Anionic ruthenium iodocarbonyl complexes as selective dehydroxylation catalysts in aqueous solution *

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Abstract

The selective dehydroxylation in aqueous solution of C_3–C_5 polyols and C_6 sugars in the presence of homogeneous ruthenium iodocarbonyl catalysts, $[Ru(CO)_3I_3]^-$ species, has been studied. Glycerol, pure or in dilute aqueous solution, is dehydroxylated to give n-propanol and its ethers with selectivities of up to 90%. Xylitol and C_6 sugars, glucose and fructose, are dehydrated and hydrogenated through initial formation of levulinic acid to give γ-valerolactone with high yields. The dehydroxylation of these polyhydroxylic substrates is made possible in water solution by the bifunctional nature (acidity and hydrogenating ability) of the ruthenium catalytic system. The requirements necessary for the catalytic system to be active and stable in water have been studied, and the mechanism of the reaction discussed.

Introduction

The catalytic activity of ruthenium iodocarbonyl systems has been extensively studied in homologation (carbonylation + hydrogenation) reactions of oxygenated substrates [1–5] and in the direct conversion of Syngas to ethylene glycol or methanol and ethanol [6–8]; their hydrogenating activities toward unsaturated and carbonylic derivatives on the contrary have generally been neglected, even though this aspect is of particular interest owing to the following features revealed during studies of their behaviour in hydrocarbonylation reactions: (a) their activity and stability in water and in donor solvents; (b) their stability in the presence of strong proton acids (the main ruthenium species detected under reaction conditions, $H^+[Ru(CO)_3I_3]^-$, is itself a strong proton acid); and (c) their activity in water–gas shift reaction.

Stability in water is an unusual property for transition metal hydrogenation homogeneous catalysts, which normally must have ionic phosphines as ligands to make them soluble and stable [9,10]. On the other hand, the water compatibility is a necessary feature for studies of their catalytic behaviour in hydrogenation, hydrocarbonylation, and dehydroxylation of polyols and sugar compounds, which have

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* Dedicated to the memory of Professor Piero Pino.

Table 1

Hydrocarbonylation of glycerol [a]

Glycerol (mmol)	412		95		98		98	
Water (mmol)	–		513		500		500	
P_{H_2} (MPa)	3		–		2		10	
P_{CO} (MPa)	10		13		10		2	
Conversion (%)	53.6		44.0		40.0		39.7	
Reaction products	mmol	Sel. (%) [b]	mmol	Sel. (%) [b]	mmol	Sel. (%) [b]	mmol	Sel. (%) [b]
^{n}PrOH	61.3	27.6	24.3	57.7	19.9	50.4	16.8	43.1
$(^n$Pr$)_2$O	4.9	4.4	0.2	0.4	0.2	0.8	0.5	2.3
α-GlycPrEther [c]	42.3	38.2	8.3	39.4	8.0	40.0	10.5	53.8
^{n}BuOH	6.2	2.8	0.8	2.0	0.5	1.3	0.2	0.5
EtCOOPr	8.5	7.7	–	–	0.7	4.3	–	–
Tetrahydrofuran	10.2	4.6	0.2	0.5	0.3	0.7	0.1	0.3
1,3-Propanediol	21.8	9.8	–	–	0.9	2.4	–	–
C_3H_8	10.8	4.9	–	–	– ·	–	–	–

[a] Reaction conditions: $Ru(CO)_4I_2$/glycerol $= 10^{-3}$; HI/Ru $= 10$; autoclave 180 ml; time 8 h, T 200 °C.
[b] Selectivity to a product: (product (mol)) × (number of C_3 groups)/Σ(formed products (mol)) × (number of C_3 groups). [c] α-GlycPrEther = α-glycerylpropyl ether.
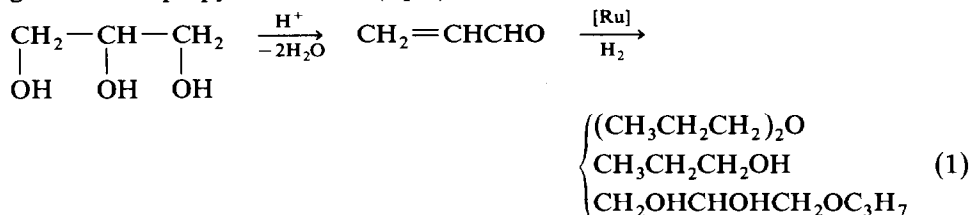
not previously been used as substrates for such reactions in the presence of homogeneous ruthenium catalysts.

