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HOMOLOGATION WITH $CO + H_2$ OF ETHYL ORTHOFORMATE IN THE PRESENCE OF RUTHENIUM CATALYSTS: A STEPWISE HYDROGENATION AND CARBONYLATION REACTION

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Summary

The reaction of ethyl orthoformate with $CO + H_2$ (P 10–15 MPa) in the presence of ruthenium carbonyl iodide catalysts at temperatures of 130–200°C has been studied. Products of hydrogenation, carbonylation and homologation of the CH, Et and EtO moieties of the ester are formed, indicating that the catalyst can activate the substrate in three ways. Diethoxymethane was the main product at lower temperatures, whereas methyl ethyl ether, methanol, and ethyl propionate predominate at higher temperatures. The formation of significant amounts of diethyl carbonate and diethoxyethane indicates the intermediate formation of EtO-Ru derivatives. Results of experiments with $CO + D_2$ suggest a step-wise process of hydrogenation and carbonylation of the substrate, and shed new light on the mechanism of activation of esters by ruthenium carbonyl iodide catalysts.

Introduction

In the course of the studies on the homologation reactions of oxygenated substrates with $CO + H_2$ catalyzed by iodocarbonyl ruthenium systems [1–3], we gave relief to the peculiar activity of the ruthenium catalyst in the hydrogenation and homologation of the formyl moiety of alkyl formates to methyl, acetyl and ethyl derivatives [3]. This prompted us to investigate the behaviour of orthoformic esters with the aim of comparing their reactivity with that of alkyl formates and gaining evidence on the mechanism of activation of such a type of substrates.

In the literature orthoformic esters are known to react with $CO + H_2$ in the presence of $Co_2(CO)_8$ as catalyst to give a mixture of aldehydes and their acetals by

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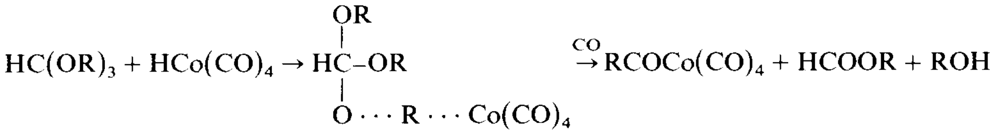
the formylation of the alkyl group of the orthoformate [4–10] (eqns. 1, 2):

$$HC(OR)_3 + CO + H_2 \rightarrow RCHO + HCOOR + ROH \quad (1)$$

$$RCHO + HC(OR)_3 \rightarrow RCH(OR)_2 + HCOOR \quad (2)$$

The study of the reaction mechanism showed that the substrate activation involves a cleavage of a C–O bond of the ester with formation of an alkyl–metal bond subsequently carbonylated and hydrogenated to aldehyde according to eqns. 3 and 4 [11]:



$$HC(OR)_3 + HCo(CO)_4 \rightarrow \begin{array}{c} OR \\ | \\ HC\text{–}OR \\ | \\ O \cdots R \cdots Co(CO)_4 \end{array} \xrightarrow{CO} RCOCo(CO)_4 + HCOOR + ROH \quad (3)$$

$$RCOCo(CO)_4 + H_2 \rightarrow RCHO + HCo(CO)_4 \quad (4)$$

No literature information is available on the use in this reaction of ruthenium catalysts which in principle should be more active in the hydrogenation steps of the process [12].

Results

Reactions of ethyl orthoformate with $CO + H_2$

In contrast to methanol, methyl ethers, methyl esters, and formic esters, which are activated towards carbonylation and homologation reactions only at temperatures > 170°C [12], ethyl orthoformate reacts with $CO + H_2$ under milder conditions and gives various products arising from different reaction pathways.

