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The cobalt-catalyzed conversion of methyl formate into acetic acid

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Abstract

Methyl formate can be selectively converted into acetic acid in quantitative yield by use of cobalt catalysts. Essential requirements include the presence of a tertiary amide as solvent, of an ionic iodide as promoter, a sufficiently high CO pressure (above 100 bar), and a reaction temperature between 160 ° and 180 ° C. Other alkyl formates are not transformed into acids. The reaction probably involves, as the key step, the reduction of the cobalt(II) catalyst to a cobaltate species, which is then transformed into alkyl and acylcobalt species. The latter reacts with lithium formate, formed *in situ*, to afford a mixed anhydride, decarbonylation of which yields acetic acid with regeneration of CO.

Introduction

In a previous study we found that the hydrocarbonylation of methyl orthoformate catalyzed by the cobalt acetate–lithium iodide system yielded acetic acid as the major by-product [1]. The acid was clearly generated via a two-step process consisting of hydrolysis of the orthoformic ester to methyl formate followed by "isomerization" of the latter. This result is in accordance with earlier reports of the iridium [2] and rhodium [3] catalyzed syntheses of acetic acid from methyl formate. We previously demonstrated that cobalt compounds show comparable activity under higher CO pressure and in specific solvents such as tertiary amides [4]. We describe here the results of a study of the effects of various parameters aimed at identifying the reaction path.

Experimental

Methyl formate and *N*-methylpyrrolidone were dried over molecular sieves. Experiments were carried out using shaken batch autoclaves designed in our laboratory. In a typical run, 66 mg (0.26 mmol) of cobalt acetate tetrahydrate and 400 mg (3 mmol) of lithium iodide were dissolved in 2.5 ml *N*-methylpyrrolidone under argon. After addition of 2.5 ml methyl formate, the autoclave was closed, pressurized with carbon monoxide and heated to 175 ° C and kept at this temperature for 2 hr. The reactor was then cooled and opened and the liquid mixture withdrawn.

GLC analysis was performed using diglyme as a standard. Typically conditions were as follows. Hewlett Packard 5700A (catharometer), injection (230 °C), detection (250 °C), column A (Hayesepp S), length (2 m), Ø (1/8″), 50–240 °C, 4 °C min^{-1}, column B (Chromosorb 101), 60–230 °C, 8 °C min^{-1} (column B was used mainly for the analysis of formic acid).

Results

The catalyst used throughout this study was cobalt acetate tetrahydrate with either lithium iodide or potassium iodide as promoter. The presence of the alkali iodide as promoter is crucial, as indicated in the earlier study [4].

Solvent effect

Methyl formate undergoes only little conversion into acid in the absence of a solvent. Several solvents were therefore examined, and as shown in Table 1, the solvent was found to play a major role. Hydrocarbons, glymes and tertiary amines are inappropriate, giving methanol as the main product, either by decarbonylation of methyl formate or its hydrolysis. Interestingly, in *N*-methylpiperidine methyl formate is decomposed to methanol and methane.

Tertiary amides such as dimethylformamide and, even better, *N*-methylpyrrolidone (NMP) selectively convert methyl formate into acetic acid. Such solvents induce a rate acceleration that limits the formation of by-products.

The promoting effect of an acid was observed in the iridium catalyzed conversion of methyl formate [2]. However, this is not the case here, and the promotional effect must be ascribed to the tertiary amide.

The volume of solvent employed can influence the reaction, as illustrated in Fig. 1. For low NMP : formate ratios, formic acid is produced. However, with a 1 : 5

Table 1

Conversion of methyl formate into acetic acid and the effect of the solvent [a]

Solvent	Conversion (%)	Selectivity [b] (%)	
		AA	MA
none	12	19	15
toluene	5	0	nd
tetraglyme	28	6	12
cyclohexanone	5	20	20
triethylamine	10	0	37
pyridine	70	0	30
N-methylpiperidine	91	0	5
N, *N*-dimethylformamide	89	85	15
NMP	96	91	9
NMP + acetic acid	85	88	12

[a] Conditions: methyl formate (42 mmol), cobalt acetate (0.25 mmol), solvent (2.5 ml), CO (150 bar), *T* (180 °C), *t* (2 h). [b] AA (acetic acid), MA (methyl acetate).

