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Hydrocarbonylation of ethyl orthoformate in the presence of rhodium catalysts

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Abstract

The reaction of ethyl orthoformate with a mixture of CO and H_2 (P 8 MPa) in the presence of various rhodium carbonyl catalysts with and without iodide promoters at temperatures of 150–170 °C has been studied. The $[Rh(CO)_2I_2]^-/CH_3I$ systems mainly catalyze the hydrogenation of ethyl orthoformate to diethoxymethane without any subsequent hydrogenation to methyl derivatives and methane. Carbonylation and hydrocarbonylation products of the ethyl moiety, i.e. ethyl propionate and 1,1-diethoxypropane together with diethyl carbonate coming from carbonylation of the ethoxy group, are produced, with a maximum selectivity of 12%. Chlorocarbonylrhodium systems without iodide promoters are active in the hydrogenation and hydrocarbonylation of the substrate, whereas carbonylrhodium derivatives without halide ligands and promoters only catalyze the hydrogenation to diethoxymethane.

IR spectroscopic studies show that the rhodium species produced under the reaction conditions are in all cases anionic halocarbonyl or carbonyl complexes, and the course of the reaction seems to depend on the hydrido character of the parent derivative.

Introduction

The hydrocarbonylation of orthoformic esters is a useful reaction for testing catalytic properties and for clarifying the mechanism of substrate activation by systems based on transition metal complexes. These esters may undergo (i) simple carbonylation at the alkyl moiety, to give esters, (ii) hydrocarbonylation with formation of aldehydes and acetals or alcohols derived from the hydrogenation of the ester, and (iii) hydrogenation of the formyl moiety, with formation of diethoxymethane, methyl ethyl ether, etc.

Carbonylcobalt catalysts have been thoroughly investigated [1], and the results demonstrate that the substrate activation involves selective cleavage of a C–O bond

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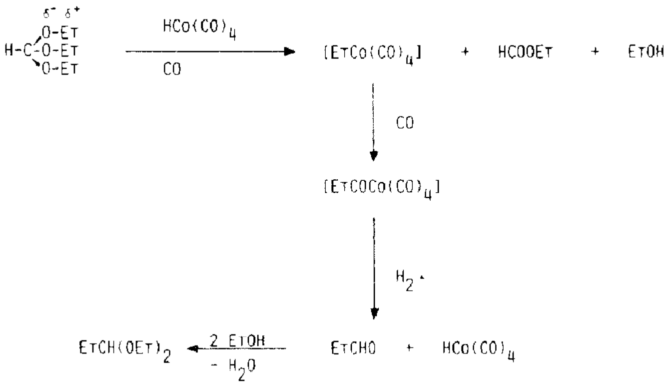


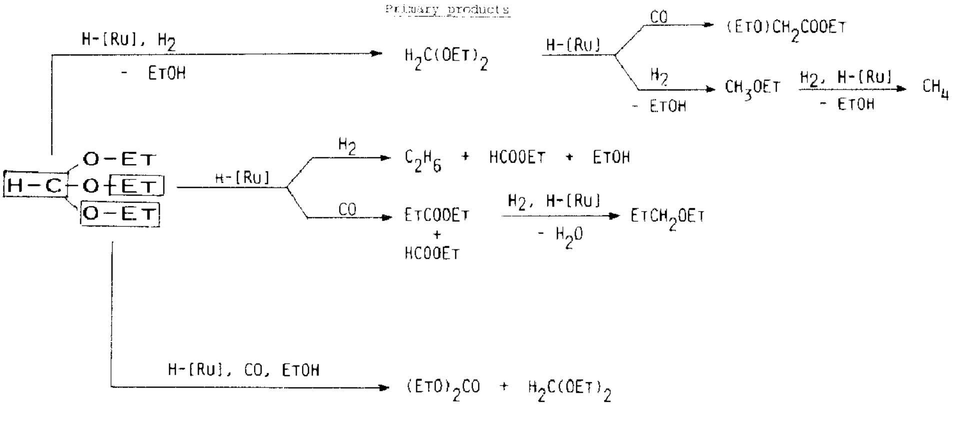
Scheme 1. Hydrocarbonylation of ethyl orthoformate with carbonylcobalt catalysts [1].

of the ester with formation of an alkylmetal intermediate, which is subsequently hydroformylated to give propionaldehyde and its diethyl acetal, as shown in Scheme 1.

