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Carbonylation of diols and their ethers and esters with ruthenium catalysts: synthesis of lactones and hydroxyacids ethers and esters

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Abstract

Diols and their formic or acetic esters can be carbonylated to give lactones or the corresponding hydroxyacid esters or ethers in the presence of carbonylruthenium iodide systems, $[Ru(CO)_3I_3]^-$/alkyl or metal iodide, at a temperature of 200 °C and CO pressure of 10–20 MPa. The reaction in the case of 1,3-propanediol gives γ-butyrolactone, with a selectivity of 60–70%. Side reactions of homologation to 1,4-butanediol derivatives and hydrogenolysis to n-propyl derivatives by H_2 produced by the water gas shift reaction (WGSR) also occur, together with acid-catalyzed dehydration to give linear polypropylene glycols, α,ω-diols with more than 3 carbon atoms in the chain preferentially give hydroxyacid esters and ethers.

The cyclic ether by-products and linear polyether by-products can be further activated and carbonylated under the reaction conditions to give lactones or hydroxy-acid derivatives thus increasing the total yield of carbonylation products. The formation of H_2 by WGSR involving water produced by the acid-catalyzed dehydration reactions, and the subsequent hydrogenolysis and homologation reactions cannot be avoided.

Introduction

Little attention has given to the carbonylation of diols because of their low reactivity and of the low selectivity of this reaction. It is only known that α,ω-diols with the hydroxyl group more than 3 carbon atoms apart can be carbonylated ($> C_3$ diols), to give 70–90% yields of α,ω-dicarboxylic acids, in the presence of nickel catalysts and iodide promoters under severe conditions (260 °C and 20 MPa) [1,2], and lower yields (30–40%) in the presence of rhodium-iodide systems under milder conditions (170 °C and 7 MPa) [3,4]. Ethylene glycol is carbonylated to give succinic acid in 15% yield in the presence of nickel catalyst [1], whereas in the presence of rhodium it is simply carbonylated to propionic acid by hydrogenolysis of one OH group by H_2 produced by the water gas shift reaction (WGSR) [5,6].

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Carbonylruthenium iodide catalytic systems consisting of a mixture of $[Ru(CO)_3I_3]^-$ with an alkyl or metal iodide, which are very active in the carbonylation and homologation reactions of alcohols, ethers and esters of low and high molecular weight [7], seemed to be a good perspect for the carbonylation of the diols because such catalysts do not require activation of the substrates by transformation into alkyl or acyl iodides, as is the case with rhodium iodide systems [8].

Results

Diols and their formic or acetic esters have been carbonylated under typical reaction conditions used for the ruthenium catalyzed homologation of esters [9] (ruthenium precursor $Ru(acac)_3$; temperature 200 °C; pressure 15 MPa) using various combinations of iodide promoters and Lewis acids as activators [10,11].

The reactions of the neat diols did not give significant yields of carbonylation products owing to the strong acidity of the catalytic system [7], which led to substantial production of polyethers and cyclic ethers. Ethylene glycol was transformed into 1,4-dioxane and a mixture of di-, tri- and poly-ethylene glycols; 1,4-butanediol was converted into tetrahydrofuran and linear polybutylene glycols.

Only in the case of 1,3-propanediol, and then only after addition of a small amount of acetic acid (in about 1/10 ratio to the diol) to promote the ruthenium catalyzed reactions, was significant formation of carbonylation products observed (Table 1).

The main product obtained with a selectivity of 10–15% was γ-butyrolactone. This is a novel reaction: it was previously only known that lactones could be obtained, generally with low selectivity, by carbonylation of unsaturated monoalcohols, esters and acids or of dienes, cyclic ethers and haloalcohols [12,13].

Along with γ-butyrolactone, small amounts of diesters of 4-hydroxybutanoic acid of type I and II were produced by a simple carbonylation of one hydroxyl group of the diol and double esterification of the alcoholic and acid moieties: $AcOCH_2CH_2CH_2COO(CH_2)_3OR$ (I, R = H; Ac) and $AcOCH_2CH_2CH_2COO[(CH_2)_3O]_2R$ (II, R = H; Ac). In addition a relevant amount of n-propyl derivatives coming from hydrogenolysis of the diol was produced in spite of the initial absence of hydrogen. The latter is, however, formed by the water gas shift reaction (WGSR), catalyzed by the same ruthenium system [14], consuming water produced in the etherification and esterification reactions. The WGSR is so favoured that gaseous hydrogen at the end of the runs can represent up to 50% of the residual gases. As a consequence of this, 1,4-butanediol derivatives arising from homologation (carbonylation + hydrogenation) of the diol were also formed: among these, tetrahydrofuran, the cyclic ether of 1,4-butanediol, was the main component.

