(PMe_3)_4$, NEt_3, MeOH, H_2 (80 atm) and CO_2 (total pressure 200–210 atm) in a 50 ml reactor. Data rounded to 2 digits. [b] Formic acid and methyl formate combined yield. [c] In a 300 ml reactor. [d] First 2 h at 80 °C. [e] With *N*-methylpiperidine rather than triethylamine. [f] With ethanol rather than methanol.

hydrogenation step. In the absence of amine, a low yield of methyl formate is obtained, albeit with complete selectivity [Fig. 2(*a*)]. Use of a weak base such as pyridine, tributylphosphine oxide or a Brønsted acid, perfluorosulfonic acid resin (Nafion 511) in place of NEt$_3$ was equally ineffective, giving low yields of methyl formate, again with complete selectivity. In the presence of NEt$_3$ (Table 1, entries 5 and 6) or *N*-methylpiperidine (entry 7), the yield is excellent. Ethyl formate can be obtained by this method, but the yield is reduced (entry 8).

At 50 °C and with methanol, we have obtained a yield of 270 TON of methyl formate (Table 1, entry 2). This is the lowest temperature at which this catalytic reaction has ever been performed. The two steps of the reaction have different temperature requirements. The esterification requires higher temperatures, while the hydrogenation step [eqn. (1)] has higher yields at lower temperatures.[4] Thus the selectivity for methyl formate rather than formic acid increases with temperature, but the maximum yield of methyl formate is obtained at an intermediate temperature of approximately 80 °C [Fig. 2(*b*)]. A reaction at 80 °C for 2 h followed by 100 °C for 15 h had the higher selectivity usually attained at 100 °C without any loss of yield (entry 4).

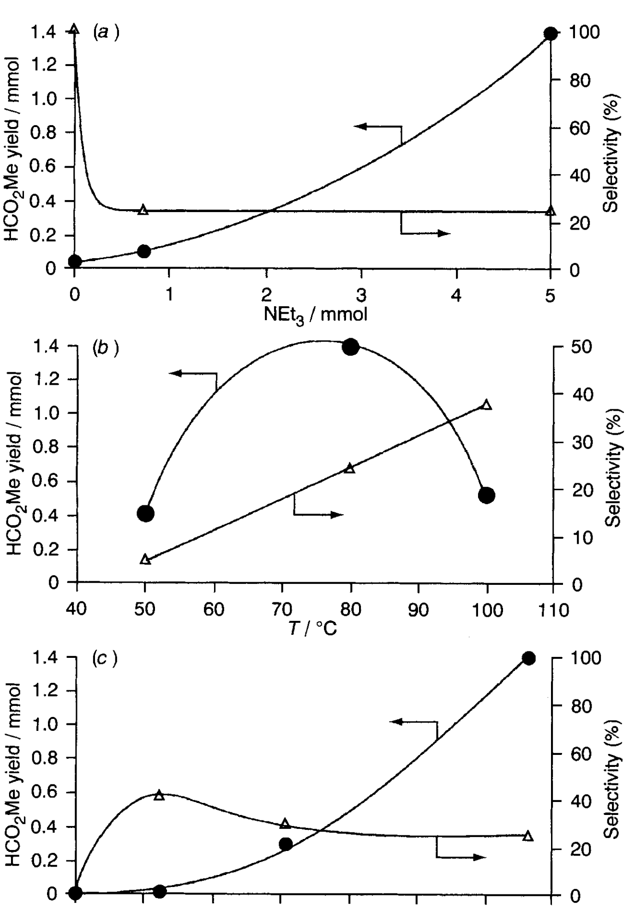

Fig. 2 The dependence of yield and selectivity for methyl formate on (*a*) the amount of amine, (*b*) the temperature or (*c*) the amount of methanol. *Conditions*: 13 mmol MeOH, 5 mmol NEt$_3$, 3–4 μmol RuCl$_2$(PMe$_3$)$_4$, 80 °C, 80 atm H$_2$, total pressure 200–210 atm, 16 h, unless otherwise stated

Methanol plays a number of roles in this reaction. In addition to its roles as the esterification agent in the second step and possibly as a kinetic promoter of the hydrogenation of scCO$_2$,[4] it also improves the final yield of formic acid at 80 °C. Attempts to prepare formic acid from scCO$_2$ at this temperature in the absence of additives such as methanol have been highly unsatisfactory, although this reaction proceeds rapidly at 50 °C.[1] A possible explanation for the favourable effect of methanol and other polar solvents on reaction (1) has been suggested.[13] A consequence of this increasing yield of formic acid is an increasing yield of methyl formate with higher methanol concentrations [Fig. 2(*c*)].

In conclusion, the use of supercritical conditions for the homogeneous hydrogenation of CO$_2$ and subsequent thermal esterification generates methyl formate at the highest yields and lowest temperatures yet reported. It is possible that the hydrogenation of CO$_2$ could, given the optimum conditions and catalyst, compete with carbonylation of methanol[14] as the industrial method for the production of methyl formate.

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Footnotes

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‡ TON = turnover number. TOF = turnover frequency.

§ Toluene was added as a standard. Identification and yields of formic acid and methyl formate were confirmed by GC–MS for the reactions which gave the highest yields of methyl formate at 50 and 80 °C.

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