Aqueous biphasic hydroformylation catalyzed by rhodium carbonyl complexes modified with bioligands

S. Paganelli [a,*], M. Marchetti [b], M. Bianchin [a], C. Bertucci [c]

[a] *Dipartimento di Chimica, Università Ca' Foscari di Venezia, Calle Larga Santa Marta 2137, 30123 Venezia, Italy*
[b] *Sezione di Sassari dell'Istituto di Chimica Biomolecolare del CNR, traversa La Crucca 3, Reg. Baldinca - Li Punti, 07040 Sassari, Italy*
[c] *Dipartimento di Scienze Farmaceutiche, Università di Bologna, via Belmeloro 6, 40126 Bologna, Italy*

Abstract

Some amino acids and oligopeptides have been used as ligands for $Rh(CO)_2(acac)$ in the aqueous biphasic hydroformylation of styrene. In particular, the amino acid L-cysteine, that presents a thiolic function, showed to be a good ligand for the rhodium carbonyl complex: in fact, the water soluble catalytic system maintained its activity practically unchanged during three recycled experiments. Also the oligopeptide glutathione in its reduced form gave good performances and the catalytic system obtained by coordination to the rhodium carbonyl showed a good activity in the aqueous biphasic hydroformylation. When other bioligands not containing the SH moiety, as L-tryptophan, L-methionine, L-cystine and vancomycin, have been used to coordinate the rhodium atom of the catalytic precursor a pronounced metal leaching occurred so preventing the possibility of recycling the aqueous catalytic phase.
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Keywords: Hydroformylation; Rhodium catalyst; Styrene; Bioligand; Aqueous biphasic catalysis

1. Introduction

Catalysis in biphasic systems has, in the last years, undergone a remarkable development and the use of environmentally more benign solvents such as water is now of considerable interest [1–6]. In this context, the hydroformylation process represents one of the most striking examples of this catalytic methodology [1–6]. Water-soluble organometallic catalysts are so far the only successful tools for implementing the idea of immobilising homogeneous catalysts with the aid of liquid supports [6,7].

In nature, reactive metal centres are located within enzymes in well defined sites, attenuating their otherwise unselective chemistry, and biopolymers can provide ideal matrices for transition metal catalysts as the access of substrates is constrained by the polymer backbone and site geometry. In this view, a combination of immobilised transition metal catalysts within molecular imprinted polymers should therefore, in theory, afford

catalytic systems that closely resemble metalloenzymes, since the catalytic process is controlled by a well-defined second coordination sphere [8].

Natural polymers as proteins have been used in α-acetamidoacrylic acid hydrogenation as water soluble chiral supports to prepare asymmetric cationic Rh(I) complexes [9]; more recently, metal complex–protein composites were used in catalytic hydrogenation and oxidation reactions [10,11]. In the last years, we reported a highly efficient and chemoselective olefin hydroformylation using water soluble complexes derived from the interaction between $Rh(CO)_2(acac)$ and human serum albumin (HSA). Styrene or 1-octene, for instance, were converted in almost quantitative yield into the corresponding *oxo*-aldehydes [12,13]; moreover, this catalytic system was active also in the hydroformylation of some functionalised olefins for the synthesis of aldehydic products, immediate precursors for fine chemicals [14,15].

In this paper we wish to report further results obtained in the hydroformylation of styrene catalyzed by rhodium carbonyl complexes modified with some amino acids present in the polymeric skeleton of HSA; in particular we used the commercially available L-tryptophan, L-cysteine and

L-methionine, the oligopeptide glutathione, both in the reduced and oxidized form, L-cystine and the glycopeptide antibiotic vancomycin.

The different coordinative properties of these bioligands were expected to give some information on the ligand capabilities of the heteroatoms present in the HSA structure. Moreover, we hoped to find new bioligands, simpler than HSA, able to modify rhodium for the aqueous biphasic hydroformylation process.

Since we suppose that HSA can coordinate the rhodium carbonyl by the indole moiety of tryptophan and by the numerous sulphur atoms present in the primary structure of the protein, we chose, besides L-tryptophan, the above mentioned aminoacids and oligopeptides because they contain in their structures a sulphur moiety. In fact, it was shown that the biocatalyst made by $Rh(CO)_2(acac)$ and human serum albumin (HSA) consists of a tetrameric structure of HSA that could bind up to 89 $[Rh(CO)_2]^+$ units. SEM observations confirmed an outstanding correspondence between the surface distribution of Rh and S atoms; this is indirect evidence that the metal ion interacts strongly mainly with the sulphur atoms [16]. Finally, our interest fell on the cyclic oligopeptide vancomycin that, even if it does not present any sulphur atom, contains some carboxylic and amino groups, possible coordinative sites for the rhodium atom.