(Iodo)(carbonyl)ruthenium systems $[Ru(CO)_3I_3]^-$ are, in contrast, non-selective catalysts, being able to activate the substrate in three different ways, involving the HC<, Et and EtO groups, and giving, as primary products, diethoxymethane and ethane by hydrogenation and ethyl propionate and diethyl carbonate by carbonylation [2] (Scheme 2). Subsequent hydrogenation of diethoxymethane and ethyl propionate produces methyl ethyl ether and then methane and n-propyl derivatives, respectively. Carbonylation of diethoxymethane gives ethoxyacetic derivatives.

No information is available in the literature on the use in this reaction of rhodium catalyst which is well known to be very active in carbonylation reactions of oxygenated substrates (carbonylation of methanol to give acetic acid [3] or of methyl acetate to give acetic anhydride [4]) and in hydrocarbonylation reactions (hydroformylation of olefins to give aldehydes [5], homologation of formaldehyde to give glycolaldehyde [6,7].

The present work was undertaken to obtain information about the activation mechanism and behaviour of rhodium-based catalytic systems involving various ligands.



Scheme 2. Hydrocarbonylation of ethyl orthoformate with ruthenium catalysts [2].

Results

Hydrocarbonylation with dicarbonyldiiodorhodate(I) catalysts $[Rh(CO)_2I_2]^-$

In the presence of the typical iodide-promoted rhodium catalysts used in methanol carbonylation [3], and involving under the reaction conditions the dicarbonyldiiodorhodate(I) anion as the main species (catalytic system precursor $RhCl_3/CH_3I$ 1/100), ethyl orthoformate is almost completely converted within a few hours at a temperature of 150 °C by reaction with $CO + H_2$ 1/1 (P 8 MPa) into the products indicated in Table 1.

The predominant reaction is the hydrogenation of $HC(OEt)_3$ to give diethoxymethane (eq. 1):

$$HC(OEt)_3 + H_2 \rightarrow H_2C(OEt)_2 + EtOH \qquad (1)$$

Smaller amounts of ethyl propionate and ethyl carbonate (eq. 2 and 3) are also obtained, by carbonylation of the ethyl and ethoxy moiety respectively:

$$HC(OEt)_3 + CO \rightarrow EtCOOEt + HCOOEt \qquad (2)$$

$$HC(OEt)_3 + CO + EtOH \rightarrow (EtO)_2CO + H_2C(OEt)_2 \qquad (3)$$

These metal-catalyzed reactions are also accompanied by some other acid (HI, $HRh(CO)_2I_2$) catalyzed reactions, such as hydrolysis, etherification, and esterification reactions, of the substrates, producing diethyl ether (eq. 4) or ethyl formate along with ethanol (eq. 5):

$$2EtOH \rightarrow Et_2O + H_2O \qquad (4)$$

$$HC(OEt)_3 + H_2O \rightarrow HCOOEt + 2EtOH \qquad (5)$$

No subsequent hydrogenation of the $H_2C\langle$ moiety to give methyl derivatives takes place even when the temperature is raised to 170 °C (run 3) and the H_2/CO ratio to 5 (run 4). The only new reaction observed at higher temperatures is the carbonylation of diethoxymethane to ethoxyacetic acid and ethyl ethoxyacetate (eq. 6 and 7):

$$H_2C(OEt)_2 + CO + H_2O \rightarrow H_2C(OEt)COOH + EtOH \qquad (6)$$

$$H_2C(OEt)_2 + CO \rightarrow H_2C(OEt)COOEt \qquad (7)$$

An increase in P_{CO} results in formation of small amounts of 1,1-diethoxypropane, formed by hydroformylation of the ethyl moiety (eq. 8), together with ethyl propionate which is the product of simple carbonylation.

$$2HC(OEt)_3 + CO + H_2 \rightarrow EtCH(OEt)_2 + EtOH + 2HCOOEt \qquad (8)$$

A clearer knowledge of the course of the reaction was obtained by following the change with time of the composition of the liquid products up to a complete conversion of ethyl orthoformate.

