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HOMOLOGATION OF CARBOXYLIC METHYL ESTERS VIA REDUCTIVE CARBONYLATION CATALYZED BY A COBALT-RUTHENIUM MIXED CATALYST

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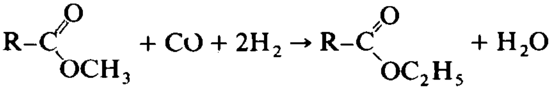
Summary

Mixtures of cobalt acetate and ruthenium acetylacetonate promote the homologation of carboxylic methyl esters to the corresponding ethyl esters by CO-H_2. The reaction of methyl formate is considered separately because of its tendency to decarboxylate. The behavior of five other methyl esters is considered as a function of the length and the size of the acyl group. In each case reductive carbonylation of the methyl ester gives methanol, ethanol, the carboxylic acid, and the ethyl ester. The formation of the last product is enhanced by the mixture of Co and Ru complexes. The mechanism is thought to be essentially the same as that previously proposed for homologation of methyl acetate.

Introduction

Ruthenium complexes have recently been reported to catalyze the homologation of methanol [1], methyl formate [2] and methyl acetate [3]. In the first and the last cases, association of the ruthenium complex with a cobalt cocatalyst (in a Co/Ru mol ratio > 1 for methanol; Co/Ru mol ratio ⩽ 1 for methyl acetate) markedly accelerates the transformation of the substrates to ethanol [1,4] and ethyl acetate [5,6] respectively. In contrast, the mixtures of cobalt and ruthenium complexes were not found to be more active than the Ru component alone in the homologation of methyl formate [2].

Following our observations on the reductive carbonylation of methyl acetate [6,7] and dimethyl ether [7], we decided to see whether the mixed Co and Ru complexes in association with iodide promoters is also effective in converting any methyl ester to the corresponding ethyl ester according to the general equation (eq. 1).



$$R\text{-}C(=O)OCH_3 + CO + 2H_2 \rightarrow R\text{-}C(=O)OC_2H_5 + H_2O \qquad (1)$$

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TABLE 1

HOMOLOGATION OF METHYL FORMATE[a]

Run	Catalyst[b]	Promoter	Addend	Liquid products (mmol)			Gaseous products (mmol)		
				CH_3OH	$HCO_2C_2H_5$	C_2H_5OH	CO_2	CH_4	C_2H_6
836[c]	(Co)	LiI	none	3.0	0.5	0	0.6	0.9	0
839	(Ru)	LiI	none	7.2	3.5	0.4	4.2	2.6	0.3
843	(Co)+(Ru)[d]	LiI	none	9.6	4.4	1.1	10.2	7.5	0.1
829[e]	(Co)+(Ru)[d]	LiI	none	11.1	8.0	1.9	10.3	7.9	0.2
847	(Co)+(Ru)[d]	CH_3I	none	12.1	1.0	0	0.2	4.1	0
856[h]	(Co)+(Ru)[d]	I_2	none	12.7	1.3	0.2	1.1	7.3	0
857	(Co)+(Ru)[d]	LiI	PPh_3[f]	7.1	4.1	0.4	34.8	1.1	0.1
861	$[Co(CO)_3(PPh_3)_2]$+(Ru)[d]	LiI	none	7.7	4.3	0.7	8.6	5.9	0.1
865	(Co)+(Ru)[d]	LiI	HCO_2H[g]	7.4	1.5	0.2	42.4	0	0

[a] Reaction conditions: Initial charge of HCO_2CH_3 (80 mmol), promoter (0.38 mmol), catalyst ($Co+Ru = 7.5 \times 10^{-5}$ mol), CO/H_2 (1/2), 200°C, 290 bar, contact time (2 h). [b] (Co) denotes cobalt acetate tetrahydrate and (Ru) ruthenium acetylacetonate, $Ru(acac)_3$. [c] Acetaldehyde was also produced in this run (3.3 mmol). [d] Mol ratio ($Co/Ru = 0.4$). [e] Contact time was 5 h. [f] PPh_3 (0.05 mmol). [g] HCO_2H (25.8 mmol). [h] Other products were also formed.

