

Iridium–formic acid based system for hydroxycarbonylation without CO gas

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Abstract

A simple method for hydroxycarbonylation of alkenes or alcohols substrates which avoids CO gas handling is reported. The proposed formic acid–iridium based system appears very attractive due to very good chemical performances for such a reaction and high stability of the catalyst. This reaction was developed for industrial purposes, but is also of interest for small scale syntheses, since it does not require expensive equipments and can be carried out easily. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The carbon monoxide chemistry has been extensively studied, leading to a wide range of methods used in small scale organic syntheses up to industrial processes [1–3]. Despite the versatility of carbonylation reactions, carbon monoxide suffers from major drawbacks that restrict its utilization. From an industrial point of view, the cumbersome handling of this toxic gas necessitates very expensive facilities which prevent its use for most of fine chemical productions.

An alternative process equivalent to a carbonylation reaction which avoids carbon monoxide introduction into the reactor and that can be used in standard polyvalent type units would be of great interest. Of

course, catalyst cost, stability and productivity should also fulfill economical requirements.

It is known that formic acid undergoes dehydration into carbon monoxide and water at elevated temperatures and under acidic conditions [4,5]. Some attempts have already been made to utilize formic acid, without need of carbon monoxide gas, for iridium [6,7] or rhodium [8] catalyzed hydroxycarbonylation, but with moderate successes. We report here the results obtained in the development of an iridium–formic acid based system for easy production of carboxylic acids from alkenes or alcohols.

2. Experimental

Hydroxycarbonylation of cyclohexene (Table 6, entry 1): cyclohexene (0.85 g, 10.3 mmol), formic acid (1.84 g, 40.0 mmol), acetic acid (2.92 g, 48.7 mmol) and IrI₄ (80 mg, 0.11 mmol) were placed into a 30 ml HB2 autoclave. The autoclave was sealed and a

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temperature reaction of 190°C was set. After a reaction time of 150 min, the autoclave was cooled to room temperature and depressurized. The homogeneous red solution was analyzed by gas chromatography (GC) using internal standards (Varian 3400 FID; column Stabilwax DA 15 m, 0.53 mm, 0.25 μm).

3. Results and discussion

Our recent studies on the isomerization of methyl formate to acetic acid showed that iridium catalysts are much more active at low CO partial pressure [9], whereas other late transition metals prefer high CO pressure [10]. We first extended the isomerization concept using various formates at low CO pressure (Table 1; Scheme 1).

During this study, we observed that no initial CO pressure is required for the reaction to start in agreement with previous results [11–13], but also that high pressure defavors the activity.

Since the reaction is carried out in carboxylic acid solvents and that *trans*-esterification is much more rapid than the isomerization reaction we investigated directly the reaction of esters with formic acid and an iridium catalyst. Results are summarized in Table 2 (Scheme 2).

Furthermore, using 1.05 equivalent of formic acid leads to a perfectly homogeneous medium with no

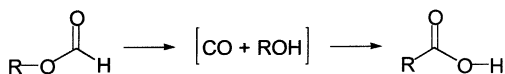
Table 1
Rearrangement of formates^a

Entry	Substrate	<i>t</i> (h)	Product	Yield (%) ^b	<i>n:iso</i> ^b
1	Ethyl formate	2	Propanoic acid	87	–
2	Butyl formate	20	Pentanoic acid ^c	78	67
3	Benzyl formate	5	Phenylacetic acid	32	–

^a Conditions: 0.5 mol% IrI₄ relative to formate; AcOH (1.0 eq.); *T* = 190°C.

^b Determined by HPLC using external standards (column: IN50D2).

^c Major isomer.



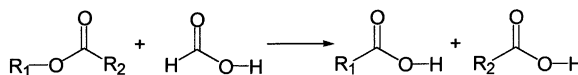
Scheme 1.