In contrast with the results obtained with (iodo)(carbonyl)ruthenium systems, the only hydrogenation reaction catalyzed by the (iodo)(carbonyl)rhodium system is the formation of diethoxymethane (Fig. 1): a control experiment showed that this substrate is completely inert under the conditions used toward further hydrogenation, and only undergoes carbonylation to give ethoxyacetic derivatives. Ethanol is consumed at the same time, to give the simple carbonylation products ethyl propionate and propionic acid.

Table 1

Hydrocarbonylation of ethyl orthoformate with $[Rh(CO)_2I_2]^-$ catalyst systems [a]

Run			1		2		3		4	
Temperature (°C)			150		150		170		150	
H_2/CO			1/1		1/2		1/1		5/1	
$HC(OEt)_3$ conv. (%)			100		100		100		100	
Part of ester involved	Type of reaction	Reaction products	mmol	Sel. (%)	mmol	Sel. (%)	mmol	Sel. (%)	mmol	Sel. (%)
CH	Hydrogenation to CH_2	$H_2C(OEt)_2$	165.1	78.3	119.7	61.9	135.2	68.3	186.0	93.0
	Hydrogenation to CH_2 plus carbonylation	$H_2C(OEt)COOEt$	–	–	–	–	4.5	2.3	–	–
		$H_2C(OEt)COOH$	–	–	–	–	3.3	1.6	–	–
	Transformation into ethyl formate	HCOOEt	45.6	21.7	73.6	38.1	55.0	27.8	14.0	7.0
Et	Hydroformylation	$EtCH(OEt)_2$	–	–	6.3	3.4	–	–	–	–
	Carbonylation	EtCOOEt	16.8	5.9	19.3	6.9	22.1	7.4	4.0	1.3
	Transformation into other ethyl derivatives	EtOH + EtI	143.0	25.1	179.1	31.9	152.5	25.4	144.7	24.2
		Et_2O	5.0	1.7	–	–	29.3	9.8	16.9	5.6
		HCOOEt	45.5	8.0	73.6	13.2	55.0	9.2	14.0	2.5
		$H_2C(OEt)_2$	165.1	58.2	119.7	43.0	135.2	45.1	186.0	66.4
		$H_2C(OEt)COOEt$	–	–	–	–	4.5	1.5	–	–
		$H_2C(OEt)COOH$	–	–	–	–	3.3	0.5	–	–
EtO	Carbonylation	$(EtO)_2CO$	2.6	0.1	4.2	1.5	3.1	1.0	–	–
Accountability [b] (%)			97		94		99		100	

[a] Reaction conditions: $HC(OEt)_3$ 200 mmol; $RhCl_3$ 0.2 mmol; CH_3I 20 mmol; time 8 h; P 8 MPa. [b] Evaluated as: $C_1 + C_2 + C_3$ groups in the products/$HC(OEt)_3 \times 4$.