In the presence of the typical ruthenium catalytic system used for the homologation reactions ($Ru(acac)_3/CH_3I = 1/10$) [3], at a temperature of 130°C, ethyl orthoformate reacts almost completely with $CO + H_2$ 1/1 (P 14 MPa) in a few hours, the predominant reaction being hydrogenation of the CH group of the substrate to diethoxymethane (eq. 5) (Table 1):

$$HC(OEt)_3 + H_2 \rightarrow H_2C(OEt)_2 + EtOH \quad (5)$$

Diethyl carbonate and ethyl propionate, which come from carbonylation of the ethoxy and ethyl moiety of the substrate, respectively, are also formed to a smaller extent (eqns. 6 and 7):

$$HC(OEt)_3 + CO + EtOH \rightarrow CO(OEt)_2 + H_2C(OEt)_2 \quad (6)$$

$$HC(OEt)_3 + CO \rightarrow EtCOOEt + HCOOEt \quad (7)$$

It is noteworthy that under these conditions significant amounts of the diethyl acetal of acetaldehyde, arising from dehydrogenation of EtO groups, are also produced (eq. 8):

$$HC(OEt)_3 \rightarrow CH_3CH(OEt)_2 + H_2 + CO \quad (8)$$

At higher temperatures, 170 and 200°C (runs 2 and 3, Table 1), products of further hydrogenation of CH_2 groups to CH_3 and CH_4 are formed (eqns. 9 and 10), with complete conversion of the orthoformate via diethoxymethane:

$$H_2C(OEt)_2 + H_2 \rightarrow CH_3OEt + EtOH \qquad (9)$$

$$CH_3OEt + H_2 \rightarrow CH_4 + EtOH \qquad (10)$$

At the higher temperatures, however, propionic esters, the products of carbonylation of ethyl groups, greatly predominate.

In all cases the presence of an iodide promoter for the ruthenium catalyst is necessary for the catalytic reactions.

The above metal-catalyzed reactions are accompanied by hydrolysis, etherification and esterification reactions catalyzed by HI formed from the iodide promoter [2,13]. The most important products of these reactions are ethyl formate and ethanol (eqns. 11 and 12), methanol (eq. 12), and diethyl ether (eq. 13):

$$HC(OEt)_3 + H_2O \rightarrow HCOOEt + 2EtOH \qquad (11)$$

$$CH_3OEt + H_2O \rightarrow CH_3OH + EtOH \qquad (12)$$

$$2EtOH \rightarrow Et_2O + H_2O \qquad (13)$$

TABLE 1

REACTIONS OF ETHYL ORTHOFORMATE WITH CO+H_2 [a]

Run			1[b]		2		3	
Temperature (°C)			130		170		200	
Time (h)			5		10		8	
$HC(OEt)_3$ conversion (%)			66		100		100	
Part of the ester involved	Type of reaction	Reaction products	mmol	Select. (%)	mmol	Select. (%)	mmol	Select. (%)
CH	hydrogenation to CH_2	$H_2C(OEt_2)$	108	81.2	–	–	–	–
	hydrogenation to CH_3	CH_3OH	–	–	57	35.7	8	5.0
		CH_3OEt	–	–	58	36.3	37	24.9
		$EtCOOCH_3$	–	–	5	3.5	10	6.5
	hydrogenation to CH_4	CH_4	–	–	5	3.5	6	3.8
	homologation to CH_3CO	CH_3COOEt	–	–	6	4.0	18	12.2
	hydrolysis	HCOOEt	25	18.8	27	17.0	72	47.6
Et	hydrogenation	C_2H_6	0.5	0.1	8	1.3	5	0.8
	dehydrogenation	$CH_3CH(OEt)_2$	4.5	3.4	–	–	–	–
	carbonylation	$EtCOOCH_3$	–	–	5	0.9	10	1.6
		EtCOOEt	5	2.6	17	5.6	82	26.9
	hydrolysis,	EtOH	111	28.8	362	59.6	148	24.5
	etherification and	Et_2O	–	–	41	13.6	59	19.3
	esterification	HCOOEt	25	6.5	27	4.4	72	11.8
		CH_3OEt	–	–	58	9.6	37	6.1
		CH_3COOEt	–	–	6	1.0	18	3.0
		$H_2C(OEt)_2$	108	56.0	–	–	–	–
	homologation	$EtCH_2OEt$	–	–	7	2.3	11	3.5
EtO	carbonylation	$(EtO)_2CO$	5	2.6	5	1.7	8	2.5
	other products	H_2O	traces		56		97	
Accountability [c] (%)			97.5		96		95	

[a] Reaction conditions: $HC(OEt)_3$ 200 mmol; $Ru(acac)_3$ 0.4 mmol; CH_3I 4 mmol; P 14 MPa; $CO/H_2 = 1$; [b] $Ru(CO)_4I_2$ 0.4 mmol. [c] Evaluated as $C_1 + C_2 + C_3$ groups in the products/$HC(OEt)_3 \times 4$.