A feature of interest is that the amounts of esterification and etherification products decreased slightly with time whereas the yields of products of the metal catalyzed reactions (carbonylation, hydrogenation and homologation) increased. This means that the dimer and oligomer ethers and esters of the diol can be further activated by the catalyst and consumed in carbonylation reactions.

To reduce the effect of unavoidable acid-catalyzed dehydration of the diols, the carbonylation runs were carried out with the mono- or di-esters of diols (formic or acetic) or with mixtures of diol and diol ester. The ester moiety of the substrate in the presence of ruthenium catalysts is practically unreactive toward simple carbony-

Table 1

Carbonylation of 1,3-propanediol (PDIOL) [a,b]

Type of reaction	Reaction products	After 6 h		After 12 h	
		meq [c]	Sel. (%)	meq [c]	Sel. (%)
Carbonylation	γ-butyrolactone	28.8	8.9	47.3	13.4
	hydroxyacid esters	8.9	2.8	7.6	2.1
	butyrates	3.5	1.1	4.0	1.1
Hydrogenolysis	n-propanol	15.8	4.9	27.5	7.8
	n-propyl ethers and esters	40.2	12.5	55.0	15.6
Homologation	tetrahydrofuran	7.0	2.2	21.8	6.2
	n-butanol	0.2	0.1	0.9	0.2
Esterification and etherification	PDIOL ethers and esters	35.8	11.1	38.5	11.0
	dimeric PDIOL ethers and ethers-esters	77.8	24.3	63.0	17.9
	trimeric PDIOL ethers and ethers-esters	55.8	17.4	44.7	12.8
	higher homologous PDIOL ethers and ethers-esters	47.1	14.7	41.8	11.9
Conversion (%)		86.6		95.7	
Accountability of PDIOL moiety		97.3		98.2	

[a] Reaction conditions: Ru(acac)$_3$ 0.36 mmol; CH_3I/Ru 10 mol; 1,3-propanediol 0.37 mol; AcOH 0.45 mol; temperature 200 °C; p 15 MPa. [b] The selectivities are calculated as (products obtained in the indicated reaction (mol)) × (number of C_3 groups)/Σ(products formed (= mol)) × (number of C_3 groups). [c] Based on C_3 groups present in the product.

lation leading to anhydride derivatives [15], such as occurs with rhodium iodide systems [16]. Accordingly, when 1,3-propanediol diformate (PDIOLDIF) containing 5% of monoformate (PDIOLMOF) was used as substrate under the most favourable reaction conditions (Table 2), there was a strong increase in the extent of formation of γ-butyrolactone and esters of 4-hydroxybutanoic acid (carbonylation products) (selectivity ca. 50%) along with a decrease in the yields of the acid catalyzed condensation products. These latter species, as well as the esters of 4-hydroxybutanoic acid, were in time further converted into γ-butyrolactone. The hydrogenolysis products of the diol (n-propyl derivatives) were produced with a lower selectivity than was observed for the neat diol, but again their concentration increased with time.

A disadvantage of the use of formic esters as substrates and formic acid as acid promoter was the lability of the formic moiety under the reaction conditions, which is partially decomposed to CO and H_2O or to CO_2 and H_2 and easily hydrogenated and homologated to give methyl and acetyl derivatives [9]. In the hope of overcoming this, acetic esters of 1,3-propanediol were examined (Table 3), either as fairly pure (97%) 1,3-propanediol diacetate (PDIOLDIAC) in the presence of acetic acid (AcOH/PDIOLDIAC = 0.22), or a mixture of propanediol with their mono- and diacetic esters (PDIOL/PDIOLMAC/PDIOLDIAC = 1.1/1.3/1) in the presence of acetic acid (AcOH/1,3-PDIOL substrates = 0.22).