2. Experimental

2.1. General remarks

L-Tryptophan, L-cysteine, L-methionine, L-glutathione (reduced and oxidized form), L-cystine and vancomycin were purchased from Aldrich. HSA was a Sigma product. $Rh(CO)_2(acac)$ was obtained by Strem. Styrene was purchased from Aldrich and distilled before use. Flash chromatographies were carried out on silica gel Merck 60, 230–400 mesh. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 300, using $CDCl_3$ or D_2O as solvent. GC analyses were carried out on an Agilent 6850A gaschromatograph, using an HP1 column (30 m × 0.32 mm × 0.25 μm). GC–MS analyses were performed by using an Agilent MS Network 5937 using an HP-5MS column (30 m × 0.25 mm × 0.25 μm). IR spectra were recorded on an FT-IR Nicolet Magna 750 instrument. CD spectra were recorded using a JASCO J-810 spectropolarimeter. The instrument was interfaced to personal computers to acquire and elaborate data. All measurements were carried out at room temperature using 1 cm path length cell. The same instrumental parameters were employed to reduce the errors: time constant 4 s, scan speed 20 nm/min, resolution 0.2 nm, sbw 1. The CD spectra were performed on the freshly prepared solutions of the catalytic complexes, and of the chiral ligands: phosphate buffer solutions, pH = 7.4, [chiral ligands] = 0.25–1 mM. The measurements were repeated over several days (up to 6) in order to check the stability of both the ligands and the catalytic complexes. Solvents were purified as described in the literature [17].
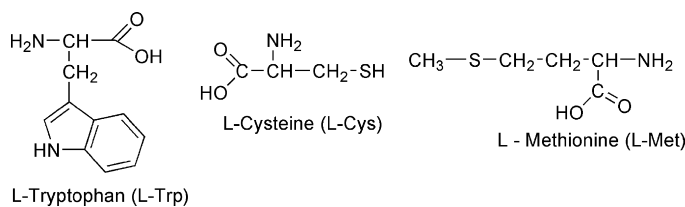

Fig. 1. Aminoacids used as Rh ligands.

2.2. Aqueous biphasic hydroformylation of styrene

In a Schlenk tube the rhodium complex $Rh(CO)_2(acac)$ (0.0096 mmol) and the bioligand of choice (see tables) were stirred under nitrogen in 3 mL of disareated H_2O until complete dissolution of the rhodium complex. A solution of styrene (**1**) (1.0 g, 9.6 mmol) in toluene (2 mL) was then added to the aqueous phase. The Schlenk tube was transferred into a 150 mL stainless steel autoclave under nitrogen, pressurized to 100 atm with syngas ($CO/H_2 = 1$) and heated at 40–80 °C for the due time (see tables). The reactor was then cooled to room temperature and the residual gases released. The organic phase was separated, dried on Na_2SO_4 and toluene removed in vacuo: the two isomeric aldehydes **2** and **3** were isolated from the reaction mixture by flash silica gel chromatography (*n*-hexane/ether 8/2) and characterized by GC–MS and ^1H NMR.

3. Results and discussion

In the search for simpler and cheaper bioligands than HSA [12–14] our choice fell on L-tryptophan (L-Trp), L-cysteine (L-Cys) and L-methionine (L-Met) (Fig. 1) which are also present in the polymeric skeleton of HSA. By using them as rhodium ligands, some useful information about the effective ligand capabilities of the heteroatoms present in the protein was sought.

These aminoacids contain in their molecules a coordinating side chain: in the protein sequence these chains contribute to determine the secondary structure of the protein and they play a fundamental role in coordinating the metal ions [18–22]. The catalytic complexes were prepared in situ by reacting, in disareated water, $Rh(CO)_2(acac)$ with the desired amount of aminoacid, and the aqueous solution obtained used as catalytic phase in the hydroformylation of styrene (**1**), chosen as model substrate (Scheme 1).