Table 2
Hydroxycarbonylation of esters^a

Entry	Substrate	<i>t</i> (h)	Product	Yield (%) ^b
1	Ethyl acetate	8	Propanoic acid	86
2	Valerolactone	3	Adipic acid	27
3	Caprolactone	2.5	Pimelic acid	31

^a Conditions: formic acid (1.3 eq.); AcOH (1.0 eq.); IrI₄/substrate: 0.8 mol%, 190°C.

^b Determined by GC using internal standards (column: Stabilwax DA).



Scheme 2.

precipitation of the catalyst. This indicates that the iridium catalyst is stable enough under these conditions and is not reduced into Ir₄(CO)₁₂ [14,15].

Therefore, we decided to investigate the hydroxycarbonylation of any carbonylatable function with this iridium–formic acid system. We found that alkenes and alcohols can also be transformed into the corresponding hydroxycarbonylated products with good yields. *n*-Hexene was carbonylated in 92% yield with a standard selectivity to linear acids neighboring 70%. When compared to the hydroxycarbonylation of *n*-hexene using CO gas and the same catalyst, this experiment gave similar results, indicating that carbon monoxide may be suitably replaced by formic acid (Table 3).

Further investigations on cyclohexene reactivity showed that the reaction is strongly temperature dependent (Table 4; Scheme 3).

Iridium is well known to be efficient for carbonylation at high temperatures (ca. 180–230°C), but

Table 3
Hydroxycarbonylation of *n*-hexene^a

Entry	Substrate	CO source	Pressure (bar)	Yield (%) ^b
1	<i>n</i> -Hexene	HCOOH	Autogeneous	92 (68)
2	<i>n</i> -Hexene	Gas	5	86 (63)

^a Conditions: *T* = 190°C; *t* = 20 h; entry 1: 3.8 eq. HCOOH, and 1 eq. AcOH relative to *n*-hexene.

^b Determined by GC using internal standards (column: Stabilwax DA); values in brackets correspond to the *n:iso* ratio.

Table 4
Influence of temperature on the hydroxycarbonylation of cyclohexene^a

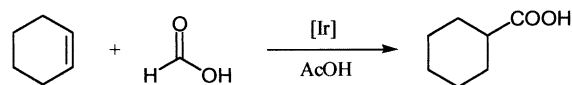
Entry	Substrate	<i>T</i> (°C)	<i>t</i> (h)	Yield(%) ^b
1	Cyclohexene	110	5	2
2	Cyclohexene	130	5	45
3	Cyclohexene	160	5	97
4	Cyclohexene	190	2.5	100

^a Conditions: cyclohexene 15.7 g; formic acid 34.1 g; acetic acid 40.4 g; IrI₄ 1 mol% relative to cyclohexene.

^b Determined by GC using internal standards (column: Stabilwax DA).

another reason for the high temperature required in our experiments comes probably from the thermal decomposition of formic acid. Evolution of the reaction mixture without substrate was analyzed at various temperatures (Table 5).

It is clearly shown that formic acid decomposition rate is slow at 110°C whereas it becomes fast upon 160°C. It can be followed both by the liquid and gas



Scheme 3.

composition analyses. Only a small amount of CO₂ gas is measured, thus water-gas shift reaction remains marginal.

Cyclohexene is quantitatively converted into carboxylic acid in 2.5 h at 190°C (Table 6, entry 1). Cyclohexanol can also be converted to cyclohexane carboxylic acid under identical conditions (entry 2). Nevertheless, its rate of carbonylation is slower when compared to that of cyclohexene and the yield is somewhat lower. It seems reasonable to assume that the alcohol is first dehydrated and then carbonylated. Similar results were obtained with linear compounds (entries 6 and 7). Unexpectedly, cyclohexanone can be directly converted to cyclohexane carboxylic acid (Table 6,

Table 5
Analysis of formic acid decomposition^a

Entry	<i>T</i> (°C)	<i>t</i> (min)	Final pressure, <i>P</i> (bar) ^b	Formic acid conversion (%) ^c	Gas composition (%)	
					CO ^d	CO ₂ ^d
1	110	180	8.8	1	17.7	0.02
2	130	245	17.1	18	53.9	0.02
3	160	180	24.6	84	80.5	0.02
4	190	150	38.5	91	84.7	0.02

^a Conditions: AcOH 0.83 mol; HCOOH 0.11 mol; IrI₄ 0.24 mmol.