(Continued on p. 251)

Table 2

Carbonylation of formic esters of 1,3-propanediol

	Run ^{a} 1			Run ^{a} 2			
Catalytic system (mmol)	Ru(acac)$_3$ CH$_3$I		0.36 3.6	Ru(acac)$_3$ KI HPF$_6$		0.36 3.6 3.6	
Reagents ^{b} (mmol)	PDIOLDIF PDIOLMOF		226 12	PDIOLDIF PDIOLMOF HCOOH		226 12 43	
p(CO) (MPa)	10			16			
p(H$_2$) (MPa)	5			–			
Time (h)	8			5.5		13	
PDIOL esters Conv. (%)	77.2			65.4		88.5	
Type of reaction	Reaction products ^{c}	meq.	Sel. (%)	meq.	Sel. (%)	meq.	Sel. (%)
Carbonylation	γ-butyrolactone	70.8	41.2	44.1	34.0	86.5	44.7
	4-hydroxybutanoic acid esters	21.4	12.4	15.4	11.8	6.0	3.1

Hydrogenolysis	n-propyl esters and ethers	26	15.1	15.3	11.7	35.9	18.5
Homologation	tetrahydrofuran	13.1	7.6	3.4	2.6	7.6	3.9
	n-butyl esters	2.1	1.2	–	–	–	–
	acetic acid + methyl acetate + $\frac{1}{2}$methylformate	78.3	–	–	–	–	–
Hydrolysis	PDIOL + PDIOLMOF	–	–	25.8	19.8	22.2	11.4
	HCOOH + $\frac{1}{2}$methylformate	156	–	6.8	–	8.2	–
Esterification and etherification	PDIOL esters + ethers	15.2	8.9	12.9	9.9	0.9	0.5
	dimeric PDIOL ethers and ethers-esters	20.0	11.6	11.8	9.1	32.6	16.8
	higher homologous PDIOL ethers and ethers-esters	3.6	2.0	1.5	1.1	2.1	1.1
Decomposition of formic groups (%)		32		50		71	
Accountability of PDIOL groups (%)		93		92.5		97.3	

[a] Temperature 200 °C. [b] PDIOLDIF = 1,3-propanediol diformate; PDIOLMOF = 1,3-propanediol monoformate. [c] See Table 1.

Table 3. Carbonylation of acetic esters of 1,3-propanediol

	Run[a] 3		Run[a] 4	
Catalytic system	Ru(acac)$_3$	0.12	Ru(acac)$_3$	0.36
(mmol)	AlI_3	0.6	CH_3I	3.6
			HPF_6	36.0
Reagents[b]	PDIOLDIAC	73.0	PDIOLDIAC	74.0
(mmol)	PDIOLMAC	2.0	PDIOLMAC	100
	AcOH	17.0	PDIOL	83
			AcOH	50
p(CO) (MPa)	14		13	
Time (h)	8	24	8	16
Conversion (%) PDIOLDIAC	11.0	28.0	31.0	40.0
PDIOLMAC	30.5	20.5	70.0	79.0
PDIOL	–	–	100.0	100.0

Type of reaction	Reaction products[c]	meq.	Sel. (%)	meq.	Sel. (%)	meq.	Sel. (%)	meq.	Sel. (%)
Carbonylation	γ-butyrolactone	1.8	26.1	12.2	60.4	39.0	25.0	54.0	33.1
	4-hydroxybutanoic acid esters	2.7	39.1	2.3	11.4	5.8	3.7	8.6	5.9
	butyrates	–	–	–	–	1.7	1.1	2.5	1.5
Hydrogenolysis	n-propyl esters and ethers	0.3	4.3	0.4	2.0	6.1	3.9	9.2	5.6
Homologation	tetrahydrofuran	–	–	–	–	0.5	0.3	0.8	0.5
Hydrolysis	PDIOLMAC	–	–	1.9	9.4	–	–	–	–
Esterification and etherification	PDIOL ethers + esters	1.7	24.7	1.6	7.9	4.5	2.8	6.9	4.2
	dimeric PDIOL ethers and ethers-esters	0.4	4.8	1.8	8.9	61.8	39.4	49.0	30.0
	higher homologous PDIOL ethers and ethers-esters	–	–	–	–	36.1	23.0	30.7	18.9
Accountability for PDIOL groups, %		98.1		99.7		92.6		89.1	

[a] Temperature 200 ° C. [b] PDIOLDIAC = 1,3-propanediol diacetate; PDIOLMAC = 1,3-propanediol monoacetate. [c] See Table 1.