In the account below, the term Co-Ru system denotes a mixture of cobalt acetate tetrahydrate and ruthenium acetylacetonate.

Homologation of methyl formate

Methyl formate, the first member of the series, is considered separately because its behavior under the conditions used to achieve homologation differs somewhat from that of the other carboxylic methyl esters. Methyl formate is known to undergo either decarbonylation (eq. 2) or decarboxylation (eq. 3), and the second reaction is highly undesirable:

$$HCOOCH_3 \rightarrow CO + CH_3OH \qquad (2)$$

$$HCOOCH_3 \rightarrow CO_2 + CH_4 \qquad (3)$$

The results are listed in Table 1. The major ($\geqslant 95\%$) liquid products were methanol, ethanol and ethyl formate. Methyl acetate was also found in some runs, but only in very minor amounts.

It will be seen that use of the Co-Ru system increases the conversion and gives maximum yields of all three products (run 843 vs. 839). This contrasts with the previously report [2] that use of the mixed system does not lead to better yields of $HCO_2C_2H_5$ than use of the Ru complex alone. Though the increase is less spectacu-

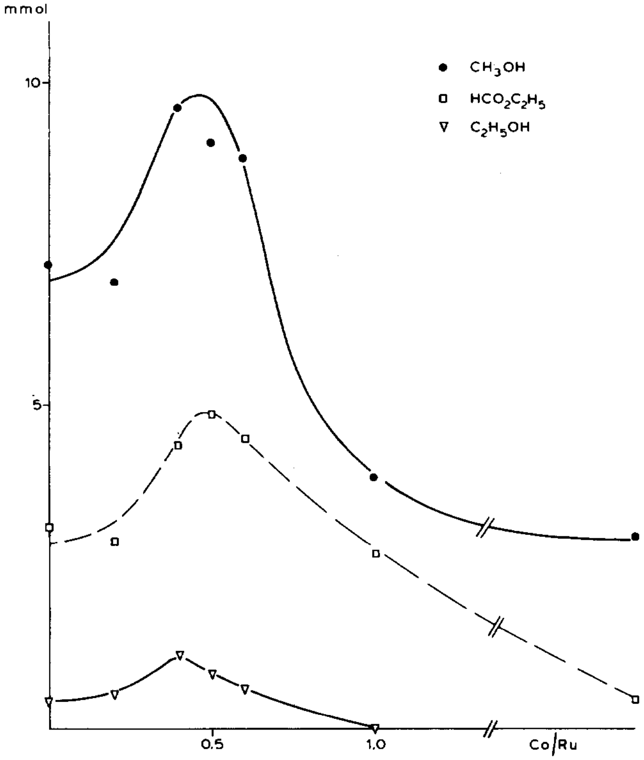

Fig. 1. Homologation of methyl formate. Influence of the composition of the catalytic system on the formation of products. (Co/Ru, mole ratio).

lar than in the homologation of methyl acetate [6], it is evident (Fig. 1). Maximum yields of CH_3OH, $HCO_2C_2H_5$ and C_2H_5OH are achieved with a mol ratio Co/Ru of ca. 0.4–0.5. It is noteworthy that this is the ratio previously found to give the best results in the synthesis of ethyl acetate.

The nature of the iodide promoter is a decisive factor in the production of $HCO_2C_2H_5$. CH_3I and I_2 show similar activities, but their use give only 25% of the proportion of $HCO_2C_2H_5$ obtained with LiI as promoter. We believe that our previous proposals concerning the mechanism for the homologation of methyl acetate still apply [7]. Addition of PPh_3 (run 857) does not significantly promote the reaction (compare run 843); instead it leads to extensive decomposition to give large amounts of CO_2 by reaction 3. Interestingly use of a cobalt complex having Ph_3P ligand bonded to Co (run 861) along with an appropriate proportion of the Ru-cocatalyst gives yields approaching those in run 843.