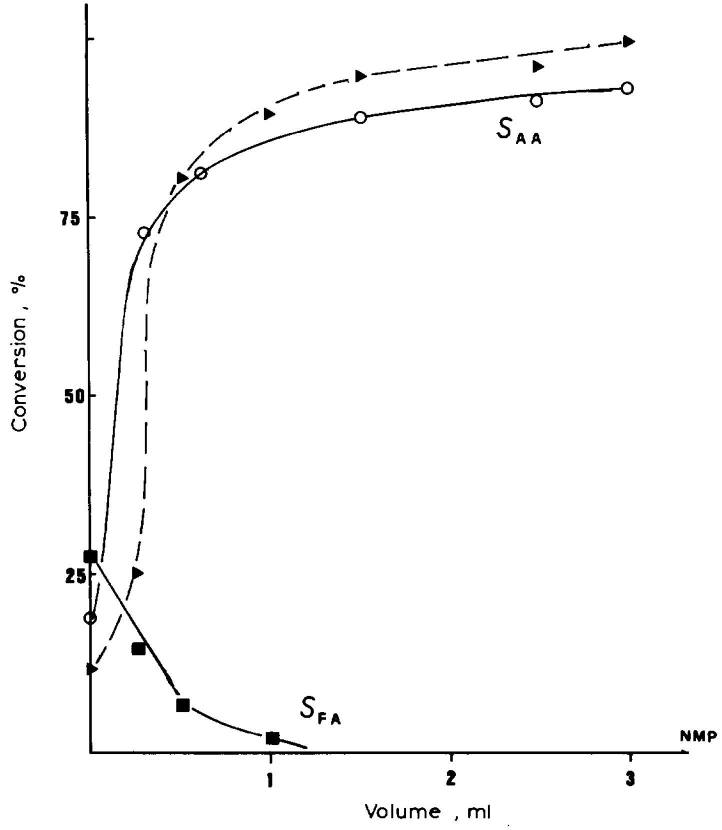


Fig. 1. Cobalt-catalyzed conversion of methyl formate into acetic acid and the effect of *N*-methylpyrrolidone (NMP). (S_{AA}, S_{FA}: selectivity for acetic acid and formic acid, respectively). Other conditions as in Table 1.

mixture, conversion and selectivity with respect to acetic acid increase sharply. Optimal values are reached for approximately equivalent volumes of solvent and substrate (Fig. 1).

Effect of promoters

The presence of a promoter is essential; no acetic acid is formed in the absence of promoters. Ionic iodides are suitable additives for the reaction. All the alkali metal iodides give comparable activity and selectivity results. Even molecular iodine can promote the reaction, presumably via formation of hydrogen iodide. On the other hand, in contrast to observations in the rhodium catalyzed reaction [3], methyl iodide is relatively ineffective.

The conversion and the selectivity are not significantly affected by the LiI concentration, though the latter should be kept as high as possible (the optimal catalyst: LiI ratio is about 1 : 10). In contrast, the concentration of the catalytic system must be correctly chosen. Increasing concentrations give higher initial rates; but lead to a loss in selectivity (Table 3).

Table 2

Conversion of methyl formate into acetic acid and the effect of promoters [a]

Promoter	Activity [b]	Selectivity (%) AA
none	0	–
CH_3I	20	73
I_2	90	89
LiI	128	94
NaI	117	92
KI	120	90
RbI	123	95

[a] Conditions as in Table 1. NMP is the solvent. [b] mol AcOH/mol cobalt/h.

The effects of pressure and temperature

As reported previously, the activity of the cobalt catalyst is very dependent on both the applied CO pressure and the temperature (Table 4). Low pressures and temperatures produce small turnovers and also lower the selectivity for conversion into acetic acid. This is due to the competitive formation of by-products, particularly methyl acetate and formic acid.

To avoid parallel reactions, it is therefore necessary to achieve a rapid carbonylation rate. This is accomplished by use of a reaction temperature of 175 °C and CO pressures above 100 bar. These effects may be related to the stability of active cobalt species such as $Co_2(CO)_8$ and $[Co(CO)_4]^-$ (*vide infra*), as in other cobalt-catalyzed carbonylations [5].

Effect of reaction time

The reaction has a short induction period, but after 20 minutes reaction, methyl formate is converted into 50% with 63% selectivity for acetic acid; complete conversion into the acid is achieved after 3 h (99% selectivity with respect to AcOH) (Fig. 2).

It should be noted that under conditions we use (equimolar volumes of NMP and formate), almost the only by-product is methyl acetate which is progressively converted into acetic acid, as illustrated in Fig. 2.

Table 3

Conversion of methyl formate into acetic acid. Influence of the concentration of catalyst and promoter [a]

$Co(Oac)_2 \cdot 4H_2O$ (mmol)	LiI (mmol)	Conversion (%)	Selectivity (%) AA
0.26	0.7	88	85
0.26	1.4	88	86
0.26	3.0	96	91
0.13	1.5	72	76
0.26	3.0	96	91
0.52	6.0	88	68

[a] See Table 1.