^b Initial pressure: *P*_{N₂} (cold) = 5 bar.

^c Determined by GC using external standards (column: Stabilwax DA).

^d In the gas phase, determined by GC (column: Carboxpack C80–100).

Table 6
Hydroxycarbonylation of various compounds^a

Entry	Substrate	<i>T</i> (°C)	<i>t</i> (h)	Product	Yield ^b (%)	<i>n:iso</i> ^b
1	Cyclohexene	190	2.5	Cyclohexane carboxylic acid	100	–
2	Cyclohexanol	160	6	Cyclohexane carboxylic acid	68	–
3	Cyclohexanone	190	66	Cyclohexane carboxylic acid	19	–
4	Cyclopentene	160	1	Cyclopentane carboxylic acid	89	–
5	Cycloheptene	160	5	Cycloheptane carboxylic acid	70	–
6	1-Hexene	190	20	Heptanoic acid ^c	92	68
7	1-Hexanol	190	8	Heptanoic acid ^c	35	73

^a Amounts of substrates are identical to that of the experimental part.

^b Determined by GC using internal standards (column: Stabilwax DA).

^c Major product.

entry 3). A possible rationale is that water-gas shift reaction produces enough hydrogen (within 66 h) to reduce the ketone into the corresponding alcohol which further reacts as previously explained.

4. Conclusions

In summary, we have shown that arduous CO gas handling can be prevented by using formic acid as a source of carbon monoxide and an iridium complex as catalyst. The activity may be increased by further optimizations (TOF >300 h⁻¹ for cyclohexene hydroxy-carbonylation) and the stability was satisfying, since more than 1000 turnovers were easily obtained by this catalytic system.²

References

- [1] H.M. Colquhoun, D.J. Thompson, M.V. Twigg, *Carbonylation: Direct Synthesis of Carbonyl Compounds*, Plenum Press, New York, 1991.
- [2] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, *J. Mol. Catal. A* 104 (1995) 17–85.
- [3] B. El Ali, H. Alper, in: M. Beller, C. Bolm (Eds.), *Transition Metals for Organic Synthesis*, VCH, Weinheim, 1998, pp. 49–67.
- [4] W. Reutemann, H. Kieczka, in: B. Elvers, S. Hawkins, M. Ravenscroft, J.F. Rounsaville, G. Schulz (Eds.), *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A12, VCH, Weinheim, 1989, pp. 13–33.
- [5] P. Mars, J.J.F. Scholten, P. Zwietering, *Adv. Catal.* 14 (1963) 35–113.
- [6] D.J. Drury, P.S. Williams, BP Chemicals, European Patent 106,656 (1983).
- [7] R.L. Pruett, P.L. Burke, EXXON, European Patent 092,350 (1983).
- [8] I.S. Kolomnikov, M.P. Erman, V.P. Kukolev, M.E. Volpin, *Kinet. Catal.* 13 (1972) 227.
- [9] C. Patois, R. Perron, RHODIA CHIMIE, European Patent 889,870 (1999).
- [10] M. Röper, *Erd. Kohle Erdg. Petrochem.* 37 (1984) 506–511 and references therein.
- [11] R.L. Pruett, R. Kacmarcik, *Organometallics* 1 (1982) 1693–1699.
- [12] M. Cheong, S. Bae, K.B. Lee, *Chem. Commun.* (1995) 1557–1558.
- [13] M. Cheong, S. Bae, K.B. Lee, *J. Mol. Catal. A* 112 (1996) 389–393.
- [14] F.P. Pruchnik, K. Wajda-Hermanowicz, M. Koralewicz, *J. Organomet. Chem.* 384 (1990) 381–383.
- [15] R.D. Pergola, L. Garlaschelli, S. Martinengo, *J. Organomet. Chem.* 331 (1987) 271–274.

² These TOF and TON data were obtained under optimized conditions: 198°C, 900 wppm Ir.