The advantage of the Co-Ru system over the Ru complex alone may be attributable to the formation of acetaldehyde (run 836), which is hydrogenated to ethanol when the Ru-cocatalyst is present. The question of the origin of the CH_3CHO is of interest; this compound may be formed simply through homologation of methanol, generated for example, in reaction 2 or by hydrogenolysis of HCO_2CH_3. However homologation experiments with MeOH under same conditions do not give significant amounts of acetaldehyde. We therefore suggest that CH_3CHO is produced in the way previously suggested for the reductive carbonylation of methyl acetate (cleavage of the acyl derivative) [7]:

$$HCO_2CH_3 + CO + H_2 \rightarrow HCOOH + CH_3CHO$$

According to the reaction scheme proposed earlier [3,7], ethyl formate could be formed by esterification of ethanol with formic acid. Ethanol is produced by hydrogenation of CH_3CHO and of the presumed intermediate species $[Ru(CH_3CO)(CO)_{x-1}I_y]$. Formic acid is not detected by GLC. Since ethanol is still present at the end of the run, it must be assumed that the acid concentration was not sufficient to lead to conversion of all the alcohol into ethyl formate; this is probably because the rate of decomposition of the acid is higher than the rate of esterification of the alcohol, since it is known that formic acid is highly unstable under the conditions used. Initial addition of formic acid does not improve the yield of $HCO_2C_2H_5$; on the contrary, there is a substantial decrease in the amounts of $HCO_2C_2H_5$ and C_2H_5OH produced (compare run 865 vs. 843) which suggests that decomposition of the acid prior to esterification produces an unfavorable dilution effect.

Analysis of the gas phase reveals that in all runs involving with Ru complexes, CO_2 is produced in large amounts along with methane (reaction 3). Even ethane is formed in some runs, possibly as a result of hydrogenolysis of an alkylruthenium intermediate or of decarbonylation of an alkoxy intermediate.

Homologation of higher methyl ester (C_3 to C_5)

In order to extend the homologation method, we investigated the reductive carbonylation of the methyl ester of propionic, butyric, valeric, isobutyric and pivalic acids, arbitrarily limiting the experiments with each methyl ester to four runs (two with each complex on its own and two with the Co-Ru system with Co/Ru

TABLE 2

HOMOLOGATION OF HIGHER METHYL ESTERS[a]

Run	Methyl ester RCO_2CH_3	Catalytic system[b]	Liquid products (mmol)					Gaseous products (mmol)	
			CH_3CHO	CH_3OH	C_2H_5OH	$RCO_2C_2H_5$	RCO_2H	CH_4	CO_2
Ref. 7	$R = CH_3$	(Co)	9.1	1.4	0.4	3.9	34.5	2.1	0
Ref. 7		(Co)+(Ru)[c]	0	3.2	4.4	14.1	15.4	3.5	0.5
Ref. 7		(Co)+(Ru)[d]	0	5.9	4.2	22.3	13.9	4.1	0.4
Ref. 7		(Ru)	0	2.4	0.7	3.1	5.8	1.8	0.3
887	$R = CH_3CH_2$	(Co)	8.7	0.9	0.2	2.0	12.2	4.3	1.9
890		(Co)+(Ru)[c]	0.3	2.4	4.6	11.6	12.8	2.4	0.3
877		(Co)+(Ru)[d]	0	5.6	3.2	9.2	9.6	7.9	0.7
882		(Ru)	0	3.2	1.6	3.2	2.2	3.0	0.9
914	$R = CH_3(CH_2)_2$	(Co)	6.5	0.3	0	1.7	14.7	6.3	0.1
916		(Co)+(Ru)[c]	0	3.1	3.4	9.6	10.3	7.6	0.8
915		(Co)+(Ru)[d]	0	3.2	3.4	8.8	10.0	7.2	0.5
917		(Ru)	0	0.8	1.0	1.9	3.0	5.9	1.3
919	$R = CH_3(CH_2)_3$	(Co)	5.9	0.3	0	0.8	10.4	6.0	1.8
921		(Co)+(Ru)[c]	0	3.0	3.5	9.4	14.1	6.4	1.7
920		(Co)+(Ru)[d]	0	2.7	3.3	9.4	10.6	7.8	3.5
922		(Ru)	0	1.3	1.3	3.3	7.1	6.3	9.2
918	$R = (CH_3)_2CH$	(Co)	6.9	0.4	0.5	2.4	13.5	3.2	0.8
924		(Co)+(Ru)[c]	0	2.3	3.6	5.9	8.2	5.2	1.0
923		(Co)+(Ru)[d]	0	2.3	3.4	6.0	7.8	2.6	0.2
925		(Ru)	0	0.8	1.4	2.0	2.3	6.9	5.0
886	$R = (CH_3)_3C$	(Co)	5.6	0	3.2	1.2	21.0	1.9	0.1
888		(Co)+(Ru)[c]	0	0.7	4.8	1.1	10.3	5.1	0.4
876		(Co)+(Ru)[d]	0	0.7	4.6	1.0	9.8	3.2	0.7
881		(Ru)	0	0.3	2.9	0.6	6.5	3.3	1.1

