New efficient catalytic system for hydroxycarbonylation without CO gas

Jean-Pierre Simonato*

Rhodia Recherches, Centre de Recherche de Lyon, Groupe Catalyse, 85 Avenue des Frères Perret, Saint Fons 69192, France

Abstract

A new rhodium-based catalytic system has been found to allow hydroxycarbonylation to proceed in good yield without the need of CO gas, without solvent and at moderate temperatures.
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1. Introduction

Amongst C1 synthons used in fine organic chemistry, alkyl formates have been the focus of intensive researches in recent years for the direct synthesis of carboxylic esters from alkenes in the absence of carbon monoxide [1–5]. Formamides, which lead to amides, have also been studied [6–8]. The use of such C1 synthons is of interest since it gives rise to reactions similar to carbonylation reactions while preventing handling of the highly toxic and explosive CO gas (Scheme 1).

Surprisingly, formic acid has not been thoroughly investigated even though it may allow the direct synthesis of carboxylic acids from alkenes or alcohols. There are very few examples dealing with the conversion of alkenes to carboxylic acids using formic acid. The Koch–Haaf acid-catalysed process leads mainly to branched products due to carbocationic rearrangements, with inevitable oligomerization [9,10]. Kolom-
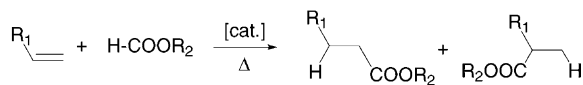
Scheme 1.

nikov et al. claimed a 10% yield for the RhCl(PPh$_3$)$_3$ catalysed addition of formic acid to cyclohexene [11]. Alper and co-workers described a remarkable palladium catalyst for hydroxycarbonylation of alkenes and alkynes by formic acid which however required the initial presence and thus the handling of CO gas for the catalysis to proceed [12–15]. Iridium-based catalyst systems were developed by Drury and Williams [16] and Pruett and Burke [17] for such a reaction. Recently, we found that this process could be easily extended to other substrates such as cycloalkenes, alcohols or esters with high yields [18–20]. Nonetheless, this reaction requires rather high temperatures, usually above 160 °C, that prevents its use for thermosensitive molecules. We report herein promising preliminary results on a new efficient catalytic system for hydroxycarbonylation using only formic acid as the C1 source and avoiding CO necessity.

* Tel.: +33-4-7289-6520; fax: +33-4-7289-6890.
E-mail address: jean-pierre.simonato@eu.rhodia.com
(J.-P. Simonato).

Table 1
Hydroxycarbonylation with formic acid

Entry	Substrate	Solvent	T (°C)	t (h)	Rh (mol%)	PPh$_3$/Rh (eq.)	Product	Yield[a] (%)	$n/(n + iso)$[b] (%)
1	Cyclohexene	AcOH	190	5	4	0	Cyclohexane	43	–
2	Cyclopentene	AcOH	190	2	2	6	Cyclopentane carboxylic acid	91	–
3	Cycloheptene	AcOH	190	2	2	6	Cycloheptane carboxylic acid	83	–
4	Cyclohexene	AcOH	190	2	2	6	Cyclohexane carboxylic acid	96	–
5	Cyclohexene	–	190	3	1	4	Cyclohexane carboxylic acid	94	–
6[c]	Cyclohexene	–	190	2	2	6	Cyclohexane carboxylic acid	20	–
7	Cyclohexene	–	110	24	2	4	Cyclohexane carboxylic acid	73	–
8	Cyclohexene	–	100	72	2	4	Cyclohexane carboxylic acid	69	–
9	Cyclohexanol	–	190	3	1	6	Cyclohexane carboxylic acid	37	–
10[d]	Cyclohexanol	–	190	3	1	6	Cyclohexane carboxylic acid	76	–
11	1-Hexene	–	160	2	1	4	Heptanoic acid[e]	55	77
12[d]	1-Hexene	–	160	2	2	4	Heptanoic acid[e]	88	71
13[d]	1-Hexene	–	110	12	2	4	Heptanoic acid[e]	54	79
14	2-Hexene	–	160	5	1	4	Heptanoic acid[e]	81	69
15	3-Hexene	–	160	5	1	4	Heptanoic acid[e]	81	66
16	2-Hexanol	–	190	3	1	4	Heptanoic acid[e]	73	63

The reactions were carried out with 4–6 MeI/Rh in a 30 ml HB2 reactor under autogenous pressure (which is lower than 30 bar).

[a] GC yield using internal standard.

[b] Linearity = (linear product/branched + linear products) × 100.

[c] CO (45 bar) and H_2O (1.1 eq.) used instead of formic acid.

[d] 1% pTsOH added.

[e] Major product.