Methyl propionate, formed by transesterification of ethyl propionate with methanol, is also present (eq. 14):

$$EtCOOEt + CH_3OH \rightarrow EtCOOCH_3 + EtOH \qquad (14)$$

In addition to these main products, small amounts of derivatives of further hydrogenation, carbonylation and homologation of methyl and ethyl substrates are also formed: among these, ethyl acetate is probably formed by carbonylation of methanol or methyl ethyl ether (eqns. 15 and 16),

$$CH_3OH + CO + EtOH \rightarrow CH_3COOEt + H_2O \qquad (15)$$

$$CH_3OEt + CO \rightarrow CH_3COOEt \qquad (16)$$

ethane by hydrogenation of EtOH (eq. 17),

$$EtOH + H_2 \rightarrow C_2H_6 + H_2O \qquad (17)$$

and ethyl-n-propyl ether by homologation of diethyl ether (eq. 18)

$$Et_2O + CO + 2H_2 \rightarrow EtCH_2OEt + H_2O \qquad (18)$$

A more comprehensive knowledge of the course of the reaction has been gained by following the change with time of the composition of the liquid products up to a complete conversion of ethyl orthoformate and diethoxymethane. The selectivities for the products coming from the CH and Et groups are shown separately in Fig. 1A and 1B, and overall balance of the products at various times in Table 2. Figure 1A clearly reveals the successive hydrogenation of the CH groups to CH_2 and CH_3 derivatives and the carbonylation of these to acetic compounds. Figure 1B shows that the Et groups, EtOH and HCOOEt, which are the primary products from the hydrogenation and hydrolysis of ethyl orthoformate (eqns. 5, 9, 10, and 11), are progressively carbonylated to propionic and homologated to n-propyl derivatives.

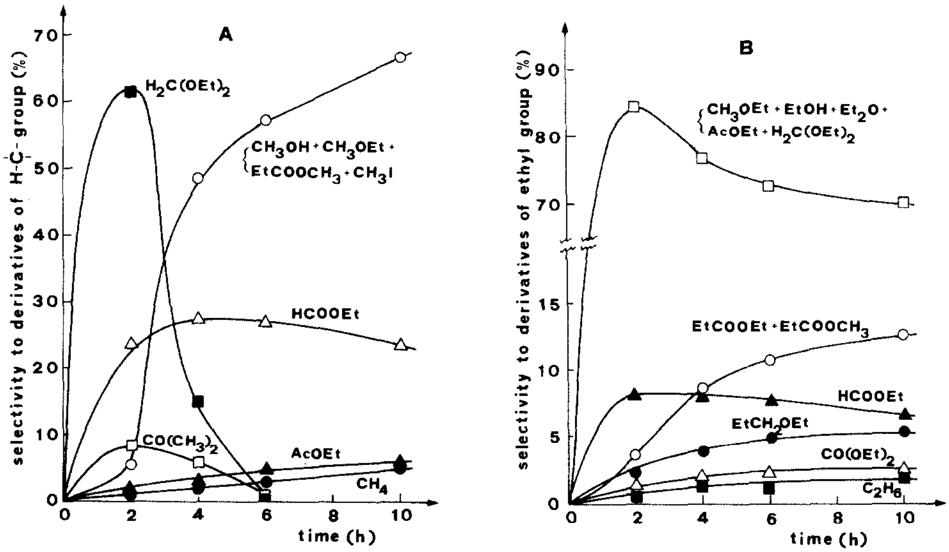


Fig. 1. Reaction of ethyl orthoformate with $CO+H_2$. $Ru(acac)_3$ 3.2 mmol; $CH_3I/Ru=10$; $HC(OEt)_3$ 1.625 mol; T 170°C; P 14 MPa; $CO/H_2=1$.