In the first case a low reactivity of the substrate (Conv. 30% after 24 h) and a high selectivity to γ-butyrolactone (≃ 70%) were observed, the composition of the side products being much simplified. Only dipropyleneglycol diacetate was present as an etherification product, and the hydrogenolysis and homologation products were practically absent.

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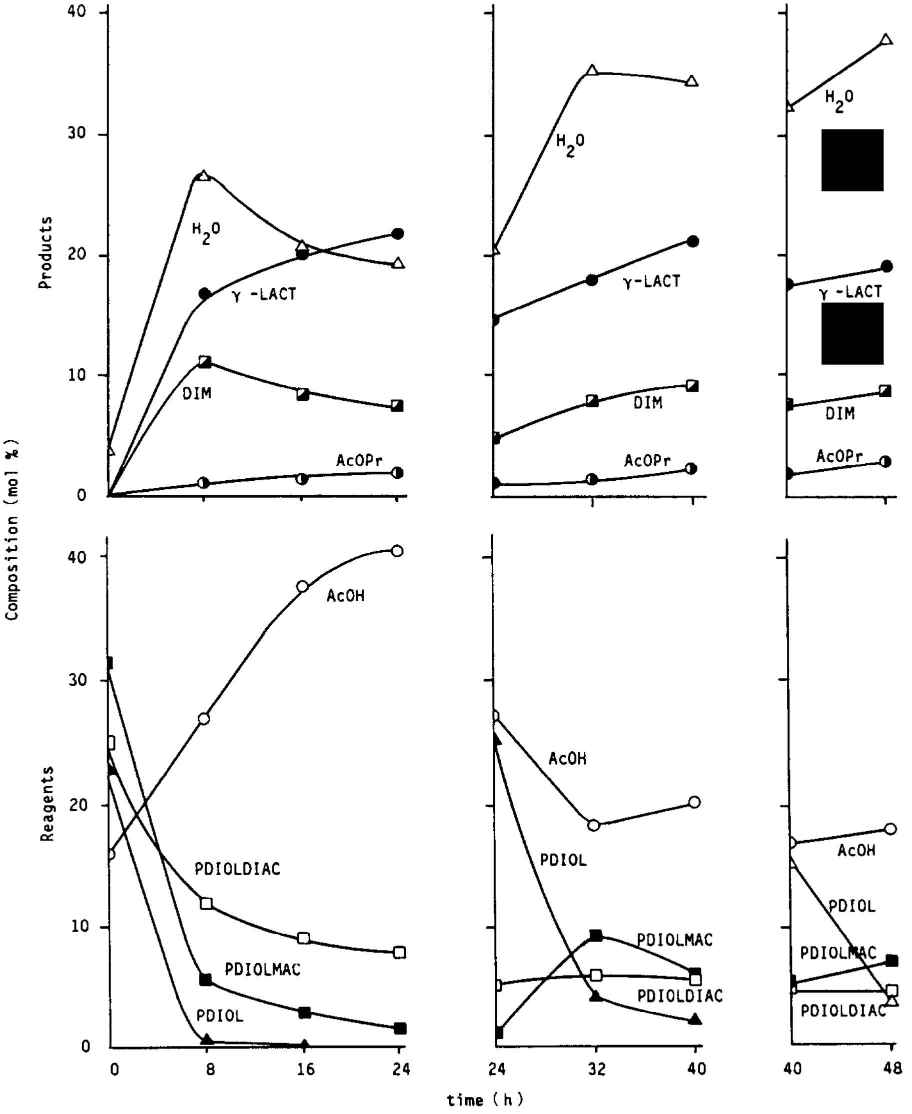


Fig. 1. Carbonylation of a mixture of 1,3-propanediol and its mono- and di-acetate. $Ru(acac)_3$ 0.36 mmol; CH_3I 3.6 mmol; AcOH 50 mmol. PDIOL 72 mmol; PDIOLMAC 94 mmol; PDIOLDIAC 75 mmol. Temperature 200 °C; $p(CO)$ 13 MPa. Addition of PDIOL: 154 mmol after 24 h and 93 mmol after 40 h. γ-LACT = γ-butyrolactone; DIM = dimer ethers and ethers-esters of PDIOL; AcOPr = n-propyl acetate.