Results

Dehydroxylation of glycerol

In an earlier study of hydrocarbonylations of diols [11] we found the ruthenium iodocarbonyl systems to be active in the carbonylation steps of the process: 1,3-propanediol was converted by carbonylation and subsequent intramolecular dehydration, into γ-butyrolactone in high yields. In an extension of this study to glycerol, pure and in dilute aqueous solution, interesting and very selective behaviour has been observed: with Syngas and also with CO and water, this substrate is selectively dehydroxylated to give n-propanol and its ethers (di-n-propyl ether and α-glyceryl-n-propyl ether [α-GlycPrEther]) (Table 1). This behaviour is strictly related to the two main characteristics of the iodocarbonylruthenium system, viz. its strong Brønsted acid character and its hydrogenating power in aqueous solution.

Glycerol is known to be easily dehydrated by acid catalysts at high temperature to give acrolein and its heavy condensation products [12] (as observed in a run carried out in absence of ruthenium catalyst). In contrast, in the presence of the hydrogenating ruthenium catalysts the unsaturated aldehyde is completely hydrogenated to n-propyl derivatives (eq. 1):
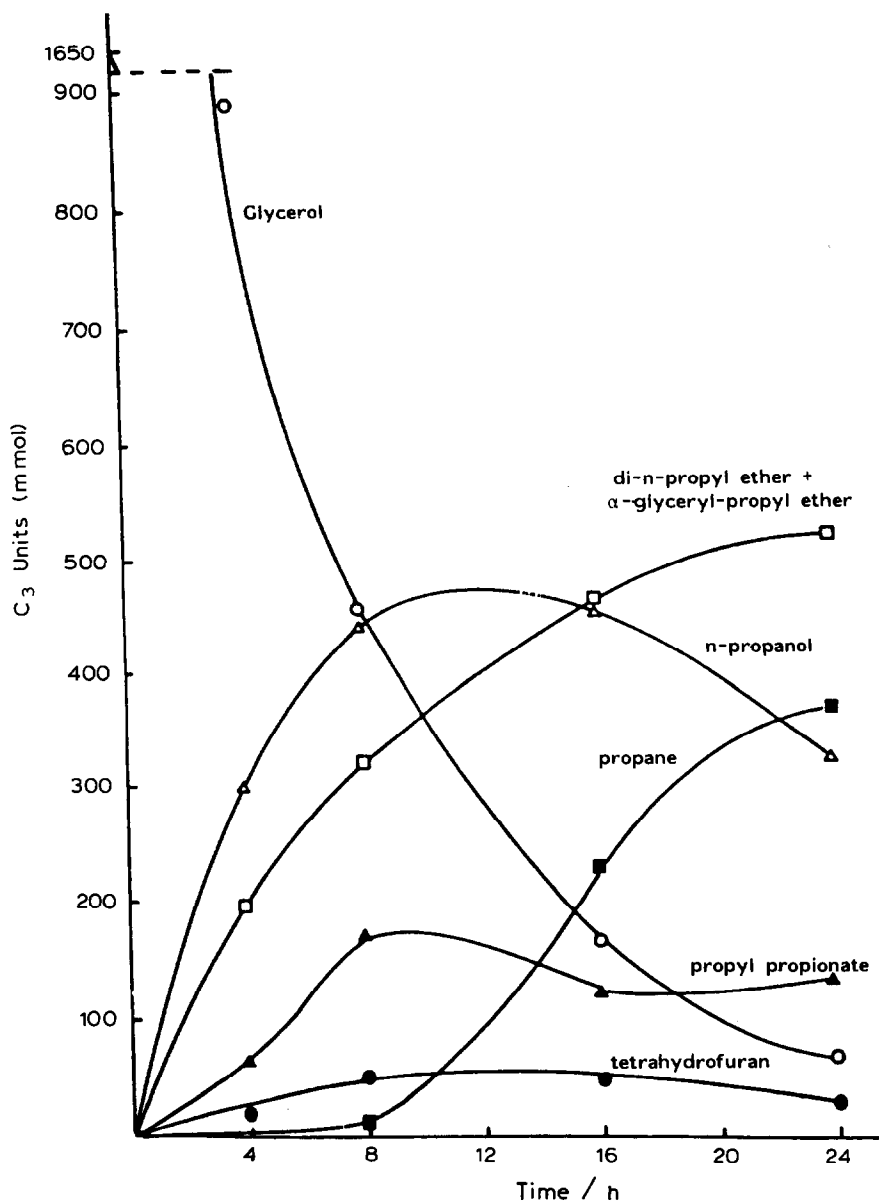
$$CH_2{-}CH{-}CH_2 \xrightarrow[-2H_2O]{H^+} CH_2{=}CHCHO \xrightarrow[H_2]{[Ru]}$$
$$| \quad | \quad |$$
$$OH \quad OH \quad OH$$