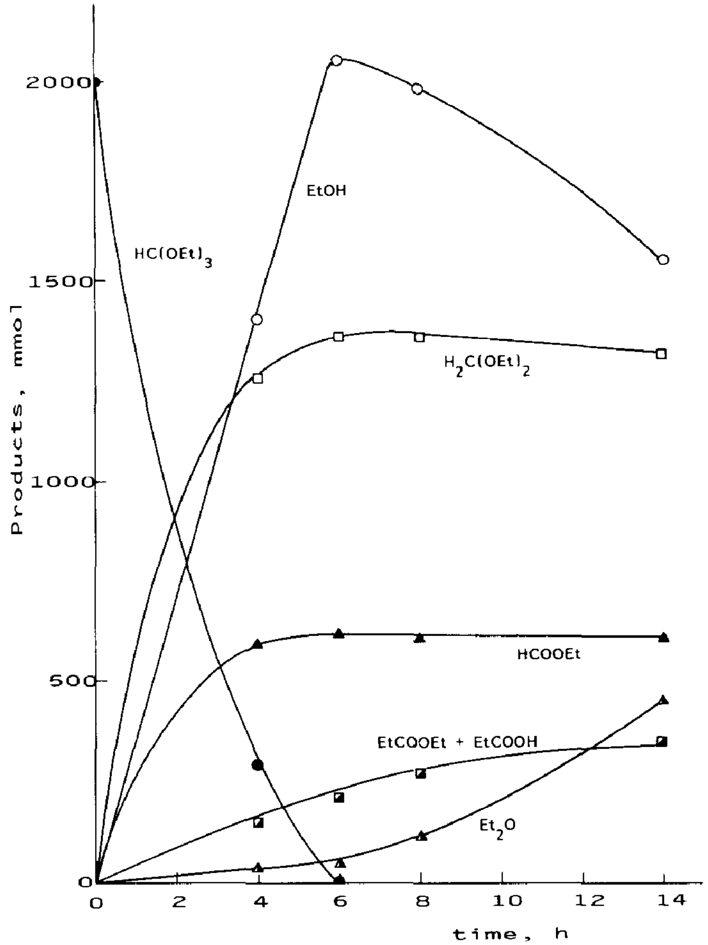


Fig. 1. Hydrocarbonylation of ethyl orthoformate in the presence of $[Rh(CO)_2I_2]^-$ catalyst. Rhodium precursor: $RhCl_3 \cdot 3H_2O$: 2 mmol; CH_3I/Rh: 100; $HC(OEt)_3$: 2 mol; T: 150 °C; P: 8 MPa; CO/H_2: 1.

The IR spectra of the solution during the reaction indicates that the sole Rh-containing species is the anion $[Rh(CO)_2I_2]^-$, the counter ion probably being H^+ solvated by the oxygenated substrate [8].

Hydrocarbonylation with (chloro)(carbonyl)rhodium(I) and carbonylrhodium species

The neutral complexes $[Rh(CO)_2Cl]_2$ and $Rh_4(CO)_{12}$ and salts of the anion $[Rh(CO)_2Cl_2]^-$ were also tried as catalysts in the hydrocarbonylation of ethyl orthoformate with the aim of decreasing the acidity of the reaction medium and suppressing the formation of hydrolysis and etherification products. Anionic chlorocarbonylrhodium(I) derivatives are reported to be involved in the hydroformylation of formaldehyde to glycol aldehyde [7], whereas the neutral complex $[Rh(CO)_2Cl]_2$ and $Rh_4(CO)_{12}$ are frequently used as rhodium precursors in hydroformylation and carbonylation reactions [5,9].

The results obtained in a series of runs carried out under the typical reaction conditions used in the previous experiments are shown in Table 2. The main reactions catalyzed by the neutral rhodium chloro carbonyl derivatives (runs 5 and

Table 2

Ethyl orthoformate reactions with $CO + H_2$ with chlorocarbonylrhodium(I) and carbonylrhodium catalysts [a]