Table 4

Carbonylation of formic and acetic esters of 1,4-butanediol and 1,5-pentanediol

	Run[a] 5		Run[a] 6	
Catalytic system (mmol)	Ru(acac)$_3$	0.23	Ru(acac)$_3$	0.36
	AlI$_3$	1.13	CH$_3$I	3.60
	AcOH	60.00	AcOH	50.00
Reagents[b] (mmol)	BDIOLDIF	131.00	PNDIOLDIAC	93.00
	BDIOLMOF	7.00	PNDIOLMAC	58.00
			PNDIOL	57.00
p(CO) (MPa)	15		15	
Time (h)	24		16	
Conversion (%)	BDIOLDIF	98.6	PNDIOLDIAC	33.0
	BDIOLMOF	32.2	PNDIOLMAC	87.0
			PNDIOL	100.0

Type of reaction	Reaction products[c]	meq	Sel. (%)	Reaction products[c]	meq	Sel. (%)

Carbonylation	δ-valerolactone	8.0	5.7	6-hydroxyhexanoic acid derivatives	34.2	24.2
	γ-valerolactone	2.4	1.7			
	5-hydroxypentanoic acid derivatives	12.8	9.1			
	n-pentanoates	4.3	3.0			
Hydrogenolysis	n-butyl esters and ethers	6.8	4.8	amyl esters and ethers	4.1	2.9
Homologation	tetrahydropyran	9.8	6.9	1,6-hexanediol diacetate	0.8	0.6
Dehydration	tetrahydrofuran	78.0	55.3	tetrahydropyran	84.3	59.6
Esterification and etherification	BDIOL esters and ethers	10.2	7.2	PNDIOL esters and ethers	12.4	8.8
	dimeric BDIOL ethers and ethers-esters	7.4	5.2	dimeric PNDIOL esters and ethers-esters	4.4	3.1
Dehydrogenation	γ-butyrolactone	1.4	1.0	δ-valerolactone	1.1	0.7

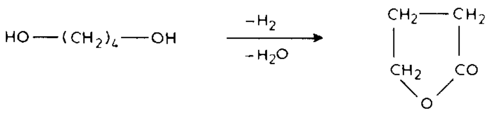
[a] Temperature 200 °C. [b] BDIOLDIF = 1,4-butanediol diformate; BDIOLMOF = 1,4-butanediol monoformate; PNDIOLDIAC = 1,5-pentanediol diacetate; PNDIOLMAC = 1,5-pentanediol monoacetate; PNDIOL = 1,5-pentanediol. [c] See Table 1.

In the second case a behaviour intermediate between that of neat PDIOL and neat PDIOLDIAC was observed there was an initial rapid consumption of the diol and of its monoacetate with formation of considerable amount of γ-butyrolactone and of dimer and oligomer etherification products, then the reaction rate strongly decreased, probably owing to the increasing concentration of the free acetic acid which, by acetylation, blocks the hydroxyl groups, with a slow consumption of both the esters and the polyethers of the diol. To overcome this and produce better yields of γ-butyrolactone, it was found effective to add additional 1,3-propanediol when its concentration became low (Fig. 1). Under these conditions, after an initial adjustment of the concentration of the acetic esters of the diol, all the diol substrates and also the dimer and oligomer ethers were consumed, and transformed mainly into γ-butyrolactone. The selectivity to γ-butyrolactone thus obtained was as high as 70%, and the concentration of the lactone reached 25% wt, the only other product in liquid phase in addition to the lactone being water, and hydrogen in addition in the gas phase.

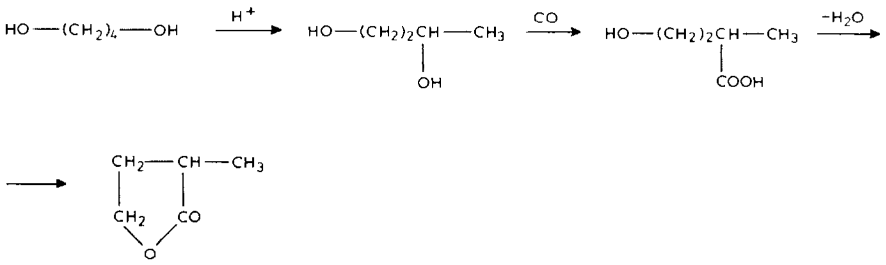
Another lactone, δ-valerolactone, was formed with low selectivity (≅ 10%) by carbonylation of formic esters of 1,4-butanediol, the esters of 5-hydroxypentanoic acid (13%) being the main carbonylation products. Secondary products were tetrahydropyran produced by homologation, n-butyl derivatives, and esters of n-pentanoic acid produced by hydrogenolysis of C_4 and C_5 bifunctional products. In this case the acid-catalyzed reactions leading to tetrahydrofuran and polybutylene glycols by intramolecular and intermolecular dehydration were the side reactions (Table 4).