Partial homologation of CH to Et groups also accounts for the deficit in the overall balance of C_1 and the small excess of C_2 and C_3 derivatives with respect to those present in the initial orthoformate.

The high reactivity of ethyl orthoformate compared with other C_2 ether and ester substrates, such as diethyl ether and ethyl formate can be seen by comparing the conversions in experiments carried out simultaneously under the same conditions (Table 3). The same products of carbonylation of the ethyl moiety are found as in the case of ethyl orthoformate, together with the products of hydrogenation of the other part of the substrate (hydrocarbons and methyl derivatives in the case of HCOOEt). In contrast, no carbonic acid esters coming from the carbonylation of the ethoxy group were formed in the runs involving ethyl formate and diethyl ether.

The results underline once more the high activity of the ruthenium catalysts in the hydrogenation reactions of various substrates and, at the same time, their poor activity in the carbonylation reactions at temperature below 170°C.

TABLE 2

OVERALL BALANCE OF THE PRODUCTS OBTAINED IN THE REACTION OF NEAT ETHYL ORTHOFORMATE WITH $CO+H_2$ AT 170°C [a]

Time (h)	2		4		10	
Conversion of $HC(OEt)_3$ (%)	100		100		100	
	mmol	Select. (%)	mmol	Select. (%)	mmol	Select. (%)
CH *groups balance*						
CH groups in HCOOEt	386	23.8	389	27.6	326	23.6
CH_2 groups in $H_2C(OEt)_2$	992	61.2	210	14.8	0	0
CH_3 groups in						
CH_3OH	32	1.9	307	21.8	314	22.7
CH_3OEt	56	3.5	338	24.0	513	37.1
$EtCOOCH_3$	0	0	37	2.6	90	6.5
CH_3COOEt	20	1.2	33	2.3	77	5.5
$(CH_3O)_2CO$	65	8.0	38	5.6	0	0
CH_4	6	0.4	19	1.3	63	4.6
Et *groups balance*						
C_2H_5 groups in						
$(EtO)_2CO$	36	1.5	41	1.7	53	2.1
C_2H_6	17	0.3	72	1.4	178	3.6
$EtCOOCH_3$	0	0	37	0.7	90	1.8
EtCOOEt	86	3.6	191	7.8	269	10.8
EtOH	1841	38.6	2555	52.0	1956	39.4
Et_2O	59	2.4	208	8.6	462	18.6
HCOOEt	382	8.1	388	7.9	326	6.6
CH_3OEt	55	1.2	338	6.9	513	10.3
CH_3COOEt	20	0.4	33	0.7	77	1.6
$H_2C(OEt)_2$	991	41.6	209	8.6	0	0
$EtOCH_2Et$	54	2.3	92	3.7	128	5.2
Accountability						
C_1 (mmol)	1620		1410		1384	
C_2 (mmol)	4765		4910		4961	

[a] Reaction conditions: see Fig. 1.

TABLE 3

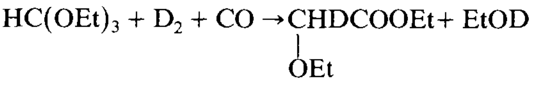
ETHYL ORTHOFORMATE, ETHYL FORMATE AND DIETHYL ETHER REACTIONS WITH $CO+H_2$ [a]

Run	4		5 [b]		6	
Substrate (mmol)	$HC(OEt)_3$, 200		HCOOEt, 400		Et_2O, 300	
Conversion (%)	100		38.5		4.5	
Reaction products [c]	mmol	Select. (%)	mmol	Select. (%)	mmol	Select. (%)
CH_3OH	24	3.1	10	3.3	–	–
CH_3OEt	33	8.2	7	4.4	–	–
$HCOOCH_3$	–	–	59	37.9	–	–
EtOH	298	37.3	84	27.2	12	53.6
Et_2O	31	7.9	9	5.9	–	–
HCOOEt	32	8.0	–	–	–	–
$EtOCH_2Et$	4	1.0	–	–	–	–
$(CH_3O)_2CO$	18	4.4	–	–	–	–
CH_3COOEt	6.5	1.5	9	5.7	3	22.3
CH_3COOH	–	–	9	2.8	–	–
$H_2C(OEt)_2$	61	23.0	–	–	–	–
EtCOOEt	15	3.7	14	9.2	2	16.1
$(EtO)_2CO$	5	1.2	–	–	–	–
$CH_4+C_2H_6$	6	0.7	11	3.6	2	8.0

