An improved catalytic homologation method for converting C_n alkyl groups into C_{n+1} groups from C_n formates
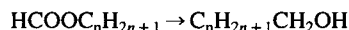
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Abstract

C_n formates can be catalytically converted to C_{n+1} alcohols and their esters in the presence of a cobalt catalyst and, optionally, of a ruthenium compound.

$$HCOOC_nH_{2n+1} \rightarrow C_nH_{2n+1}CH_2OH$$

The reaction occurs under modest CO pressure in the presence of lithium iodide and tributylphosphine. It is promoted by an onium salt. The reaction is highly selective with respect to the formation of the next higher homologues (alcohols + esters). The method is general and permits homologation of alkyl groups other than methyl, though turnovers are sharply depressed with increasing chain length of the alkyl group. The reaction occurs via a complex pathway differing from typical mechanisms previously proposed for the hydrocarbonylation of methanol and higher alcohols.

1. Introduction

The homologation of alcohols to their higher homologues has been the subject of numerous academic and industrial laboratories [1], especially the hydrocarbonylation of methanol to ethanol [2]. The last reaction takes place under cobalt catalysis and iodine promotion. Significant rates are achieved only under high syngas pressure (200–300 bar) [3]. Lower pressures (70 bar) are possible only in the synthesis of ethanol from methanol provided that the reaction is carried out in the presence of CH_3I and diphosphine ligands [4] whereas iodine-free binary Co–Ru catalysts show activity only at 300 bar syngas pressure [5].

We have recently proposed another method based on a decarbonylation–hydrocarbonylation sequence of aqueous alkyl formates [6]. The advantage of the process is that it requires neither iodine promotion, nor initial gas pressure. In addition, selectivity to the higher alcohol is high (ROH not taken into account):

$$HCOOR \xrightarrow{\text{H}_2\text{O, catal.}} RCH_2OH$$
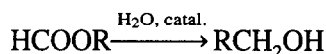
The major drawback is the relatively low yield of the desired alcohol. For example, methyl formate leads to a maximum yield of 28% of ethanol, limiting the potentiality for industrial application. This has prompted us to investigate the above reaction involving formic esters under low CO pressure and in the presence of a promoting agent, lithium iodide.

2. Experimental section

Standard conditions have been determined: ethyl formate (37.2 mmol), $Ru_3(CO)_{12}$ (0.015 mmol), $P(nBu)_3$ (0.76 mmol) Bu_4PBr (0.34 mmol), H_2O (8.3 mmol), toluene (2 ml), 200°C, 5 h. Compared to the former work [9], additional catalyst and promoter have been introduced: $CoBr_2 \cdot xH_2O$ (0.09 mmol), and LiI (0.44 mmol). These conditions hold for all tables and figures except where otherwise indicated.

The experiments have been done under CO pressure (usually 60 bar). Under these conditions, the products are distributed as ethanol, propanol, n-propyl formate, ethyl propionate, propyl propionate, ethane, CO_2, CO, H_2. Experimentally, the reactions were run as described earlier [6].

The liquid phase was collected and submitted to gas chromatography under following conditions: Hewlett-Packard 5700A; Hayesepp S; 2.5 m × 1/8 in.; 50–240°C; 4°C min^{-1}. Analysis of gases was done with an IGC 120ML apparatus; Hayesepp D (80–100 mesh); 8 m × 1/8 in.; methane and helium as successive carrier gases.

The yield is defined as the ratio of moles of formate converted to propanol to moles of formate charged. Total propyl groups means the 'available' propanol: free propanol + propyl groups in esters.
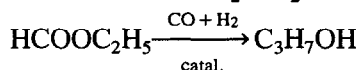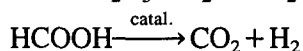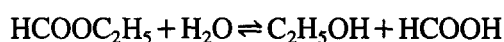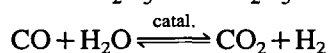
3. Results