Run			5		6		7		8		9	
Catalyst			$[Rh(CO)_2Cl]_2$		$[Rh(CO)_2Cl]_2$		$[NBu_4][Rh(CO)_2Cl_2]$		$Rh_4(CO)_{12}$		$Rh_4(CO)_{12}/NBu_4Cl$ [c]	
$HC(OEt)_3$ conv. (%)			100		90.2		10.0		55.0		60.1	
H_2/CO			1		1/2		1		1		1	
Part of the ester involved	Type of reaction	Reaction products	mmol	Select. (%)	mmol	Select. (%)	mmol	Select. (%)	mmol	Select. (%)	mmol	Select. (%)
CH	Hydrogenation to CH_2	$H_2C(OEt)_2$	156.1	78.8	109.0	61.8	11.5	48.9	104.1	100	103.7	84.6
	Transformation into ethyl formate	HCOOEt	41.9	21.2	67.5	38.2	12.0	51.1	–	–	18.8	15.4
Et	Hydroformylation	$EtCH(OEt)_2$	21.5	11.3	30.0	16.8	–	–	–	–	–	–
	Transformation into other ethyl derivatives	EtOH	142.5	25.0	152.6	28.5	28.4	44.8	94.7	30.0	103.8	28.6
		Et_2O	–	–	–	–	–	–	6.2	3.9	16.7	9.2
		HCOOEt	42.0	7.4	67.5	12.6	12.0	18.9	–	–	18.8	5.1
		$H_2C(OEt)_2$	156.1	54.8	109.0	40.8	11.5	36.3	104.1	66.1	103.7	57.1
	Homologation	PrOH	8.7	1.5	6.5	1.2	–	–	–	–	–	–
Accountability [b] (%)			96.0		98.5		100		95.2		100	

[a] Reaction conditions: $HC(OEt)_3$ 200 mmol; $[Rh]/HC(OEt)_3$ 1×10^{-3}; T 150 °C; P 8 MPa; time 8 h. [b] Evaluated as: $C_1 + C_2 + C_3$ groups in the products/$HC(OEt)_3 \times 4$. [c] $Rh_4(CO)_{12}/NBu_4Cl$ molar ratio: 1/2.

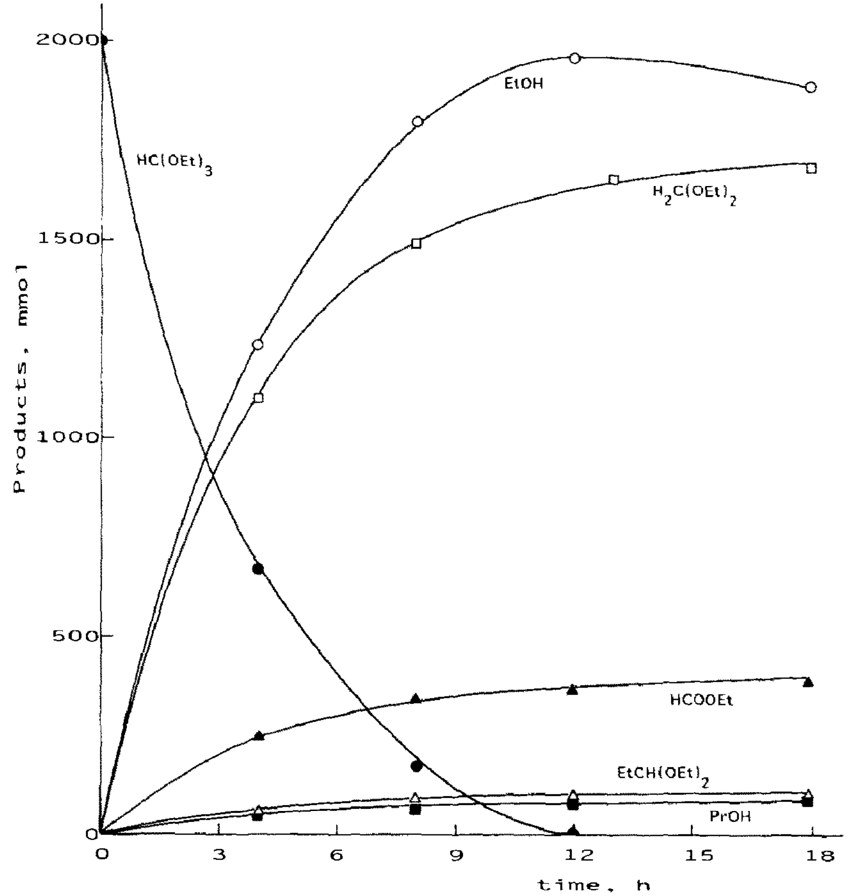


Fig. 2. Hydrocarbonylation of ethyl orthoformate in the presence of $[Rh(CO)_2Cl]_2$ catalyst. $[Rh(CO)_2Cl]_2$: 1 mmol; $HC(OEt)_3$: 2 mol; T: 170 °C; P: 8 MPa; CO/H_2: 1.