[a] Reaction conditions: $Ru(acac)_3$ 0.4 mmol; CH_3I/Ru 10; T 170°C; P 15 MPa; $CO/H_2=1/1$; Time 5 h. [b] $Ru(acac)_3$ 0.8 mmol; [c] $\text{Select. (\%)} = \frac{[(\text{product,mol}) \times (\text{number of } C_1 \text{ and } C_2 \text{ groups})]}{\Sigma[(\text{product,mol}) \times (\text{number of } C_1 \text{ and } C_2 \text{ groups})]} \times 100.$

Reactions of ethyl orthoformate with $CO + D_2$

To gain a better understanding of the catalytic steps of the process, ethyl orthoformate was treated with $CO + D_2$ at different temperatures and partial pressures P_{CO} and P_{D_2} (Table 4). Deuterated products from the orthoformate, $HDC(OEt)_2$, CHD_2OD, CHD_2OEt, all arising from deuteration of the CH group were observed. In addition, EtOD, co-product of the hydrogenation reactions (eqns. 5, 9 and 10), and D_2O, formed in etherification, hydrogenation, homologation and esterification reactions (eqns. 13, 17, 18 and 15), were also detected. Moreover at the higher P_{CO} used in the deuteration experiments ($CO/D_2 = 2.5/1$), two new carbonylation products appeared, namely (a) ethyl ethoxymonodeuteroacetate $HDC(OEt)COOEt$, coming from deuteration and carbonylation of the CH moiety (eq. 19)



$$HC(OEt)_3 + D_2 + CO \rightarrow \underset{\displaystyle OEt}{\underset{|}{CHDCOOEt}} + EtOD \qquad (19)$$

and (b) di-deuteromethylcarbonate, $CO(OCHD_2)_2$, coming from the carbonylation of CHD_2O derivatives. In contrast, there were no significant amounts of products arising from H/D exchange reactions at C–H bonds of the ethyl groups of the orthoformate. The other identified non-deuterated products arising from carbonylation (EtCOOEt, HCOOEt, $CO(OEt)_2$) and dehydrogenation ($CH_3CH(OEt)_2$, CH_3COOEt) of the ethyl and ethoxy groups of the substrate were the same as those formed in the experiments with $CO + H_2$.

TABLE 4

REACTION OF ETHYL ORTHOFORMATE WITH CO + D_2 [a]

Run	7	8	9
Reagent	$HC(OEt)_3$	Products of run 7	Products of run 8
CO/D_2 (MPa)	2.5 (14)	2.5 (10)	1.0 (8)
Temperature (°C)	150	170	200
Time (h)	4	4	6
Conversion of $HC(OEt)_3$ (%)	20	38.5	100
	Mol. % in solution	Mol. % in solution	Mol. % in solution
Deuterated products			
$HDC(OEt)_2$	5.6	12.0	3.0
 $\mathrm{HD}\underset{\substack{\vert\\ \mathrm{OEt}}}{\mathrm{C}}\mathrm{COOEt}$	–	1.5	1.0
$CHD_2OD + CHD_2OH$	–	–	1.5
CHD_2OEt	–	–	7.0
$(CHD_2O)_2CO$	–	–	0.3
$EtOD + EtOH + Et_2O$	17.8	28.6	40.0
$D_2O + DHO + H_2O$	1.3	2.5	16.5
Other products			
HCOOEt	9.0	10.8	13.0
$(EtO)_2CO$	–	1.8	1.8
CH_3COOEt	0.7	0.9	0.9
$CH_3CH(OEt)_2$	1.0	1.4	–
EtCOOEt	0.6	2.0	15.0

[a] Reaction conditions: $Ru(acac)_3$ 0.4 mmol; CH_3I 4 mmol; $HC(OEt)_3$ 0.2 mol.