The reaction involving ethyl formate was chosen as the standard reaction to yield n-propanol:

$$HCOOC_2H_5 \xrightarrow{\text{catal.}} C_3H_7OH$$
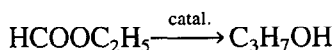
At first, it must be emphasized that the homologation of ethyl groups to propyl groups via hydrocarbonylation is extremely hard to achieve. Literature references are rather scarce [1,7]. Ethanol could be homologated to propanol with iodine promoted cobalt–ruthenium catalysts only under high pressures (400–600 bar) [8]. Under these conditions, propanol was produced in 35% yield and 55% selectivity. This alcohol was

formed in 15% yield and 76% selectivity in the ruthenium catalyzed decarbonylation–hydrocarbonylation reaction involving aqueous ethyl formate [9]. The complex catalytic system consisted of $Ru_3(CO)_{12}$, an onium salt, a phosphine $(C_4H_9)_3P$ (abbreviated $P(nBu)_3$) and hydrochloric acid.

Keeping nearly the same catalytic conditions, we have studied the effect of additional parameters with the aim to improve the yield of propanol. The process is sequential and presumably involves generation of CO and H_2 from the aqueous solution of ethyl formate via decarbonylation and water gas shift reaction [10], or hydrolysis to formic acid and decarboxylation:

$$HCOOC_2H_5 \xrightarrow{\text{catal.}} C_2H_5OH + CO$$

$$CO + H_2O \xrightleftharpoons{\text{catal.}} CO_2 + H_2$$

$$HCOOC_2H_5 + H_2O \rightleftharpoons C_2H_5OH + HCOOH$$

$$HCOOH \xrightarrow{\text{catal.}} CO_2 + H_2$$

$$HCOOC_2H_5 \xrightarrow[\text{catal.}]{CO + H_2} C_3H_7OH$$
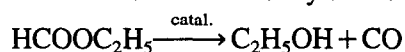
3.1. Effect of catalyst composition

In our former work [9], the catalyst was $Ru_3(CO)_{12}$. In the present study, using LiI as promoter, we reasoned that since in the typical methanol homologation process cobalt catalysts are strongly activated in the presence of iodine, association of a cobalt catalyst with $Ru_3(CO)_{12}$ could be beneficial for the reaction. We have therefore carried out experiments with $CoBr_2 \cdot xH_2O$ ($Co_2(CO)_8$ is also appropriate and probably other cobalt compounds could be used in the reaction). Keeping constant the concentration of the cobalt catalyst (0.09 mmol), we have investigated the effect of increasing amounts of $Ru_3(CO)_{12}$ (Table 1).

In contrast to our former study [6], under the present conditions the cobalt catalyst is *able to induce homologation of ethyl to propyl groups.* This is a quite interesting, unprecedented result.

Addition of the ruthenium catalyst results in a slight increase of the propanol yield, but promotes

Table 1
Effect of $Ru_3(CO)_{12}$ concentration [a]

$Ru_3(CO)_{12}$ 10^3 mmol	Formate conversion (%)	Yields (%)	
		n-propanol	total propyl groups
0	84	17	26
7.5	92	18	37
15.0	98	22	37.5
24.0	98	19	35.5
37.5	94.5	19	32
37.5 [b]	93	15	27

[a] Standard conditions.
[b] $Ru_3(CO)_{12}$ alone.

Table 2
Effect of CO pressure [a]

CO (bar)	Formate conversion		Yields (%) n-propanol		Total propyl groups	
	(a) (%)	(b)	(a)	(b)	(a)	(b)
0	71	71	6	5	10	8
30	98	–	6.5	–	11	–
60	98	98	10	22	16	38
80	98	–	12	–	18	–
130	98	98	14	10	33	25

(a) Catalyst: $Ru_3(CO)_{12}$ (0.039 mmol), no cobalt compound. Other conditions are standard as described in the experimental part.
(b) Catalyst: $Ru_3(CO)_{12}$ (0.015 mmol), $CoBr_2$ (0.09 mmol) (standard conditions).