All the experiments were carried out in the biphasic system water/toluene at 60–80 °C and 100 atm of syngas ($CO/H_2 = 1$) for 16–24 h with a substrate to rhodium catalyst molar ratio = 1000 (see Table 1).

In all cases, independent of the nature of the aminoacid ligand, the chemoselectivity of the reaction was always complete,
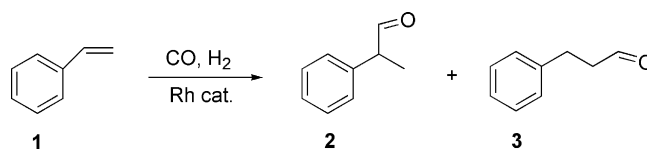
Scheme 1. Hydroformylation of styrene.

Table 1
Hydroformylation of styrene catalyzed by Rh(CO)$_2$(acac) modified with water soluble aminoacids

Run	Aminoacid	Rh/ligand (molar ratio)	T (°C)	t (h)	Conversion (%)	Aldehydes yield (%)	b/n (%)
1	L-Trp	1:9	60	16	>99	>99	98/2
2[a]	L-Trp	1:9	60	16	0	–	–
3	L-Cys	1:1	60	24	32	32	100
4	L-Cys	1:2	60	24	31	31	100
5[a]	L-Cys	1:2	60	24	30	30	100
6[a]	L-Cys	1:2	60	24	30	30	100
7[a]	L-Cys	1:2	60	24	27	27	100
8	L-Cys	1:6	60	18	0	–	–
9	L-Cys	1:6	80	18	0	–	–
10	L-Met	1:6	60	21	>99	>99	96/4
11[a]	L-Met	1:6	60	21	4	4	100

Substrate = 9.6 mmol; substrate/Rh (molar ratio) = 1000; solvent = water/toluene (3/2 mL); p(CO) = p(H$_2$) = 50 atm. L-Trp, l-tryptophan; L-Cys, l-cysteine; L-Met, l-methionine.

[a] Reaction carried out by using the aqueous catalytic phase recovered from the previous experiment.

leading to the exclusive formation of the *oxo*-products **2** and **3** (Scheme 1), hydrogenation side products being absent.

The hydroformylation process carried out in the presence of the catalytic system Rh(CO)$_2$(acac)/L-Trp (1/9 molar ratio) proceeded smoothly with quantitative substrate conversion and aldehyde yield and the regioselectivity towards the branched aldehyde **2** was very high (98%). Disappointingly, a recycle experiment carried out under the same reaction conditions (run 2 of Table 1) showed that the aqueous catalytic phase completely lost its activity: evidently, the coordination between the rhodium atom and L-tryptophan is not as strong as to maintain the metal in the aqueous phase. In fact, atomic absorption measurements carried out on the organic phase after the reaction, demonstrated the complete leaching of the metal from the aqueous phase to the organic solution.

The amino acid L-cysteine, with a thiolic function in its molecule, showed to be a better ligand for the rhodium complex: the great affinity of "soft" metals such as rhodium, for the thiolic group is well known [23], e.g. dinuclear thiolato-bridged rhodium complexes showed to be very active in the oxo process [24–26]. Even if the conversions obtained were rather low (runs 3 and 4 of Table 1), the activity of the catalytic system Rh/L-Cys remained practically unchanged after three recycles and showed a complete chemoselectivity and a total regioselectivity towards the branched aldehyde, 2-phenylpropanal (**2**) (runs 4–7 of Table 1). L-Cysteine gave rise to active catalytic systems only at rather low Rh/L-Cys molar ratio: when the oxo process was carried out in the presence of a strong excess of cysteine the catalytic activity was practically suppressed (runs 8 and 9 of Table 1).

Finally, we used L-methionine as water-soluble ligand for the rhodium carbonyl complex: this aminoacid does not contain a thiolic group but it presents a sulphur bridge between a methyl and a methylenic group of the side chain. Also in the presence of this catalytic system the chemoselectivity of the process was still complete and the regioselectivity towards **2** very high (96%) but analogously to the system Rh/L-Trp, an attempt to reuse the aqueous catalytic phase in a recycle experiment gave a very disappointing result (run 11 of Table 1). This confirms that the presence of a SH moiety is fundamental to coordinate the

metal atom. All the aminoacids employed are enantiomerically pure compounds and therefore, in principle, able to induce optical activity in 2-phenylpropanal (**2**) produced: disappointingly, chiral GC analysis carried out by using a beta dex capillary column, showed that **2** had been obtained as a racemic product. Next, we drove our attention towards some simple oligopeptides constituted by a small number of aminoacids: L-cystine and glutathione, the latter in both oxidized and reduced form (Fig. 2).