[a] Reaction conditions as in Table 1. Initial charge of ester (5 ml). No attempt to optimize the ethyl ester yield was made. Contact time in runs with $CH_3CO_2CH_3$ was 5 h, with the other esters 2 h. [b] See footnote [b] in Table 1. [c] Mol ratio (Co/Ru) = 1.0. [d] Mol ratio (Co/Ru) = 0.4.

ratios of 0.4 and 1.0). In each case the reaction gives only four liquid products [9]: methanol, ethanol, the ethyl ester and the corresponding carboxylic acid. In addition, acetaldehyde is produced in all runs in the presence of the cobalt complex alone. The results are listed in Table 2.

The following observations can be made:

(a) With the cobalt catalyst alone, large amounts of the corresponding acid are formed in each case, reflecting the well established effectiveness of the cobalt catalysts for carbonylation. Acetaldehyde is produced in every reaction, in keeping with our previous assumption that CH_3CHO is formed from the ester by the action of CO-H_2.

(b) Use of the ruthenium complex alone leads to the lowest total conversion for the four runs for each methyl ester.

(c) With the majority of esters, in the homologation the highest yields of methanol, ethanol, and especially the corresponding ethyl ester are obtained, when the Co-Ru systems are used. Only pivalic ester provides an exception; this is due to the steric hindrance to esterification induced by the bulk of the t-butyl group. At the same time production of ethanol is optimal for Co/Ru ratios of 0.4 to 1.0, thus compensating for the small extent of ethyl ester formation, so that the overall conversion of the pivalic ester is comparable with that from the other esters.

The increased formation of the ethyl ester can be attributed to the reduction of acetaldehyde which is produced when the cobalt cocatalyst is present. However, the maximum conversion depends on the Co/Ru ratio. For methyl formate, acetate and propionate, only values in a narrow region around 0.4 give optimal yields, whereas for the higher methyl esters the ratio is less critical, as long as both components are present.

(d) If the reaction scheme proposed in our former work [7] is valid, we can expect that the size of the alkyl group will affect the formation of ethanol little if at all. This was found to be the case for all runs conducted with a given catalytic system. However, the bulk of R should modify the yields of the acid and consequently of the corresponding ethyl ester, because of the steric effect during the formation of acid and the subsequent esterification; this was the case, especially for the pivalate methyl ester.

(e) The variations of the amounts of formed CH_4 and CO_2 on variations of the catalyst and the length and size of R show no consistent pattern. The reaction with methyl valerate gives large amounts of CO_2 (especially with Ru complexes), comparable to those shown in Table 1 for methyl formate.

Pressure effect

Because the production of the ethyl ester seems to involve esterification of ethanol formed in the reaction with the corresponding acid, we thought that an increase in pressure might shift the equilibrium toward the ester. The results are shown in Table 3.