Table 3
Effect of H_2 partial pressure [a]

H_2 (bar)	Formate conversion (%)	Yields (%)	
		n-propanol	total propyl groups
0	98	22	37.5
30	88	20	38
40	83	20	41
60	84	17	53
90	87	11	52

[a] CO (60 bar). Other conditions are standard.

much more the formation of propyl esters (carbonylation), probably in relation with the carbonylation tendency of $Ru(CO)_3I_3^-$ active species [11]. There is an optimal Co:Ru composition, since for higher concentration of $Ru_3(CO)_{12}$, the yield of total propyl groups decreases.

3.2. Effect of total and partial CO and H_2 pressure

In order to illustrate the effect of CO pressure, two series of experiments are listed in Table 2: the first concerns runs carried out with $Ru_3(CO)_{12}$ alone and the second runs with the standard Co + Ru catalytic system. Without initial CO pressure, but in the presence of LiI, ethyl formate yields only 6 and 5% propanol, respectively. This is in agreement with former results emphasizing the detrimental effect of either iodine or iodide ion on the reaction [6]. Increase in CO pressure results in better propanol yields up to 14%. The same trend is observed for propyl groups. With $Ru_3(CO)_{12}$ as catalyst, under 130 bar CO pressure, ethyl formate is converted to 33.5% to propyl groups (14% propanol, 0.5% propyl formate, 14% ethyl propionate, 5% propyl propionate). A lower yield (25%) is obtained with the mixed catalytic system.

Initial CO pressure is therefore essential to stabilize catalytic species which are responsible for the formation of propyl derivatives. For example, under nitrogen pressure (130 bar), the yield of propanol is only 6% as under atmospheric pressure. Replacing CO by initial H_2 pressure (80 bar), other conditions being similar leads to only 1.1% yield (free propanol only) (both runs being carried out with the Ru catalyst).

CO–H_2 mixtures improve significantly the yield of propyl groups, however not toward propanol, but mostly to ethyl and propyl propionate (Table 3). We decided therefore to run our exper-

Table 4
Effect of iodide promoters [a]

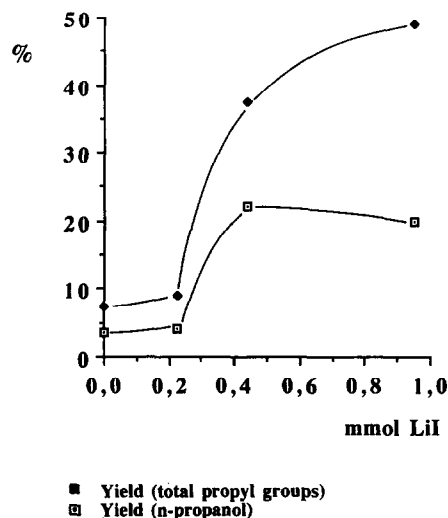| Promotor	Formate conversion (%)	Yields (%)	
		n-propanol	total propyl groups
none	46	3.5	7.5
LiI	98	22	37.5
C_2H_5I	80	13	22
I_2	84	13	36

[a] Standard conditions.

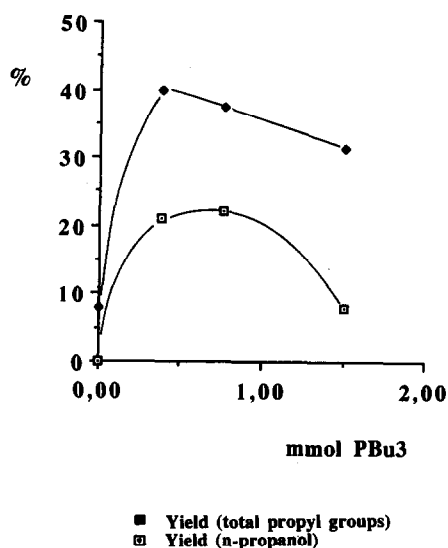Fig. 1. Effect of the concentration of LiI (standard conditions).

Fig. 2. Effect of the concentration of tri-n-butylphosphine (standard conditions).

iments only under CO pressure (60 bar), in the presence of the standard Co + Ru catalytic system.