These oligopeptides contain heteroatoms able to coordinate the Rh(I) complex. L-Cystine is the dimeric form of the aminoacid L-cysteine and it presents a sulphur–sulphur bond. Reduced glutathione is an oligopeptide formed by three aminoacids as glutamic acid, cysteine and glycine, and it presents a terminal SH group. The oxidized form of glutathione is a dimer of the reduced glutathione and the SH group is not present because of the formation of a S–S bond. We also evaluated the ligand capability of the antibiotic glycopeptide vancomycin (Fig. 2) whose structure presents, besides many heteroatoms, also a 22- and a 17-member ring that, in principle, could host the rhodium carbonyl complex. These catalytic systems were also prepared in situ by reacting the rhodium complex with the desired bioligand in disareated water and the aqueous phase used as catalyst in the hydroformylation of styrene. All the reactions were carried out in the biphasic system water/toluene at 40–80 °C and 100 atm of syngas (CO/H$_2$ = 1) for 17–20 h with a substrate to rhodium catalyst molar ratio = 1000 (see Table 2).

From the data reported in Table 2, we can observe that the catalytic system Rh(CO)$_2$(acac)/L-cystine was not active at 60 °C (run 1 of Table 2) and only carrying out the hydroformylation at 80 °C we observed a complete conversion of styrene into the corresponding *oxo*-aldehydes (run 2 of Table 2); in this case, however, the catalytic activity is imputable to the non-coordinated rhodium carbonyl. In fact, the organic phase recovered from this experiment, analysed by atomic absorption, showed the presence of 10 ppm of rhodium, due to pronounced metal leaching. More active was the catalytic system obtained from Rh(CO)$_2$(acac) and the reduced form of glutathione; after 18 h at 60 °C and 100 atm of syngas (CO/H$_2$ = 1) styrene was converted at 50% with complete chemo- and regioselectivity.
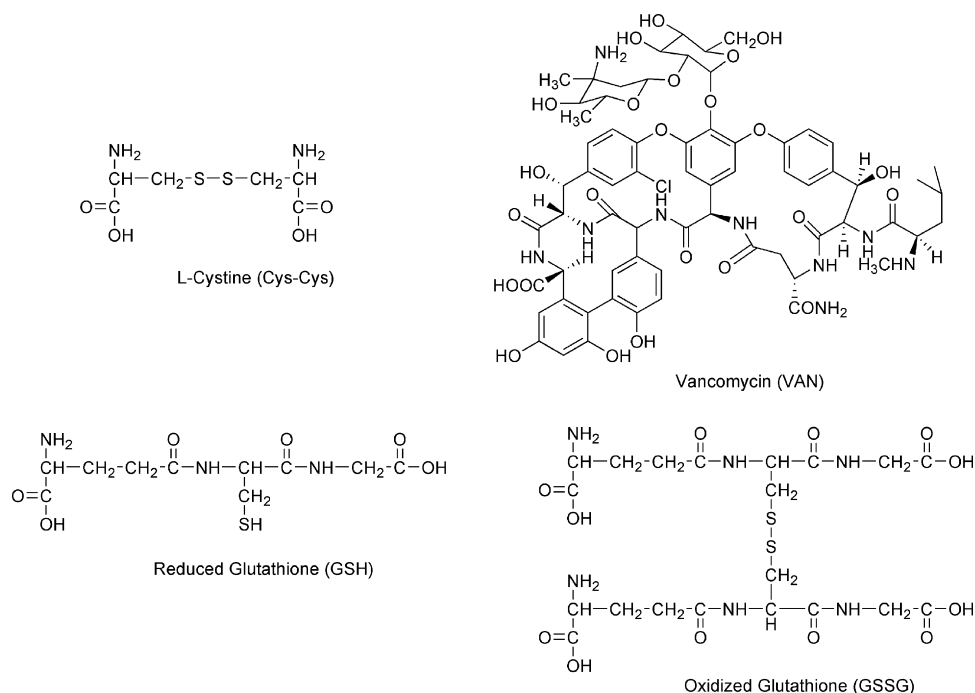
Fig. 2. Oligopeptides used as Rh ligands.