Small amounts of γ-butyrolactone produced by dehydrogenation and dehydration of the 1,4-diol (eq. 1) and of γ-valerolactone, arising from isomerisation and carbonylation of the substrate (eq. 2), were also found.

In contrast, lactones were from among the products of carbonylation of 1,5-pentanediol and 1,6-hexanediol, for which the esters and ethers of the corresponding 6- and 7-hydroxyacids were the only carbonylation products (Table 4). In these cases the very stable cyclic ethers, tetrahydropyran and hexamethylene oxide, produced by intramolecular dehydration, were the main products.



(1)



(2)

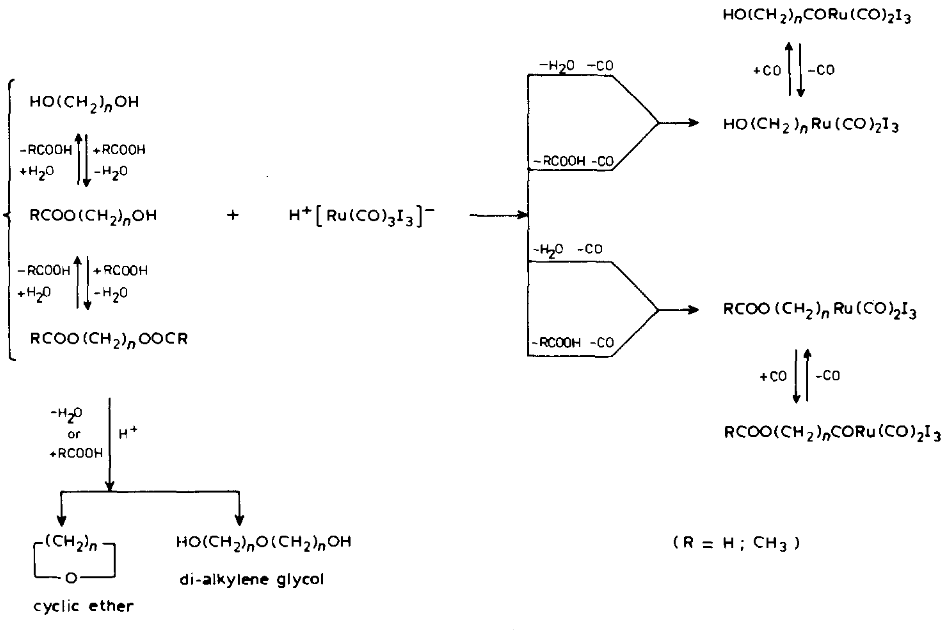
Higher α,ω-diols such as 1,12-dodecanediol, were practically unreactive under the usual reaction conditions, whereas the secondary diols gave a very complex mixture containing carbonylation products (lactones and hydroxyacids) both of the two non-equivalent hydroxyl groups together with products coming from intramolecular and intermolecular dehydration followed by hydrocarbonylation of the unsaturated intermediate products.

Discussion

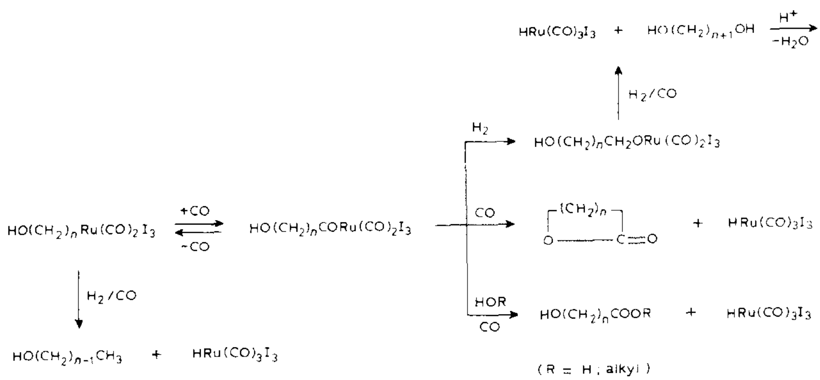
The unusual behaviour of the carbonylruthenium iodide systems in activating the weakly reactive diols and their ester derivatives towards carbonylation reactions may be related to the presence in solution of the strong acid hydride $HRu(CO)_3I_3$ or its salts [7]. This hydride is able to activate a large number of oxygenated substrates, to form, after an initial protonation step, alkyl- and acyl-ruthenium intermediates (Scheme 1), and is also responsible for the intramolecular and intermolecular etherification reactions leading to cyclic ethers and polyalkylene glycols. The acyl intermediate lactones are produced by an intramolecular nucleophilic attack with ring closure, and the hydroxy-acid derivatives by a nucleophilic attack by water or alcohols, the ring closure being favoured for C_4 or C_5 compounds (Scheme 2).