$$\begin{cases} (CH_3CH_2CH_2)_2O \\ CH_3CH_2CH_2OH \\ CH_2OHCHOHCH_2OC_3H_7 \end{cases} \quad (1)$$

Fig. 1. Hydrocarbonylation of glycerol. Reaction conditions: glycerol 1.63 mol; H_2O 8.5 mol; HI/Ru = 10; $Ru(CO)_4I_2$ 1.6 mmol; T 200 °C; P 9 MPa; $H_2/CO = 0.5$.

Very high selectivities (> 90%) to n-propyl derivatives ($^nPrOH + (^nPr)_2O + \alpha$-GlycPrEther) were found when aqueous solutions of glycerol (50% wt) were used with Syngas having a low H_2 content when the glycerol conversion was limited to < 75% (Fig. 1). At higher conversions, n-propanol becomes the main product in the reaction solution, and the well-known reactions of alcohols are observed [3]: thus hydrogenation to give propane, homologation to give n-butanol, and carbonylation

to give butyric esters take place (eqs. 2–4):

$$C_3H_7OH + H_2 \longrightarrow C_3H_8 + H_2O \tag{2}$$

$$C_3H_7OH + CO + 2\,H_2 \longrightarrow C_4H_9OH + H_2O \tag{3}$$

$$2\,C_3H_7OH + CO \longrightarrow C_3H_7COOC_3H_7 + H_2O \tag{4}$$

In addition a small amount of tetrahydrofuran (THF) is produced, probably by hydroformylation of the intermediate acrolein, successive hydrogenation of the aldehyde to 1,4-butanediol, and dehydration (eq. 5):

$$CH_2{=}CHCHO \xrightarrow{CO/H_2} CHO(CH_2)_2CHO \xrightarrow{H_2} CH_2OH(CH_2)_2CH_2OH \tag{5}$$

$$H^+ \Big\downarrow -H_2O$$
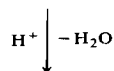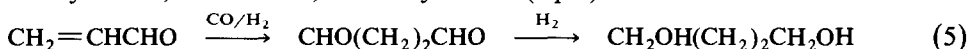
These reaction occur even when aqueous solutions of glycerol are exposed to CO in the absence of hydrogen, because of the formation of hydrogen in the water–gas shift reaction.
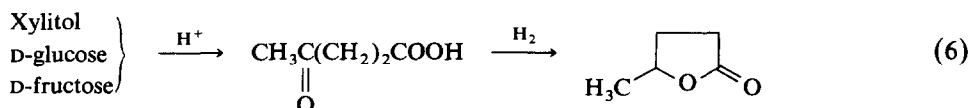
Another noteworthy aspect of this ruthenium-catalyzed dehydroxylation is the complete absence of carbon–carbon bond cleavage products (ethylene glycol, ethane and methane), which, in contrast, are the main products when heterogeneous Ru, Ir or Rh catalysts are used [13].