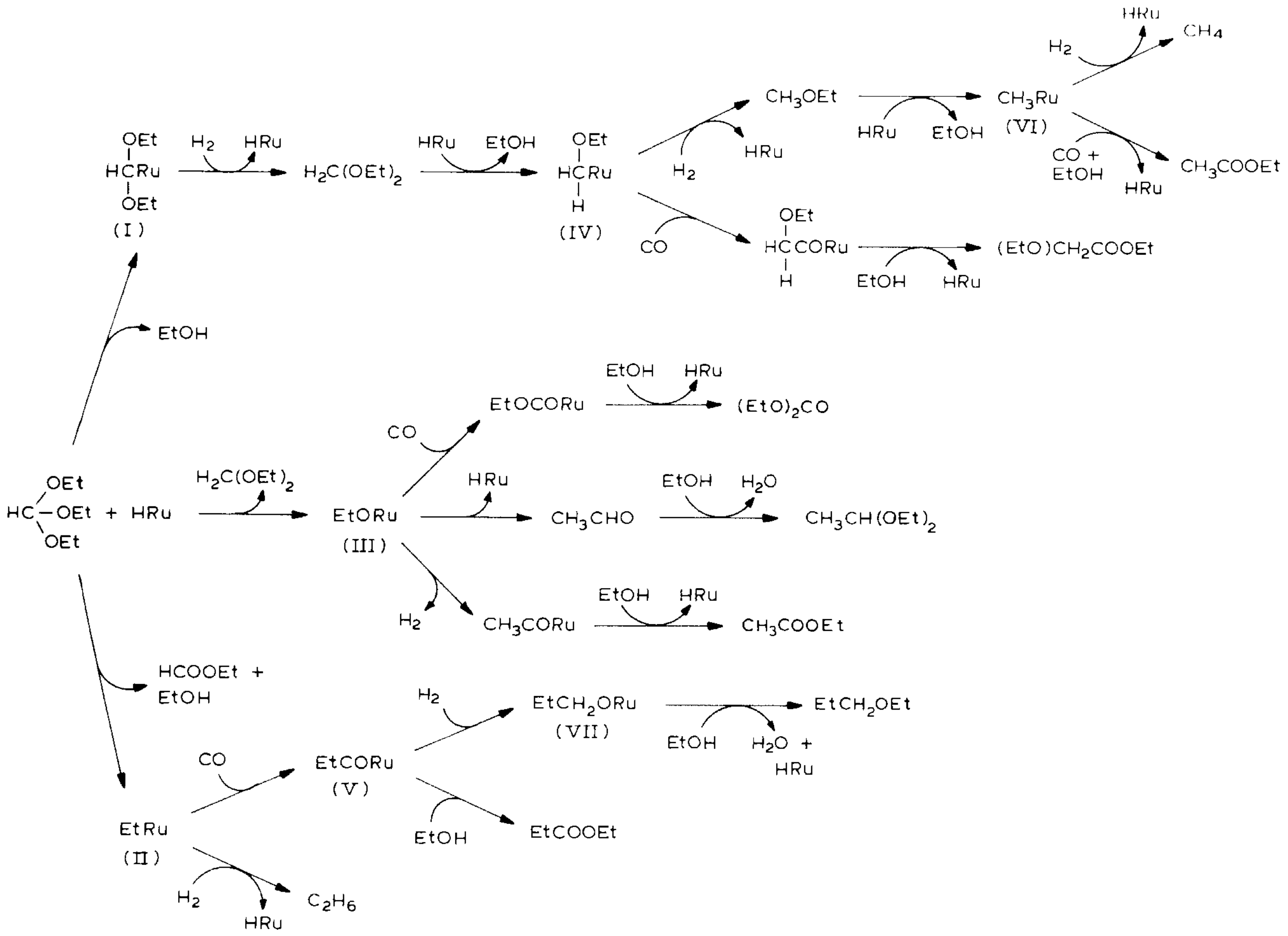
Discussion

Because of its high reactivity, ethyl orthoformate reacted with CO + H_2 or CO + D_2 under mild conditions and this allows the detection and identification of well defined stable intermediate products which shed new light on the pathways of activation of ester substrates by the ruthenium carbonyl iodide systems.