6) are hydrogenation of the HC$\lessdot$ moiety to give diethoxymethane (selectivity 60–80%), and hydroformylation of the ethyl group to give 1,1-diethoxypropane (selectivity 10–20%). Significant amounts, increasing with time, of n-propanol produced by hydrogenation of the propionaldehyde derivatives are also formed (Fig. 2). Acid-catalyzed reactions, e.g. the etherification of ethanol, do not occur with this system.

From the solution after the reaction at room temperature under atmospheric CO pressure, most of the rhodium catalyst separates in form of black crystals of the $Rh_6(CO)_{16}$ carbonyl cluster (ν(CO) 2073s, 2026m, 1800s cm^{-1}) [10]. This is not surprising since the runs were carried out under the typical conditions used for the formation of this compound [11]. Very small amounts of another unidentified yellow-green carbonylrhodium species are present in the solution (ν(CO) terminal: 2035s, 1990sh, 1925s). Attempts to isolate this compound, probably an anionic (chloro)(carbonyl)rhodium cluster, from the reaction mixture failed, in accord with the known instability of such derivatives [12] and with the existence of a complex equilibrium between the neutral and anionic carbonyl- and chlorocarbonyl-rhodium cluster complexes [8]. The chlorocarbonylrhodium salt $[NBu_4][Rh(CO)_2Cl_2]$ is a very poor catalyst, active only in the hydrogenation of ethyl orthoformate to give diethoxymethane (run 7 Table 2); no hydroformylation or carbonylation products of the ethyl moiety were detected.

The IR spectrum of the catalytic solution indicates the predominant presence of the tetrabutylammonium salt of the anionic cluster $[\mathrm{Rh_5(CO)_{15}}]^-$ (ν(CO): 2045s, 2010s, 1870m, 1838m, 1785m [13]), in accord with the known tendency of anionic chlorocarbonylrhodium(I) species to undergo cluster formation under the reaction conditions [7].

More active in the catalysis, but showing analogous behaviour is $\mathrm{Rh_4(CO)_{12}}$ in the absence of chloride promoters or in the presence of a chloride salt such as $\mathrm{NBu_4Cl}$. Only the hydrogenation to diethoxymethane is observed and no hydrocarbonylation products are detected. This is a very striking result in view of the high catalytic activity of the carbonyl rhodium derivatives in olefin hydroformylation [5].

From the reaction solution of run 8 some neutral $\mathrm{Rh_6(CO)_{16}}$ separated out, and the IR spectrum of the solution indicated the presence of only the anionic carbonylrhodium cluster $[\mathrm{Rh_5(CO)_{15}}]^-$. The formation of the anion $[\mathrm{Rh_5(CO)_{15}}]^-$ may be related to the condensation of the $[\mathrm{Rh(CO)_4}]^-$ species, produced by action of $\mathrm{H_2}$ on the polynuclear Rh species [14], with its parent complex (eq. 9) [13].

$$\mathrm{Rh_4(CO)_{12}} + [\mathrm{Rh(CO)_4}]^- \rightarrow [\mathrm{Rh_5(CO)_{15}}]^- + \mathrm{CO} \qquad (9)$$

Practically the same catalytic behaviour and IR pattern were observed when $\mathrm{NBu_4Cl}$ was added to $\mathrm{Rh_4(CO)_{12}}$ in a molar ratio of 2/1.