Dehydroxylation of > C₃ polyols and sugars

In view of the selective dehydroxylation observed for glycerol, aqueous solutions of higher polyols and sugars were treated with CO/H_2 in the presence of the same bifunctional ruthenium iodocarbonyl catalyst. The results obtained (Table 2) parallel those for glycerol, but the selective dehydroxylation can take place only when the first step of the process, the acid-catalyzed dehydration, gives intermediate species containing unsaturated or carbonyl groups which can undergo hydrogenation catalysed by the ruthenium derivatives.

In this respect erythritol ($C_4H_{10}O_4$) and mannitol ($C_6H_{14}O_6$), which by an intramolecular acid-catalyzed etherification give the very stable internal ethers 1,4-anhydro-erythritol and 1,4–3,6-di-anhydro-mannitol, respectively, are dehydroxylated only to a small extent (< 4%) in the presence of the ruthenium iodocarbonyl catalysts.

In contrast, xylitol ($C_5H_{12}O_5$) and especially D-glucose and D-fructose can in aqueous dilute solution give the dehydroxylation product, γ-valerolactone, in moderate yields, through ruthenium-catalyzed hydrogenation of levulinic acid (eq. 6) formed by well-known acid-catalyzed dehydration and internal oxidation–reduction reactions [14,15]:

$$\left.\begin{array}{l}\text{Xylitol}\\ \text{D-glucose}\\ \text{D-fructose}\end{array}\right\} \xrightarrow{H^+} CH_3C(CH_2)_2COOH \xrightarrow{H_2} \tag{6}$$
with $\parallel$ over O below, yielding the lactone drawn as $H_3C{-}O{-}O$ ring

Of special interest is the possibility of dehydroxylating sugars, e.g. glucose or fructose in dilute aqueous solution (10–30% wt) to γ-valerolactone with selectivities

Table 2

Dehydroxylation of C_4–C_6 polyols with ruthenium iodocarbonyl catalysts [a]

Polyol	wt. % in water solution	Acid promoter	P_{H_2} (MPa)	P_{CO} (MPa)	Conversion (%)	Products (mol.%)	
Erythritol	33	HI	3	6	83	1,4-anhydro-erythritol	95.0
						tetrahydrofuran	3.5
						n-butanol	1.0
						n-pentanol	0.5
Xylitol	39	HI	3	6	90	1,3-4,6-anhydro-xilitol	90.7
						γ-valerolactone	9.0
						n-pentanol	0.1
						2-methyl-tetrahydrofuran	0.2
D-glucose	35	HI	3	6	99	γ-valerolactone	39.5
						"humin" [b]	
D-glucose	35	Nb_2O_5 (1 g)	3	6	98	γ-valerolactone	38.5
						levulinic acid	2.5
						"humin" [b]	
D-fructose	35	HI	6	3	95	γ-valerolactone	18.0
						levulinic acid	5.5

[a] Reaction conditions: T 200°C; $Ru(CO)_4I_2$ 2 mM; HI/Ru = 50; time 8 h. [b] Solid products of condensation.

as high as 40–50%. This reaction may, with advantage, be carried out without the use of soluble protonic acids (HCl or HI) that are normally used, by attaching the ruthenium iodocarbonyl system to the heterogeneous acidic support Nb_2O_5, the solid acid with the highest Brønsted acidity [16]. Furthermore, under these conditions no hydrogenolysis of the C–C bond occurs, in contrast to what happens when heterogeneous ruthenium hydrogenation catalysts are used [17].