3.3. Effect of the iodide promoter (Table 4)

Under carbon monoxide pressure, lithium iodide is a good promoter as shown in Fig. 1 which reports the effect of LiI concentration. Without LiI, ethyl formate is mostly decarbonylated to eth-

anol and decarboxylated to ethane. For a LiI concentration of 0.44 mmol, there seems to be an optimum regarding the yield of propanol. Further increase of concentration has a beneficial effect on the formation of propyl ester: 50% of ethyl formate are converted to propyl groups for LiI = 0.95 mmol.

Other iodide compounds are also suitable as promoters (C_2H_5I, I_2). However ionic iodides lead to the highest yield of free propanol.

3.4. Effect of water concentration

Water is supposed to generate hydrogen via the WGS reaction or formation of formic acid. However, hydrogen is formed even without initial addition of water, suggesting that ethyl formate itself is a source of hydrogen. In fact, in that case the reaction takes place, yielding mostly propyl ester (Table 5). Increasing amounts of water increase the yield and selectivity of free propanol.

3.5. Effect of phosphines

The effect of tributylphosphine $P(nBu)_3$ was compared to that one of tricyclohexylphosphine PCy_3 which was found to have the best promoting effect in the decarbonylation of methyl and ethyl formate [10,12]. With PCy_3, only 11% free propanol and 33% propyl groups were obtained vs. 22% and 37.5%, respectively, in the case of PBu_3. A comparable situation was observed when methyl formate was converted into ethyl groups. Accordingly, we adopted PBu_3 as the promoting phosphine.

Table 5
Effect of initial water concentration [a]

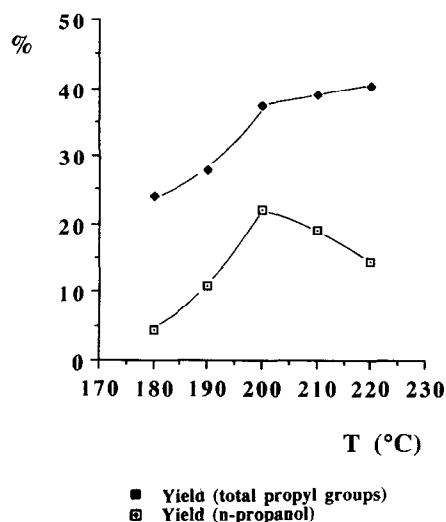| Water (mmol)	Formate conversion (%)	Yields (%)	
		n-propanol	total propyl groups
0	74	6	32
4.4	92	13	40
8.3	98	22	37.5
16.6	94	22	31

[a] Standard conditions.

Fig. 3. Effect of temperature (standard conditions).

The phosphine was found to be essential to the reaction. Without phosphine, there is little reaction: only 8% total propyl groups are formed and no propanol at all. The reaction is strongly dependent on the concentration of the phosphine (Fig. 2). There is a maximum in yield of C_3 products corresponding to a concentration of PBu_3 of 0.60 mmol (e.g. for a $Ru:PBu_3$ ratio of 1:120 and formate: $PBu_3 = 60:1$). For higher concentrations of phosphine, yields of both propanol and total propyl groups are depressed.

3.6. Temperature and miscellaneous effects

The effect of temperature is shown in Fig. 3. The reaction becomes significant only from 180°C. At 200°C, the yield of propanol is maximum, whereas at higher temperatures, there is only a slight increase in the yield of C_3 products (mostly as esters).

The reactions described until here were carried out in toluene as solvent. Two other solvents were examined (Table 6). In N-methylpyrrolidone, the yield of propanol is lower, however the overall yield of C_3 products is a little higher. Clearly, pyridine is not the appropriate solvent.

In our former work, the presence of an onium salt was found to be an absolute condition. Under the present conditions, it plays also the role of a promoting agent, however the homologation reaction occurs even without the phosphonium salt, indicating that another mechanism takes place.

3.7. Extension to other alkyl formates

In the subsequent step, we turned to the reactions involving methyl, n-propyl, isopropyl, n-butyl and n-amyl formate. We adjusted the initial water concentration in the following way. In the ethyl formate reaction, the best selectivity with respect to free propanol was obtained in the run carried out with 16.6 mmol water (Table 5). We adopted these conditions for the reactions of other formates (Table 7). However, in the same way as for ethyl formate (Table 5), this is not the optimal condition for the highest conversion to C_{n+1} groups. As an illustrative example, methyl formate could be converted to 38% ethanol and 86% ethyl groups, when lowering the initial water concentration to 5.5 mmol (instead of 16.6 mmol).