The recovered catalytic aqueous phase was reused in three recycle experiments: there was a very little loss of activity and both chemo- and regioselectivity remained practically unchanged (runs 4–6 of Table 2). Moreover, we can observe that the reaction rate is strongly dependent on the ligand concentration: going on from a Rh/ligand molar ratio = 1/6 to 1/12 the catalytic system becomes practically inactive.

The catalytic system obtained from the rhodium carbonyl complex and the oxidized form of glutathione (1/6 molar ratio) was much more active affording, after 18 h at 60 °C and 100 atm of syngas (CO/H_2 = 1), a total styrene conversion into oxo-aldehydes with complete chemoselectivity and high regioselectivity towards the branched isomer **2** (run 8 of Table 2). Disappointingly, also in this case, the metal leaching was pronounced as evidenced by an atomic absorption analysis (10.4 ppm of Rh with respect to 20 ppm of the total). Very interestingly, vancomycin, reacts with Rh(CO)$_2$(acac) to give almost instantaneously a water soluble complex: this catalytic system was very active but it was sensitive to the reaction conditions, and even at only 40 °C after 17 h, formed a milky emulsion, probably due to a deterioration of the antibiotic. Analogously to the amino acids previously employed as ligands for the rhodium complex, also these oligopeptides were not able to promote an enantioselective process.

Aiming to obtain more information on the nature of the coordination between the metal centre and these water-soluble bioligands, we carried out a preliminary and merely explorative NMR study of some catalytic solutions. On the basis of the results obtained in the hydroformylation experiments we chose for our investigation the two catalytic systems Rh(CO)$_2$(acac)/L-cysteine and Rh(CO)$_2$(acac)/GSH, respectively, dissolved in disareated deuterated water.

Table 2
Hydroformylation of styrene catalyzed by Rh(CO)$_2$(acac) modified with water soluble oligopeptides

Run	Ligand	Rh/ligand (molar ratio)	T (°C)	t (h)	Conversion (%)	Aldehyde yield (%)	b/n (%)
1	Cys–Cys	1:6	60	18	0	–	–
2	Cys–Cys	1:6	80	18	>99	>99	85/15
3	GSH	1:6	60	18	50	50	100
4[a]	GSH	1:6	60	18	47	47	100
5[a]	GSH	1:6	60	18	43	43	100
6[a]	GSH	1:6	60	18	38	38	100
7	GSH	1:12	60	18	1	1	100
8	GSSG	1:6	60	20	>99	>99	96/4
9	VAN	1:3	60	17	>99	99	100
10	VAN	1:3	40	17	41	41	100

Substrate = 9.6 mmol; substrate/Rh (molar ratio) = 1000; solvent = water/toluene (3/2 mL); p(CO) = p(H$_2$) = 50 atm; Cys–Cys, cystine; GSH, reduced glutathione; GSSG, oxidized glutathione; VAN, vancomycin.

[a] Reaction carried out by using the aqueous catalytic phase recovered from the previous experiment.

The ^{1}H NMR spectrum of L-cysteine shows multiplets at 2.88–3.06 ppm and at 3.87–3.91 ppm assigned to –CH$_2$ and –CH protons, respectively. The ^{1}H NMR spectrum of the complex obtained by reacting Rh(CO)$_2$(acac) and L-cysteine in a molar ratio 1/2, shows a clear shifting and splitting of the signals as compared with the spectrum of the free aminoacid. In particular, the peaks of the protons of the –CH$_2$ moiety are shifted from 2.88–3.06 to 3.05–3.34 ppm and those assigned to the –CH group from 3.87–3.91 to 4.00–4.06 ppm. Moreover, the ^{13}C NMR spectrum of the complex Rh/L-Cys shows, as compared with the spectrum of free cysteine, a shift from 36.7 to 42.3 ppm for the signal assigned to the carbon atom bound to –SH and from 49.5 to 68.9 ppm for the carbon atom bound to the amino group. On the basis of these results, we can assume that the shifting of the aminoacid peaks is due to the proximity of the rhodium. We can hypothesize the formation of a chelate complex due to an interaction of the rhodium atom with both sulphur and nitrogen. In order to further support our hypothesis, FT-IR spectra of Rh/L-Cys complex and of the free aminoacid in the range of 4500–600 cm^{-1} were recorded. We can observe that the band present in the cysteine spectrum at 2550 cm^{-1}, due to the S–H stretching, is absent in the Rh/L-Cys spectrum, so confirming the Rh–S interaction; moreover, the strong band at 3427 cm^{-1} possibly indicates a coordination of the amino group to the metal atom [27].