Working mechanism of the iodocarbonyl/ruthenium system

To provide better understanding of the special hydrogenation ability of the iodocarbonyl/ruthenium system towards the polyol substrates in aqueous solution (an indispensable requirement for sucrochemistry), the two steps of process, dehydration and hydrogenation, are better studied separately.

Information on the dehydration step was gained by carrying out some blank runs on aqueous glucose solutions under the dehydroxylation conditions in the absence of any ruthenium compounds but in the presence of catalytic amounts of HI (the iodide promoter for the ruthenium catalysts) or of the heterogeneous niobic acid. Transformation of glucose into levulinic acid with the same yields and selectivities as found for γ-valerolactone was observed in all cases.

Information on the second step was obtained by studying the hydrogenation of levulinic acid to give γ-valerolactone. The hydrogenation in hydrocarbon solution of this keto-acid catalyzed by ruthenium-phosphine complexes, particularly $H_2Ru(PPh_3)_4$, has been previously reported, and activation of the keto-acid by formation of an alkoxy and carboxylato complex, subsequently converted into γ-valerolactone by a reductive elimination, observed [18]. Such catalysts are, however, decomposed by addition of small amounts of water and up to now the only ruthenium homogeneous complexes found to catalyze (and then with only a very

low activity) the hydrogenation of keto acids in aqueous solution were those containing sulphonated-triphenylphosphine ligands (i.e. $HRuCl(Dpm)_3$) (Dpm = sulphonated triphenylphosphine) [19].

To establish the requirements for making the ruthenium systems active in hydrogenation of levulinic acid in aqueous solution, a series of runs was carried out (Table 3), and the results led to the following conclusions:

(i) Water-soluble ruthenium species containing carboxylato ligands, such as $[Ru_3O(OCOCH_3)_6(OH)(H_2O)_2]$, either decompose rapidly and completely to metal in the absence of CO even in the presence of an external acid (runs 1 and 2), or give inactive carboxylato species (run 10). In the presence of CO such species are transformed into inactive carbonyl carboxylato derivatives (run 3).

(ii) Ruthenium carbonyl or hydrido carbonyl species containing no other ligands are practically insoluble in water and can be used in hydrogenation only in hydrocarbon or organic solvents, as previously reported (runs 4, 5) [20].

(iii) The simultaneous presence of carbonyl and iodide ligands in the coordination sphere of ruthenium is the essential requirement for an active hydrogenation catalyst soluble in water.

(iv) The carbonyl ligands may either be present in a carbonyl precursor complex, i.e. $Ru(CO)_4I_2$, or be taken up *in situ* from CO/H_2 mixtures (runs 6, 7, 9). However, high CO pressures lower the rate of hydrogenation (compare runs 6 and 7).

(v) The iodide ligands must be supplied as HI or NaI in the appropriate amount to generate the anionic iodocarbonyl species $[Ru(CO)_3I_3]^-$, always detected in solution when hydrogenation reaction takes place (runs 6, 8, 9). When $Ru(CO)_4I_2$ is used alone, without an excess of I^-, it decomposes under the reaction conditions to give ruthenium metal (runs 11 and 12).

(vi) The presence of H^+ or of an alkali metal cation (Na^+) enhances the activity of the system. This effect, previously observed in hydrogenations of others aldehydes and ketones, can be attributed to polarization by the cations of the keto group, which facilitates the coordination to the metal center and accelerates the hydrogenation [21].

The results reveal the involvement of an iodocarbonyl-ruthenium species, namely $H^+[Ru(CO)_3I_3]^-$, in the hydrogenation of the ketonic substrates and its role may be represented as shown in the following scheme:
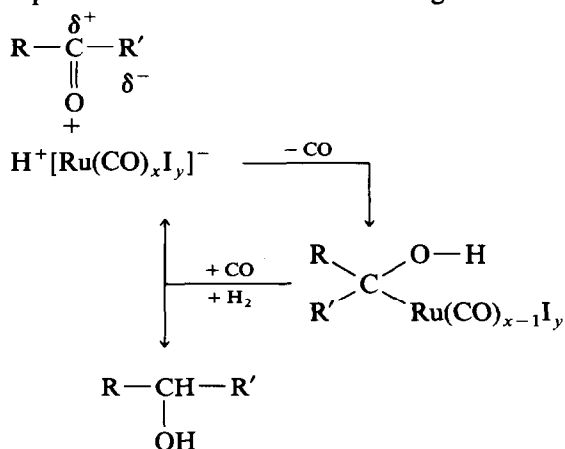
Table 3