Table 6
Effect of solvent and phosphonium salt [a]

Solvent	Bu_4PBr (mmol)	Formate conversion (%)	Yields (%)	
			n-propanol total	propyl groups
Toluene	0.34	98	22	37.5
N-methylpyrrolidone	0.34	98	14	40
Pyridine	0.34	91	0	8
Toluene	0.0	76	13	23

[a] Standard conditions

Table 7
Generalization of the homologation reaction[a] $HCOOR \rightarrow RCH_2OH$

R	Catalyst	Formate conversion (%)	Yield of RCH_2OH (%)	$C_{n+1}OH$ $(n:n + iso)$ [e]	Yield of total C_{n+1} groups (%)
methyl	Co [b]	100	26	-	51
methyl	Co + Ru	100	33	-	55
ethyl [c]	Co + Ru	98	22	-	31
n-propyl	Co + Ru	92	20	0.54	21
i-propyl	Co + Ru	83	3	0.36	3
n-butyl [d]	Co + Ru	88	17	0.56	17
n-amyl	Co + Ru	87	3	?	?

[a] Standard conditions. Formate (3 ml), H_2O (16.6 mmol).
[b] No $Ru_3(CO)_{12}$. Cobalt catalyst in all runs is $CoBr_2 \cdot xH_2O$ (0.10 mmol).
[c] Reference (see Table 5).
[d] Xylene (2 ml) was the solvent.
[e] Ratio of linear vs. linear + branched alcohols.

For the case of methyl formate, formate conversion is total under conditions shown in Table 7. It slightly decreases with increasing chain length of the alkyl group, whereas turnovers are sharply depressed in accordance with all earlier works reporting the homologation of alkyl groups [1,7,13]. In contrast, selectivity to the higher alcohol increases, when higher alkyl formates are considered. This is obviously due to the lower tendency of higher alkyl groups to be carbonylated into esters. In the case of C_4 and C_5 formates, only

the corresponding alkanes could be detected as side products.

Table 8 lists comparative turnover and selectivity data according to the process involved. (A) represents the $Co-Ru-I_2$ hydrocarbonylation of alcohols [13], (B) corresponds to the alkyl formate process with no CO pressure and without addition of iodine [9], (C) refers to this work (initial water concentration is 5.5 mmol).

Though the experimental conditions (even temperature) are different, the data listed in Table 8 refer to those obtained under optimal conditions and thus can be compared to each other. The results indicated that from both standpoints (TN and selectivity), the present method emerges as a pertinent process to convert C_n alkyl groups into C_{n+1} groups. The advantage of methods B and C over method A is mainly due to the quasi absence of the dialkyl ether R_2O which forms in substantial amount in procedure A.

Table 8
Homologation of C_n groups into C_{n+1} groups[a,b]
$HCOOC_n \rightarrow C_{n+1}OH$
(C_n: alkyl group)

Method	[c]	Cn			
		Methyl	Ethyl	n-Propyl	n-Butyl
A	TN	no run	69	28	19
	ΣT		65	67	72
B	TN	256	140	60	40
	Σ_T	75	79	78	65
C	TN	508	166	79	52
	Σ_T	86	90	92	92

[a] For exact conditions, see [13] for A and [9] for B.
[b] TN refers to the total number of C_{n+1} groups/mol catalyst Co for A and C, Ru for B.
[c] Σ_T is the molar selectivity (%) of total C_{n+1} groups (all liquid products + gaseous alkanes when formed are taken into account except alcohol C_nOH).

4. Discussion

The present homologation reaction can be related a priori to our previous works reporting the homologation of methyl to ethyl formate [14] and to the reductive carbonylation of carboxylic esters [15]. As a matter of fact, these reactions

involve also the cobalt–ruthenium tandem catalytic system and iodine promotion.