Very interesting has been the comparison of the ^{1}H NMR spectrum of the catalytic system Rh(CO)$_2$(acac)/L-cysteine with that of free L-cystine. The presence of many superimposed signals indicates that the rhodium complex Rh(CO)$_2$(acac) has promoted the dimerization of L-cysteine to L-cystine. It is in fact known that some metals are able to catalyze the oxidation of aminoacids containing an SH– group, as L-cysteine, bringing to the formation of S–S bonds [18].

As far as the ^{1}H NMR spectrum of the catalytic system Rh(I)/GSH is concerned, by comparison with that of the free oligopeptide, it shows a clear shifting and splitting of the signals. In particular, the peaks of the protons of –CH$_2$ bound to –SH are shifted from 2.34–2.44 to 2.43–2.52 ppm and the triplet centred at 4.40 ppm, due to –CH bound to –CH$_2$SH, is shifted to 4.50 ppm; moreover, the triplet at 3.67, assigned to –CH bound to –NH$_2$ is shifted to 3.74 ppm and the multiplet due to –CH$_2$ bound to –CHNH$_2$ group is shifted from 1.94–2.06 to 2.05–2.14 ppm. Also in this case, we can assume that the shifting of the peaks is imputable to the formation of a complex by interaction of the rhodium atom with both sulphur and nitrogen. Moreover, analogously to what observed with the Rh/L-cysteine system, by comparison with the NMR spectrum of oxidized glutathione, we can suppose that the rhodium complex has promoted the oxidation of reduced glutathione in its dimeric form.

Circular dichroism (CD) was then used to demonstrate the Rh(I) binding to the chiral ligands and to give information on the stability of the catalytic systems in solution. In particular, CD spectra of GSH and GSSG were carried out in buffer solution, either isolated or complexed to Rh(CO)$_2$(acac). A bisegnate induced CD spectrum was observed between 450 and 350 nm, for the two complexes (Fig. 3).
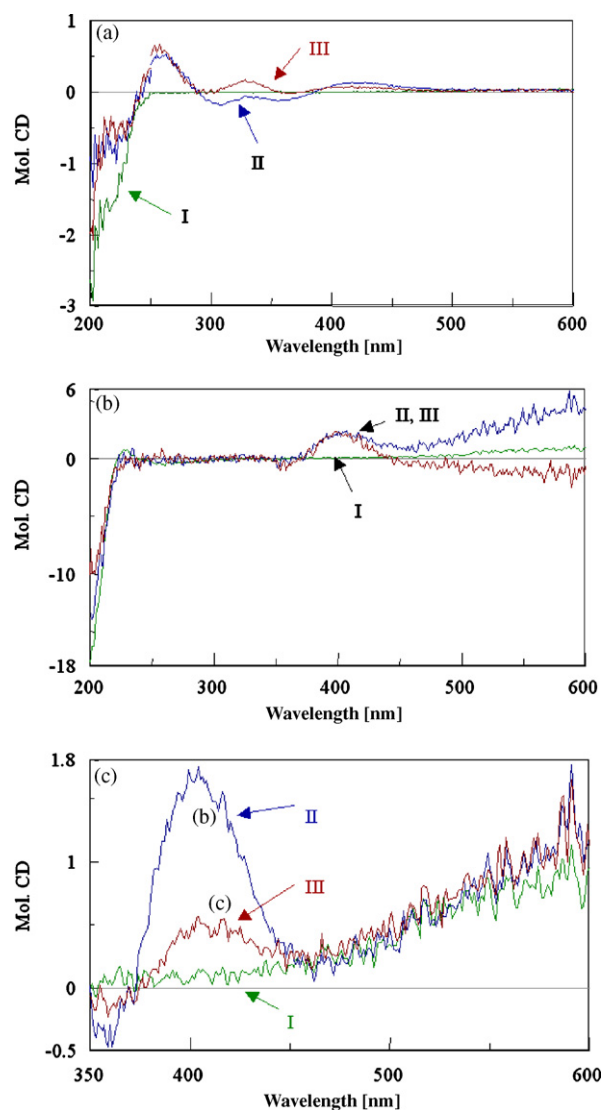