Homologation products, mainly detected as cyclic ethers of the homologous $n+1$ diol, can be also formed by hydrogenation of the acylruthenium intermediate, probably through an alkoxyde derivative [15].

Hydrogenolysis of the alkyl intermediate leads, on the other hand, to monohydric alcohols derivatives and then to their carbonylation and homologation products. To



Scheme 1. Activation of diols and diol esters by ruthenium catalysts.

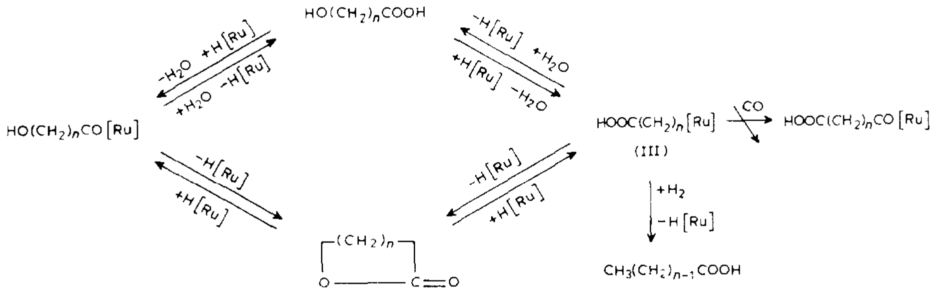


Scheme 2. Reactions of hydroxy-alkyl- and -acyl-ruthenium intermediates.

reduce this side reaction it is important to have present typical Lewis acids or alkali cations which in the same way act as Lewis acids, to accelerate the carbonyl insertion-alkyl migration step and so reduce the life of the alkyl intermediates and so the extent of their hydrogenolysis [10,11].

The complete absence among from reaction products of dicarboxylic acid derivatives, which are produced in high yields when nickel and rhodium catalysts are used [1–5], emphasizes once again the relatively weak carbonylation activity of the ruthenium systems. It seems likely that an alkylruthenium carboxylate intermediate (III, Scheme 3), arising from activation of a lactone or of a hydroxyacid derivative, preferentially undergoes an intermolecular nucleophilic attack by H_2O or alcohols or intramolecular attack by a COOH group, regenerating the monocarboxylic acid derivatives, rather than undergoing a CO insertion necessary to produce dicarboxylic acids.

Finally, the ruthenium catalysts readily activate the by-product cyclic ethers and linear polyethers, to give hydroxyalkyl intermediates which may go on to give lactones or hydroxy-acid derivatives.



Scheme 3. Pathways in carbonylation with ruthenium catalysts.

Experimental section

Materials

Tris(acetylacetonato)ruthenium(III) $Ru(acac)_3$, was prepared by a published procedure [17] starting from $RuCl_3$ hydrate (Ind. Engelhard S.p.A.). $Ru(CO)_4I_2$ was prepared from $Ru(acac)_3$ [18]. CH_3I, KI, AlI_3 (Merck), AcOH, HI 57%, HCOOH (Carlo Erba), ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol (Fluka) and HPF_6 (Aldrich) were used as received. Diol diformates and diacetates were prepared by the general esterification procedure, described by Vogel [19].

Apparatus and procedure

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

Analysis

Gas products were analyzed by GLS by use of a Perkin–Elmer Sigma 3B chromatograph fitted with a thermal conductivity detector, as previously described [10].

Liquid products were identified by mass spectrometry (Hewlett–Packard spectrometer 5995 A) and quantitatively determined by GLC (Perkin–Elmer Sigma 3B) after calibration with authentic samples of the products. The best chromatographic resolutions were obtained with Tenax GC (60–80 mesh) columns and SE-54 capillary columns.

Acknowledgements

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