In the first case, it was shown that:

$$HCOOCH_3 + CO + H_2 \rightarrow HCOOH$$
$$+ CH_3CHO$$

$$CH_3CHO + \tfrac{1}{2}H_2 \rightarrow C_2H_5OH$$
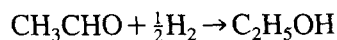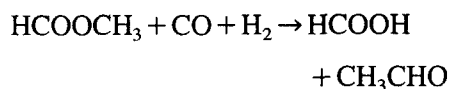
However, with our catalytic system, HCOOH is largely decomposed into CO_2 and H_2, whereas $HCOOCH_3$ decarbonylates into CH_3OH.
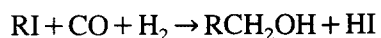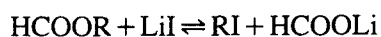
In the second case, the mechanism was supposed to involve, at least in part, an olefinic intermediate, such as in the hydrocarbonylation of alcohols [13].

However, under the conditions of this paper (and under $CO + H_2$ pressure), alcohols are not hydrocarbonylated to higher homologues, meaning that there must be a specific homologation route involving the formate. In addition, it is worthwhile to note that, unlike process A, the homologation stops at the C_{n+1} level. No C_{n+2} alcohol or any other C_{n+2} product, is formed from C_n formate. This is another line of evidence for a distinct pathway.
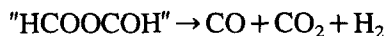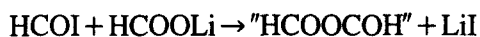
In the present process, several conditions are required in order to produce the higher alkyl group:

(i)   The substrate must be the formate and not the alcohol
(ii) A phosphine must be present
(iii) CO pressure, LiI and, to a lesser extent, presence of an onium salt, are highly favourable for the reaction.

The mechanism is not clear. A first step probably involves the well known equilibrium [16] producing the alkyl iodide which would undergo homologation possibly through hydrogenation of an acyl cobalt intermediate under CO/H_2 pressure.

$$HCOOR + LiI \rightleftharpoons RI + HCOOLi$$

$$RI + CO + H_2 \rightarrow RCH_2OH + HI$$

Other possible reactions could be:

$$HI + CO \rightleftharpoons HCOI$$

$$HCOI + HCOOLi \rightarrow ''HCOOCOH'' + LiI$$

$$''HCOOCOH'' \rightarrow CO + CO_2 + H_2$$

This scheme explains also the origin of H_2 when the reaction is carried out without adding water. CO also originates from decarbonylation of the formate [12] and H_2 from the WGSR or from HCOOH. The slight synergistic effect observed when combining the cobalt and the ruthenium catalyst in the appropriate ratio may be related to our former studies [13,15]. In this respect, we proposed an olefinic intermediate which could be evidenced in the hydrocarbonylation of ethanol [13]. In the present work, we could detect a low amount of ethylene in some runs involving ethyl formate, thereby suggesting the formation of the higher alcohol via hydroformylation (also possibly starting from the formate [17]).

Catalytic species may be hydruro–metal carbonyls or hydruroiodometal–carbonyls: $Co(CO)_4^-$, $H(CH_3)CoI(CO)_3$, $HRu(CO)_xI_y$, $HRu_3(CO)_{11}^-$. Initial CO pressure contributes to stabilize the cobalt species. As H_2 is rapidly generated in the process, it is not necessary to introduce hydrogen pressure. The phosphonium salt serves as a counter-ion for anionic species [18].

Finally, it must be observed that phosphine is an indispensable additive. No higher alcohol is formed in the absence of tri-n-butylphosphine in probable relation to its role in formate decarbonylation [12,19]. Another possible explanation can be given via our previous scheme in which the phosphine was shown to be an integral part of the reaction sequence [6].

5. Conclusion

In the long standing problem of the conversion of C_n alkyl groups to C_{n+1} groups, alkyl formates appear as a mean to orchestrate the homologation reaction. It is particularly worthwhile to point out the apparent facility of the method: low CO pressure, cobalt catalysis, iodine and phosphine pro-

motion, when compared to previous methods [1,3,8].

Acknowledgements

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