The simultaneous formation of hydrogenation and carbonylation products from the CH, Et and EtO groups of the substrate reveals the peculiar ability of the ruthenium catalyst to activate the orthoformic ester in three different ways, involving formation of diethoxymethyl (I), ethyl (II), and ethoxy (III) ruthenium intermediates, respectively (Scheme 1). As postulated for other oxygenated substrates [9,12], a ruthenium hydrido species is probably involved in the activation of the ethyl orthoformate. The hydride atom can be transferred both to the oxygen atoms with releasing of EtOH or HCOOEt + EtOH and formation of the intermediates I and II, and to the carbon atom of the CH group, with release of $H_2C(OEt)_2$ and formation of the intermediate III.

The evolution of these ruthenium intermediates by reaction with H_2 or CO leads to primary products of hydrogenation (diethoxymethane from I, and ethane from II) and of carbonylation (ethyl propionate from II and diethyl carbonate from III). Dehydrogenation products, such as acetaldehyde diethylacetal can be also produced from III when the P_{H_2} is kept low.

The higher concentration in the reaction mixture of $H_2C(OEt)_2$, $HDC(OEt)_2$; and propionic esters compared to $CO(OEt)_2$ and $CH_3CH(OEt)_2$ seems to indicate



SCHEME 1. General scheme for hydrogenation, carbonylation and homologation of ethyl orthoformate.

that the intermediates I and II are formed more readily than III and are more reactive. The formation of an alkylruthenium intermediate of type II has previously been proposed and indirectly confirmed by consideration of the products obtained in the homologation of methanol [14], ethers [2], alkyl formates, and other carboxylic acid esters [3] in the presence of the same ruthenium carbonyl iodide catalysts. The diethoxymethylruthenium intermediate I has not been previously observed or proposed, even though a HCO-Ru intermediate, the parent of I, seems to be involved in the homologation of alkyl formates [3]. The alkoxyruthenium derivative III, through which diethyl carbonate can be formed, has been suggested to be one of the possible intermediates involved in the hydrogenation of carbon monoxide to methanol in the presence of ruthenium catalysts [15–17].

The oxygenated primary products of the reaction can be further activated towards subsequent hydrogenation and carbonylation reactions. Thus diethoxymethane can be hydrogenated, through an ethoxymethylruthenium intermediate IV, to methyl ethyl ether or carbonylated to ethyl ethoxyacetate, whereas the propionyl derivatives can be hydrogenated, through an n-propoxyruthenium intermediate VII, to n-propyl compounds (ethyl-n-propyl ether). A third process of activation of the products coming from the CH moiety is observed at the level of methyl derivatives, and leads to methane by hydrogenation and acetic derivatives by carbonylation of the methylruthenium intermediate VI.

The formation of non-deuterated ethyl acetate in the deuterocarbonylation of ethyl orthoformate indicates that the acetic derivatives can be also produced by dehydrogenation of an ethoxyruthenium intermediate [18].

Experimental section

Materials

Tris(acetylacetonato)ruthenium(III), Ru(acac)$_3$, was prepared by a published procedure [19] starting from RuCl$_3$ hydrate (Ind. Engelhard S.p.A.).

Methyl iodide (Merck), ethyl orthoformate (Merck), ethyl formate (Carlo Erba) and diethyl ether (Carlo Erba) were commercial products, and were distilled before use

Deuterium (Matheson) 99.7%, was used as supplied.

Apparatus and procedure

The experiments were carried out either in a 190 ml Hastelloy C rocking autoclave, heated in an oil bath, or in a 1 l Hastelloy C reactor, magnetically stirred and electrically heated, equipped with devices for collecting liquid and gas samples during the runs (Brignole).

Analysis

The liquid products of the catalytic runs were qualitatively identified by mass spectrometry (Hewlett Packard Spectrometer 5995 A) and quantitatively determined by GC using a Carlo Erba Fractovap Model 2450 (with a thermal conductivity detector) and Porapak PS columns. Because of the complexity of the liquid mixture a standardization procedure was used for quantitative analysis [20].

Gas products were analyzed by GC using columns of 5 Å molecular sieves and silica gel (35 mesh).

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