Table 4

Conversion of methyl formate into acetic acid and effect of pressure and temperature [a]

P(CO)	*T* (°C)	Conversion %	Selectivity % AA	Activity
45	175	48	38 [b]	20
85	175	80	64	nc
150	175	96	91	128
250	175	100	96	nc
150	160	35	26 [b]	15
150	175	96	91	128
150	185	100	63 [b]	94

[a] Conditions as in Table 1. [b] By-products are formic acid, methanol, methane, and CO_2.

Extension to other alkyl formates

We were interested in the possible generalization of the process and so subjected other alkyl formates to the same conditions, but the results were not promising

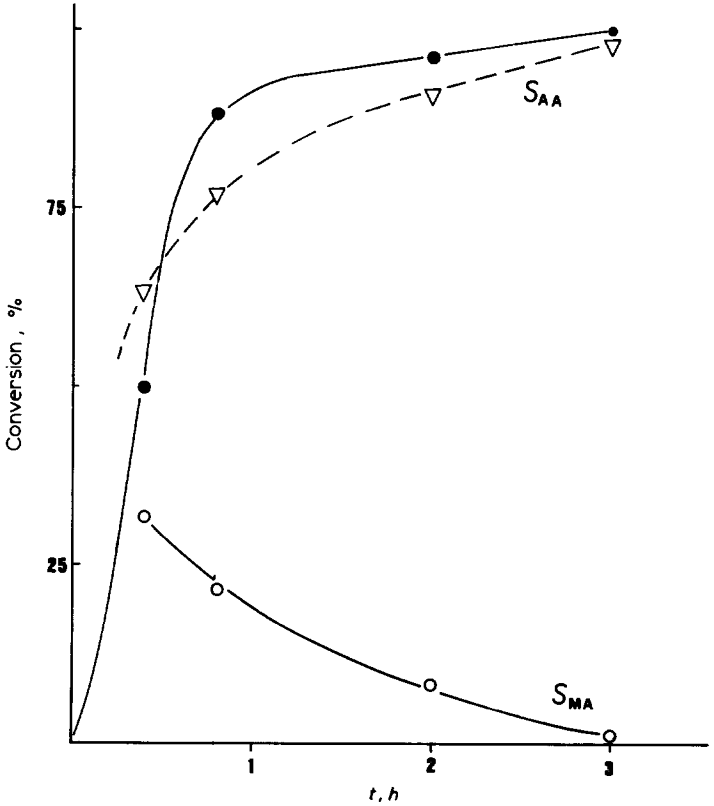


Fig. 2. Cobalt-catalyzed conversion of methyl formate into acetic acid and the effect of reaction time. Other conditions as in Table 1 (the solvent was *N*-methylpyrrolidone). (S_{AA}, S_{MA}: selectivity for acetic acid and methyl acetate, respectively).

Table 5

Cobalt-catalyzed reaction of various alkyl formates (HCOOR) [a]

Formate R	Catalyst	Conversion %	Selectivity %		
			ROH	RCOOH	RCOOR
C_2H_5	Co	30	1	54	45
	Pd	12	26	18	38
n-C_3H_7	Co	23	14	16	51
	Pd	11	57	6	19
n-C_4H_9	Co	48	6	54	27
i-C_4H_9	Co	11	73	0	0
	Pd	2	100	0	0

[a] Alkyl formate (2.5 ml), NMP (2.5 ml), $Co(OAc)_2 \cdot 4H_2O$ (0.26 mmol) or $Pd(OAc)_2$ (0.26 mmol), LiI or KI (3 mmol), T (175° C), CO (150–300 bar), t (4 h).

(Table 5). The reactions proceeded very slowly (especially that of isobutyl formate), and so the acids were produced in low yield; in the case of isobutyl formate no acid at all could be detected. Increase in the CO pressures did not improve the results, nor did the replacement of the cobalt compound by a palladium catalyst, which was found to be twice as active as cobalt in the conversion of methyl formate to acetic acid [4].

Simultaneous formation of derivatives of formic and acetic acid

Under the homogeneous catalytic conditions used methyl formate can be employed as the starting material for the synthesis of both acetates and acetamides. However, the reaction is not selective, because the reaction conditions also induce the formation of formates or formamides (transesterification or aminolysis) (Table 6).

$$HCOOCH_3 + ROH \longrightarrow \begin{cases} HCOOR \\ + \\ CH_3COOR \end{cases}$$

$$HCOOCH_3 + RNH_2 \longrightarrow \begin{cases} HCONHR \\ + \\ CH_3CONHR \end{cases}$$

Acetates and formates are produced in nearly equal yields. With amines, methyl formate reacts preferentially to yield formamides (formylation reaction) [6].