Discussion

The behaviour of the rhodium catalytic systems in the hydrocarbonylation of ethyl orthoformate differs from that observed for the corresponding cobalt [1] and ruthenium systems [2] in the following respects:

(i) hydrogenation of the substrate to give $\mathrm{H_2C(OEt)_2}$ predominates over carbonylation to give propionyl derivatives and/or hydroformylation to give propionaldehyde and its acetals;

(ii) only one hydrogenation step of the $\mathrm{HC}\leqslant$ moiety to $\mathrm{H_2C}<$ occurs with no subsequent hydrogenation of $\mathrm{H_2C(OEt)_2}$ to give methyl derivatives or methane.

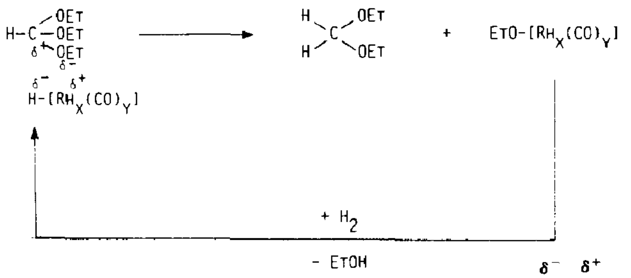
Moreover the observed catalytic behaviour, which is strongly affected by the nature of the anionic carbonylrhodium species formed from the precursor complexes and actually present in the reaction solutions, indicates that:

(i) simple carbonylation of the Et moiety to give ethyl propionate occurs only in the presence of iodocarbonylrhodium species, i.e. $[\mathrm{Rh(CO)_2I_2}]^-$.

(ii) hydrocarbonylation to give propionaldehyde probably requires the presence of a chlorocarbonyl species, as in the case of the hydrocarbonylation of formaldehyde to give glycol aldehyde.

(iii) carbonylrhodium complexes without halide ligands can only hydrogenate the substrate to give $\mathrm{CH_2(OEt)_2}$.

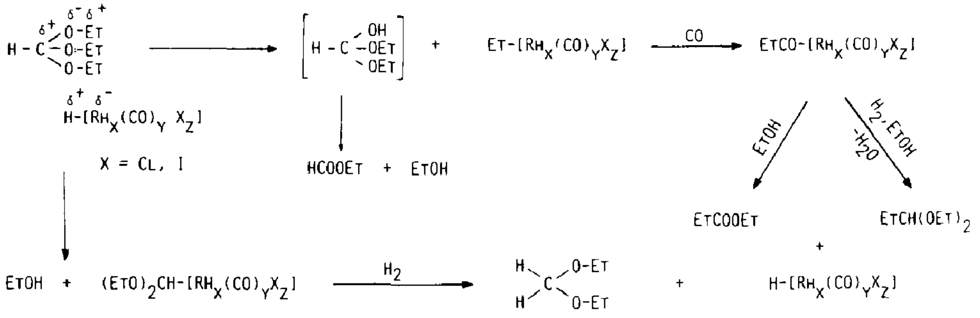
Another important aspect is the apparent necessity of the formation of a hydridorhodium derivative for catalytic activation of the substrate. The hydridic character of this intermediate depends on the type and number of metal ligands. Thus preformed salts of anionic (chloro)(carbonyl)rhodium derivatives, e.g. $[\mathrm{NBu_4}][\mathrm{Rh(CO)_2Cl_2}]$, are practically inactive (run 7 Table 2) and unable to produce hydrido species. Furthermore, the selectivity of the reaction seems to be related to



Scheme 3. Hydrogenation of ethyl orthoformate with H–[Rh] carbonyl catalysts.