Raising the pressure from 29 to about 65–70 MPa leads to a favorable shift of the esterification equilibrium. However, the results depend on the ester used: while the yield of ethyl ester is doubled for $R = H$ and $R = (CH_3)_3C$, the increase is small for the other esters. The formation of ethanol is increased with increasing pressure in all cases, while the yield of the appropriate carboxylic acid, with the exception of pivalic

TABLE 3

PRESSURE EFFECT IN THE HOMOLOGATION OF METHYL ESTERS[a]

Run	Methyl ester RCO_2CH_3	Pressure (MPa)	Liquid products (mmol)			
			CH_3OH	C_2H_5OH	$RCO_2C_2H_5$	RCO_2H
843	R = H	29	9.6	1.1	4.4	–
926		71	12.1	1.8	8.7	–
877	$R = CH_3CH_2$	29	5.6	3.2	9.2	9.6
927		70.5	4.7	4.7	12.0	8.3
915	$R = CH_3(CH_2)_2$	29	3.2	3.4	8.8	10.0
928		66.5	3.3	4.4	10.0	7.3
920	$R = CH_3(CH_2)_3$	29	2.7	3.3	9.4	10.6
930		67	3.4	4.9	10.2	7.0
923	$R = (CH_3)_2CH$	29	2.3	3.4	5.9	7.8
929		71.5	2.2	4.9	6.5	7.3
876	$R = (CH_3)_3C$	29	0.7	4.6	1.0	9.8
895		65	1.1	9.0	2.0	15.9

[a] Reaction conditions as in Table 1. Contact time 2 h, Co/Ru ratio 0.4.

acid, is decreased. In the light of earlier results [11] we thought that the presence of bulkier substituents would induce a greater pressure dependence, but the situation in the systems studied in the present work is more complicated, since the homologation reaction does not take place in isolation but is part of a catalytic cycle for which the pressure effects are unknown.

Conclusion

On the basis of the results of Tables 1 and 2 together with those previously obtained in the reductive carbonylation of methyl acetate [7], we conclude that the Co-Ru system in the appropriate ratio (which may depend on the alkyl moiety) promotes the homologation of a carboxylic ester to the corresponding ethyl ester and that the mechanism is common to all reactions, involving: (i) formation of the active anionic species $[Ru(CO)_xI_y]^-$; this process is favored by the presence of an ionic iodide (LiI); (ii) formation of the corresponding acid and the intermediate $[RuCH_3(CO)_{x-1}I_y]$; (iii) reductive carbonylation of this intermediate to C_2H_5OH.

The procedure provides a general method for homologation of methyl esters to the corresponding ethyl esters.

Depending on the structure of the substrate, optimization of the reaction is a complex problem, involving several parameters such as pressure, temperature, contact time, catalyst and promoter concentration.

Experimental section

Chemicals

Ruthenium(III) acetylacetonate was supplied by Degussa and cobalt acetate tetrahydrate was obtained from Prolabo. Lithium iodide and the methyl esters were purchased from Fluka.

Batch autoclave runs

The 15 ml-autoclave consisted of a multilayered vessel with a liner made from a special titanium steel [10]. In a typical run the vessel was filled with argon and then the catalyst together with lithium iodide (50.3 mg, 0.38 mmol), was placed in the autoclave. 5 ml of the ester were introduced. The autoclave was closed, filled with the CO/H_2 mixture up to the desired pressure, and then heated. After reaching the required temperature, the reaction was allowed to proceed for 2 h. After cooling to 20°C, the pressure was slightly released, a gas sample was taken and the autoclave opened. 200 μl of an internal standard (3-methyl-1-butanol for all runs, except those involving with methyl isobutyrate, for which 2-pentanol was used) were added to the mixture. The liquid phase was at the end analyzed by GLC: Hewlett-Packard 5700, column (Porapak R-4 m, inox, 1/8″, 80–100 mesh, 60–230°C, 4°C/mn).

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