Table 6

Formic and acetic acid derivatives formed in the reaction of methyl formate with alcohols or amines [a]

Substrate	Yields of derivatives (%)	
	acetic acid	formic acid
1-propanol	34 [b]	28 [b]
1-butanol	33 [b]	30 [b]
2-methyl-1-propanol	32 [b]	34 [b]
n-propylamine	29 [c]	71 [c]

[a] Conditions of Table 1. Solvent (NMP). [b] Ester. [c] Amide.

Discussion

The present study outlines the importance of three controlling factors: i) the presence of the cobalt catalyst; ii) the nature of the promoting agent; and iii) the use of a basic solvent such as *N*-methylpyrrolidone. CO pressure and temperature are important secondary parameters.

Depending on the catalyst used, several mechanisms have been proposed for the conversion of methyl formate to acetic acid. Bryant favoured the decarbonylation of methyl formate to methanol followed by carbonylation [7]. However, this cannot be the case here, since cobalt complexes are generally poor decarbonylation catalysts [8] and there is no acid formation from higher formate esters. Wegman suggested an alternative route for the rhodium catalyst via a mixed anhydride produced by reaction of lithium formate and acetyl iodide formed *in situ* [3].

For the cobalt-catalyzed reaction, we suggest that the initial step is the reaction of methyl formate with LiI:

$$HCOOCH_3 + LiI \rightleftharpoons CH_3I + HCOOLi \qquad (1)$$

This reaction is known to occur with organic esters [9] and we have detected methyl iodide in the reaction mixture.

The second step would be the crucial one, the reduction of the cobalt(II) catalyst to a cobaltate ion. This reaction is known to occur under base-catalyzed conditions, as shown by Steinmetz [10]. The base here is NMP and the counterion could be Li^+ or Co^{2+} formed via the sequence:

$$Co^{2+} \underset{\substack{H^+ \\ \text{excess}}}{\overset{CO}{\rightleftharpoons}} Co_2(CO)_8 \xrightarrow{\text{base catalysis}} Co^{2+}[Co(CO)_4{}^-]_2 \qquad (2)$$

The salt $Li[Co(CO)_4]$ was shown to be formed in a complex reaction involving, *inter alia*, cobalt acetate, lithium iodide, and CO [11]. The IR spectrum of the mixture after the reaction shows the characteristic bands of $Co(CO)_4{}^-$ (1895–1904 cm^{-1}). The occurrence of reaction 2 accounts for the need to use a high CO pressure, which prevents decomposition of $Co_2(CO)_8$ and of $Co(CO)_4{}^-$ at the high reaction temperature.

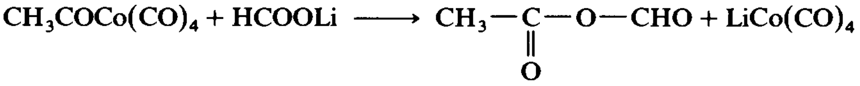
Following the reactions shown in equations 1 and 2, it is easy to envisage the classical oxidative addition followed by acylation of the alkyl cobalt species:

$$CH_3I + Co(CO)_4{}^- \longrightarrow CH_3Co(CO)_4 + I^- \qquad (3)$$

$$CH_3Co(CO)_4 \xrightarrow{CO} CH_3COCo(CO)_4 \qquad (4)$$

The difficulty of forming the alkyl-cobalt bond with alkyl groups other than the methyl group may account for the disappointing results shown in Table 5.

The acylcobalt species in eq. 4 then reacts further with lithium formate formed in eq. 1 according to:



$$CH_3COCo(CO)_4 + HCOOLi \longrightarrow CH_3-\underset{\substack{\| \\ O}}{C}-O-CHO + LiCo(CO)_4 \qquad (5)$$

The mixed anhydride is very unstable under the reaction conditions [12], and decomposes into acetic acid with liberation of carbon monoxide [3]:

$$CH_3COOCHO \longrightarrow CH_3COOH + CO \qquad (6)$$

In this scheme it is easy to recognize the roles of LiI, CO pressure, and solvent (NMP). The presence of water raises the reaction rate, as shown by the effect of using the hydrated cobalt catalyst $Co(OAc)_2 \cdot 4H_2O$; the conversion and the selectivity for the isomerization are increased from 72 to 96% and 62 to 91% by switching from $Co_2(CO)_8$ to $Co(OAc)_2 \cdot 4H_2O$. Initial addition of water in the $Co_2(CO)_8$ catalyzed reaction (the amount of H_2O added corresponding to that contained in cobalt acetate tetrahydrate) raises the yield of acetic acid to 100%, thus bringing about complete and fully selective reaction.

In conclusion, like the recently reported nickel-tin catalytic system [13], cobalt compounds can replace the costly rhodium and iridium catalysts in the conversion of methyl formate into acetic acid.

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