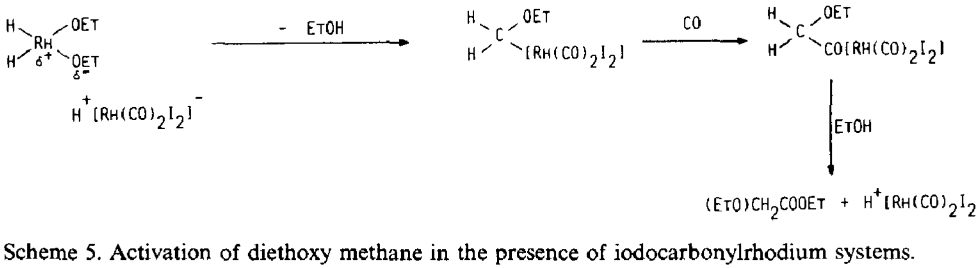
the polar character of the H–Rh bond. Thus the highly polarized orthoformate substrate [15] can react with the hydridic rhodium intermediate to give only the hydrogenation product $H_2C(OEt)_2$ when H–Rh is polarized, as indicated in Scheme 3: this happens with the carbonylrhodium catalysts containing no halide ligands and is in accord with the detection in solution solely of the cluster $[Rh_5(CO)_{15}]^-$, whose parent hydride probably does not have strong H^+ character. Only at very high $P(H_2)$ and temperatures is it possible to bring about declusterization of the polynuclear rhodium derivatives and produce the acid hydride $HRh(CO)_4$ [14] which might catalyze the hydrocarbonylation reactions.

On the other hand an acidic hydride such as $HRh(CO)_2I_2$, formed in the typical "Monsanto catalytic systems" [8], and a (chloro)(carbonyl)rhodium derivative $HRh_x(CO)_yCl_z$, probably generated from the Vallarino complex, can activate the ethyl moiety of the orthoformate to give the ethylrhodium intermediate, which is subsequently carbonylated to give propionate or propionaldehyde derivatives, as depicted in Scheme 4 (Table 1). The other possible addition of the H^+–Rh ion to the orthoformate might result in the formation of an $(EtO)_2CHRh$ intermediate readily hydrogenated to $CH_2(OEt)_2$.



Scheme 4. Carbonylation and hydrocarbonylation of ethyl orthoformate in the presence of iodo- and chloro-carbonylrhodium derivatives.

Only the strong acid $HRh(CO)_2I_2$ is able to activate diethoxymethane to give, in a subsequent carbonylation step, the ethoxyacetic derivative actually found when the "Monsanto catalytic system" is used (Scheme 5).



Scheme 5. Activation of diethoxy methane in the presence of iodocarbonylrhodium systems.

The formation of ethyl propionate instead of propionaldehyde derivatives observed with the (iodo)(carbonyl)rhodium catalysts is also in accord with the high acidity of the corresponding hydrido species which promotes the nucleophilic attack by ethanol on the acyl intermediate [16,17].

In conclusion, the use in hydrocarbonylation reactions of the selected oxygenated substrate ethyl orthoformate has provided information about the role played in the activation of the substrate by the hydridorhodium intermediates involved in the catalysis. In this case an activation pathway involving oxidative addition of an iodo- or chloro-alkyl derivative generated by reaction of orthoformate with HI or HCl seems very unlikely. The reaction of HX with $HC(OEt)_3$ leads only to EtX + HCOOEt, and this does not account for the hydrogenation to give $H_2C(OEt)_2$ and the carbonylation to give ethoxyacetic derivatives.

Experimental

Materials

$Rh_4(CO)_{12}$ [18], $[Rh(CO)_2Cl]_2$ [19] and $[NBu_4][Rh(CO)_2Cl_2]$ [20] were prepared by the published procedures. $RhCl_3$ hydrate (Ind. Engelhard S.p.A.) was used as received. Methyl iodide (Merck) and ethyl orthoformate (Merck) were distilled before use.

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 Hastelloy C reactor, magnetically stirred electrically heated, and equipped with devices for collecting liquid and gas samples during the runs (Brignole).

Analysis

Liquid products from the catalytic runs were identified by mass spectrometry (Hewlett Packard Spectrometer 5995 A) and quantitatively determined by GLC using a Perkin–Elmer Sigma 3B Hwd chromatograph and Porapak PS columns; a standardization procedure was used for the quantitative analysis.

IR spectra under reaction conditions were recorded by use of a high pressure heated cell with KBr windows with a Perkin–Elmer 283B spectrometer coupled to a 3600 Data Station.

Aknowledgments

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