2. Experimental

Hydroxycarbonylation of cyclopentene (Table 1, entry 2): cyclopentene (1.00 g, 14.7 mmol), pure formic acid (2.71 g, 58.9 mmol), acetic acid (3.53 g), [RhCl(CO)$_2$]$_2$ (59 mg, 0.15 mmol), methyl iodide (0.22 g, 1.6 mmol) and triphenylphosphine (462 mg, 1.76 mmol) were placed into a 30 ml HB2 autoclave. The autoclave was sealed and a temperature reaction of 190 °C was set. After a reaction time of 120 min, the autoclave was cooled to room temperature and depressurised. The homogeneous solution was analysed by gas chromatography using internal standards (Varian 3400 FID; column Stabilwax DA 15 m, 0.53 mm, 0.25 μm).

3. Results and discussion

Amongst several metallic precursors examined, rhodium was found to be a suitable metal source. The oxidation state of the rhodium precursor was of limited impact since [Rh^{I}Cl(CO)$_2$]$_2$, [Rh^{II}(OAc)$_2$]$_2$ and Rh^{III}Cl$_3$ gave nearly identical results. Addition of iodide was shown to have a positive effect by stabilising the catalytic species against precipitation and increasing its activity. A minimum of four iodide per rhodium was necessary to fully stabilise the catalyst. We found that the best iodide source was methyl iodide, which is carbonylated in situ into acetic acid according to Scheme 2 (confirmed by GC/MS analysis) [21].

The catalysis works without phosphines (entry 1) but these ligands were found to have an accelerating effect. The best compromise (activity/selectivity/cost) was obtained with triphenylphosphine. Bidentate phosphines such as 1,2-bis-(diphenylphosphino)-methane, 1,2-bis-(diphenylphosphino)-ethane and 1,2-bis-(diphenylphosphino)-propane gave acids in only 1–4% yield, whereas 1,2-bis-(diphenylphosphino)-

$$HCOOH \xrightarrow{\Delta,\ H^+} CO + H_2O$$

$$CH_3\text{-}I + CO + H_2O \xrightarrow{\Delta,\ [Rh]} CH_3COOH + HI$$
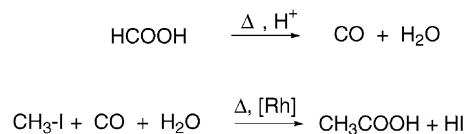
Scheme 2.

butane and 1,2-bis-(diphenylphosphino)-pentane gave results in the same range than those obtained with triphenylphosphine, probably through hemilability phenomenon (at P/Rh ratio = 6). No ligand synergism, as mentioned for palladium catalysis, between mono and diphosphines was observed [13]. It is also noteworthy that replacement of formic acid by carbon monoxide and water leads to a much lower yield (Table 1, entries 5 and 6).

Contrary to the previous iridium system which needed solvent to prevent iridium reduction by formic acid into the inactive $Ir_4(CO)_{12}$ species [22,23], the rhodium-based catalytic system gives identical results without solvent for cyclohexene and even better yields for 1-hexene hydroxycarbonylation (Table 1, entries 4, 5 and 11). Obviously, this is interesting in the development of solvent-free reactions, but is also advantageous from an industrial point of view since higher volumetric efficiency allows larger amount of products to be made with lower investment.

First experiments at lower temperatures gave acceptable results, even at 100 or 110 °C (Table 1, entries 7, 8 and 13) with longer reaction time. Addition of some acidic species (e.g. *para*-toluenesulfonic acid) in the medium was found to accelerate the overall kinetics of the reaction, presumably through catalytic decomposition of formic acid into water and carbon monoxide (Scheme 3, Table 1, entries 10 and 12) [24–26].

An intrinsic advantage of the metallocatalyzed hydroxycarbonylation method with respect to the acid-catalysed process is that mainly linear carboxylic acids are obtained. Even internal olefins like 2-hexene and 3-hexene were converted mostly into linear acids, this system promoting also double bond isomerisation (Table 1, entries 14 and 15). The reaction was also found to proceed well with alcohols (Table 1, entries 9, 10 and 16). Moreover, this system provides a new easy route to cycloalkane carboxylic acids, which are not readily accessible in one step from the corresponding cycloalkenes or cycloalcohols (Table 1, entries 2, 3, 4 and 9).

4. Conclusions

In conclusion, the results presented herein show that this new catalytic system allows hydroxycarboxylation to proceed in good yields without handling and introduction of CO gas into the reactor, without solvent and at moderate temperatures. It is of interest for fine chemical synthesis both on laboratory scale since it does not require expensive facilities, up to industrial processes which can be carried out using this technique in a standard polyvalent type unit.

Acknowledgements

$$HCOOH \xrightarrow{\Delta, H^+} CO + H_2O \quad (1)$$

Scheme 3.

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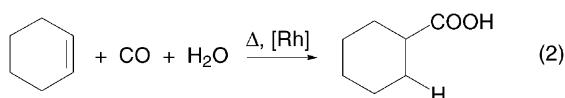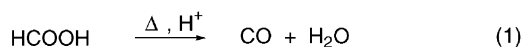
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