Activities of various ruthenium catalyst systems in the hydrogenation of levulinic acid [a]

Run	Ruthenium precursor	Iodide promoter	I/Ru	External acid	P_{CO} (MPa)	Reaction medium	Conversion (%)	Remarks/Species in solution
1	$Ru_3O(AcO)_6OH(H_2O)_2$	–	–	–	–	Water	100	Complete decomposition to metal
2	$Ru_3O(AcO)_6OH(H_2O)_2$	–	–	HPF_6	–	Water	100	Complete decomposition to metal
3	$Ru_3O(AcO)_6OH(H_2O)_2$	–	–	HPF_6	3	Water	0	Formation of inactive carbonyl carboxylato species
4	$Ru_3(CO)_{12}$	–	–	–	3	Toluene	5	Formation of $[HRu_3(CO)_{11}]^-$ species
5	$Ru_3(CO)_{12}$	–	–	HPF_6	3	Toluene	70	Formation of $[HRu_3(CO)_{11}]^-$ species
6	$Ru(CO)_4I_2$	HI	10	–	–	Water	85	Formation of $HRu(CO)_3I_3$
7	$Ru(CO)_4I_2$	HI	10	–	3	Water	24	Formation of $HRu(CO)_3I_3$
8	$Ru(CO)_4I_2$	NaI	10	–	–	Water	87	Formation of $NaRu(CO)_3I_3$
9	$Ru_3O(AcO)_6OH(H_2O)_2$	HI	10	–	3	Water	15	Mixture of $HRu(CO)_3I_3$ and carbonyl-acetate species
10	$Ru_3O(AcO)_6OH(H_2O)_2$	HI	10	–	–	Water	0	Inactive iodo carboxylato species
11	$Ru(CO)_4I_2$	–	–	–	–	Water	18	Partial decomposition to metal
12	$Ru(CO)_4I_2$	–	–	HPF_6	–	Water	86	Substantial decomposition to metal

[a] Reaction conditions: T 150°C; P_{CO+H_2} 10 MPa; time 8 h; external acid/Ru = 10.

It is the acidic nature and hydrogenating ability of the ruthenium iodocarbonyl species that are responsible for its ability to bring about the hydrogenation of the carbonyl group and double bond of the organic substrates in aqueous solution that are required for the dehydroxylation of the sugars.

Experimental

Materials

$Ru(CO)_4I_2$, $Ru_3(CO)_{12}$ and $[Ru_3O(AcO)_6(OH)(H_2O)_2]$ were prepared by published procedures [22–24]. Organic and other inorganic reagents were from commercial suppliers (Merck and Fluka).

Apparatus and procedures

The reactions were carried out in a glass vial contained in a 180-ml Hastelloy C rocking autoclave heated in an oil bath.

The experiment carried out to study the change in the product composition with time was carried out in a 1-l Hastelloy C reactor, magnetically stirred and electrically heated, and equipped with devices for removing liquid and gas samples.

Analysis

Products from the catalytic runs on glycerol were identified by GC-MS (Hewlett Packard spectrometer 5995 A) and quantitatively determined by GLC with a Perkin–Elmer Sigma 3B Hwd chromatograph fitted with Porapak PS (80–100 mesh) and Tenax GC (60–80 mesh) columns.

Products from the catalytic runs on polyols and sugars were identified and their yields determined by GLC-MS and GLC of their O-trimethylsilyl (Me$_3$Si) derivatives on OV-17 columns. 1-Trimethylsilyl imidazole (Fluka) was used for the silylation.

Acknowledgements

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