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Decarbonylation of Alkyl Formates Catalysed by Osmium Complexes

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Abstract: *In dimethylformamide or polar solvents , Osmium compounds in the presence of amines as promotor are very good catalysts for decarbonylation of methyl formate.*

In recent years much attention has been focused on decarbonylation of formic acid esters catalysed by organometallic complexes.

$$\mathrm{HCOOR} \xrightarrow{[M]} \mathrm{ROH} + \mathrm{CO} \qquad (1)$$

In addition to the theoretical aspect, this interest is certainly due to the great advantage, especially in Fine Chemistry, which would be to produce directly CO in a reaction medium,[1] and therefore avoiding storage and handling of this toxic gas.

Basic catalysts such as alkaline methoxides, (which are effective at moderate temperature) are known for a long time.[2] However, as these bases are often incompatible with subsequent reaction, organometallic catalysts have been researched. In this trend, different catalytic systems based on Ir,[3] Rh[4] or Ru[5] have recently been described. All of them however are not very active and/or selective towards methyl formate decarbonylation (the most current and important formate ester) despite the use of high reaction temperature (180-220°C).

We report here the results obtained in this context by using an osmium catalytic system in an amide as solvent.

Thus, when a solution of methyl formate in dimethyl formamide (DMF) is heated at 190°C with a catalytic amount of $OsCl_3$ (0.015 mole %), for 1 hour, under nitrogen in an autoclave, the liquid phase analysis shows the presence of methanol (yield 87%, selectivity up to 99%) together with unreacted methyl formate. The gas phase analysis revealed a 97% selectivity in carbon monoxide, the only by-products beeing CO_2 and CH_4 (the thermodynamically favoured reaction[6]).

Table 1, which lists some results obtained under different reaction conditions, shows that different osmium salts or complexes present almost equivalent activities. The favourable effect of the solvent is also obvious: the reaction does not occur in pure methyl formate or even in a polar compound like γ butyrolactone (runs 1 and 2). In contrast, amides like NMP (N-methyl pyrrolidone) and DMF give satisfactory results.

Table 1 : Decarbonylation of alkyl formates [a]

Runs	HCOOR R=	Solvent	Temp. (°C)	t (h)	Conv. (%)	MeOH Sel. (%)	CO Sel. (%)[g]
1[b]	Me	none	190	2	0	---	---
2[b]	"	γ butyrolactone	"	"	0	---	---
3[b]	"	NMP	"	1	70	≈100[f]	96
4[b]	"	DMF	190	1	78	≈100[f]	99
5[c]	"	"	"		78	≈100[f]	97
6[d]	"	"	"	"	87	≈100[f]	98
7[e]	"	"	"	"	80	≈100[f]	95
8[b]	"	"	170	"	71	≈100[f]	96
9[e]	"	"	150	"	1	---	---
10[b]	Et	"	190	4	11	≈100[f]	99

(a) Conditions : HCO_2R = 270 mmol; solvent = 30 mL; catalyst : (b) Os $(NH_4)_2Br_6$ = 0.005 mmol , (c) $OsCl_3$ = 0.005 mmol, (d) $Os(NH_4)_2Br_6$ = 0.04 mmol , (e) $Os(NH_4)_2Br_6$ = 0.02 mmol. (f) The only product observed by GPC. (g) by -products : CO_2, CH_4.

This solvent effect does not seem to be linked with its polarity: this obviously should come from other characteristics of the amides, for which some possibilities are analyzed below:

i) At these high reaction temperatures, a very little part of solvent could decompose into CO and amines. The latter are known to catalyse alkyl formate decarbonylation, particularly in the presence of epoxides[7]. Besides, osmium could catalyse this decomposition of the amide leading to an appreciable amount of amine which accordingly would favour formate decarbonylation.

ii) It is also possible that the slight amount of amine produced by this decomposition could combine with Os to form a catalytic species particularly active towards decarbonylation of formate.

To check these hypotheses, different reactions have been conducted without osmium in DMF, with or without amine (runs 11 and 12). Under these conditions the rate of decarbonylation increases with the amine concentration. In this case, the decarbonylation is certainly due to the incipient production of MeO^- by the equilibrium described in eq.2[8]

$$NEt_3 + CH_3OH \rightleftharpoons HNEt_3^+ + CH_3O^- \qquad (2)$$

However, the results remains drastically lower than those observed in the osmium catalysed reaction. So the osmium contribution to the overall catalytic decarbonylation process becomes evident.

Table 2 : Influence of amine on the decarbonylation of methyl formate[a]

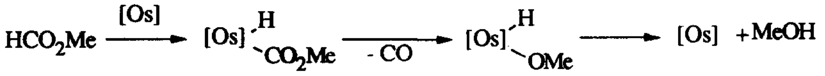
Runs	Solvent	Catalytic system	Temp. (°C)	t (h)	Conv. (%)	MeOH Sel. (%)	CO Sel. (%)
11	DMF	none	190	1	1	---	*b*
				2	4	98	
12	"	NEt_3[c]	"	1	8	99,5	*b*
13	γ butyrolactone	NEt_3[c]	"	1	2	---	*b*
				2	5	≈100	95
14	"	$Os(NH_4)_2Br_6$ = 0.11 mmol NEt_3[c]	"	1	52	≈100	97
15	DMF	$Os(NH_4)_2Br_6$ = 0.005 mmol NEt_3[c]	150	1	10	≈100	97
				2	27	≈100	96

(a) HCOOMe = 270 mmol., solvent =30 mL, (b) not determined, (c) NEt_3 = 1.6 mmol.

At this stage, to estimate the influence of the amine, DMF (a potential source of amine) has been replaced by γ butyrolactone (another polar solvent) to which "catalytic" quantities of amine have been added. With this solvent (runs 2, 13 and 14) a good activity is also observed, provided both the osmium and the amine are present.

So we can deduce that a combination of an osmium salt associated with catalytic amounts of amine (in a polar solvent in order to solubilize the catalyst) leads to a catalytic system especially active for methyl formate decarbonylation. This system can be obtained by in situ production of amine resulting of a very weak decomposition of amide such as DMF or by direct addition of an amine to the reaction medium. In this last case, the reaction temperature can be notably reduced (compare runs 9 and 15). Indeed, decomposition of the amide into the amine, which is the first step of catalyst production in pure amide solvents, happens only at high temperatures (> 180°C) in contrast with the catalytic formate decarbonylation.

From a mechanical point of view, a specific experiment was conducted at 190°C to produce the active species and followed by a decrease of reaction temperature at 120°C. Under such conditions the reaction stopped immediately. This fact leads us to the conclusion that the rate determining step of the process might be the oxidative addition of H-COOMe on the metal center, an elementary step which requires probably high temperature conditions on this system.



$$\mathrm{HCO_2Me} \xrightarrow{[\mathrm{Os}]} [\mathrm{Os}]\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{CO_2Me}} \xrightarrow[-\mathrm{CO}]{} [\mathrm{Os}]\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{OMe}} \longrightarrow [\mathrm{Os}] + \mathrm{MeOH} \qquad (3)$$

To our knowledge, this osmium-amine system is much more active and selective for methyl formate decarbonylation than other organometallic catalysts already reported[4,5]. Apart from the fact that it allows to synthesize the CO/MeOH mixture from liquid methyl formate, a process which can be done easily by sodium methoxide[2], this system could present a synthetic interest for the *in situ* production of methanol and carbon monoxide during carbonylation reactions were the substrates, products and/or the catalyst are not compatible with the presence of alcoolates.

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