Fig. 3. (a) CD spectra of GSH, immediately after the dissolution (I), and of the GSH/Rh(CO)$_2$(acac) 1/1 complex [immediately after the dissolution (II), and after 72 h (III)]; (b) CD spectra of GSSG, immediately after the dissolution (I), and of the GSSG/Rh(CO)$_2$(acac) 1/1 complex [immediately after the dissolution (II), and after 72 h (III)]; (c) CD of GSSG (I), CD of the GSSG/Rh(CO)$_2$(acac) 1/1 (II), and CD of the GSSG/Rh(CO)$_2$(acac) 1/10 (III). Phosphate buffer solutions, pH 7.4, 1 cm cell.

The monitored CD signals at wavelength longer than 300 nm demonstrate the complexation of the metal to the oligopeptides: indeed, no CD contribution is shown by the oligopeptides in this spectral range, and the free Rh(CO)$_2$(acac) cannot show any intrinsic CD signal. Furthermore the induced CD spectra result quite stable over 48 h for the GSSG/Rh(CO)$_2$(acac) complexes (Fig. 3a), while a significant change has been observed in the case of GSH/Rh(CO)$_2$(acac) complexes (Fig. 3b). This behavior is in agreement to the NMR and catalysis data, suggesting a rapid oxidation of GSH, as accelerated by the presence of the metal atom. The instability of GSH has been monitored also in buffer solution. Indeed, the CD spectrum of GSH changes over the time (Fig. 4a), resembling, after 6 days, that one of GSSG (Fig. 4b), this last remaining almost unchanged after the same time of monitoring (Fig. 4c).
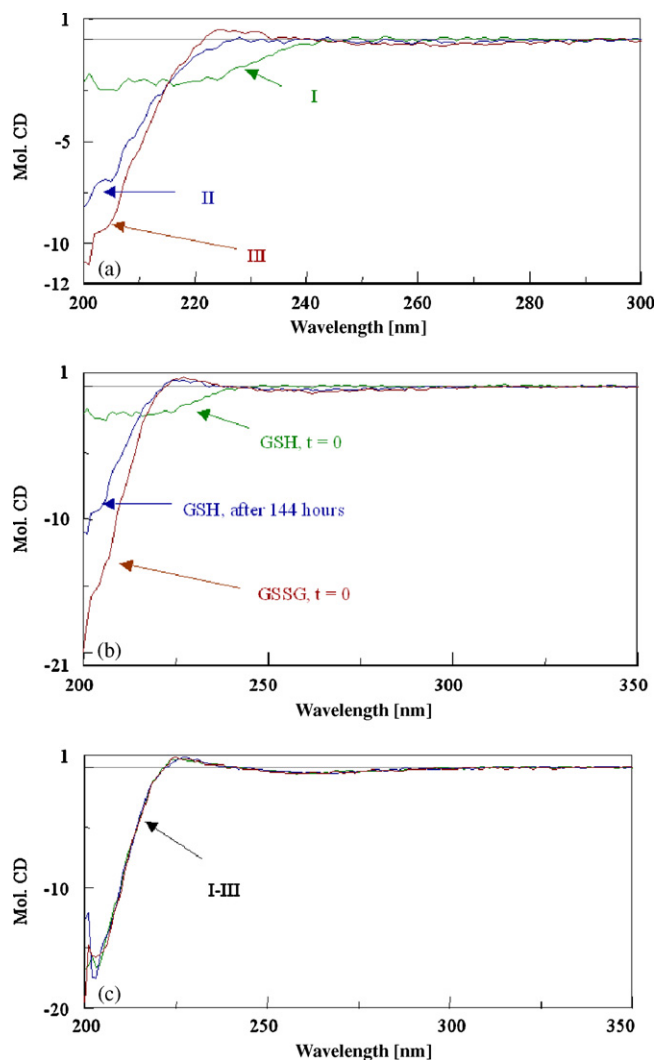
Fig. 4. (a) CD spectra of GSH, phosphate buffer, pH 7.4, immediately after the dissolution (I), after 72 h (II), and after 144 h (III); (b) CD spectra of GSSG, immediately after the dissolution, of GSH immediately after the dissolution, and of GSH after 144 h; (c) CD spectra of GSSG, immediately after the dissolution (I), after 72 h (II), and after 144 h (III): the three CD spectra are almost superimposable. Phosphate buffer solutions, pH 7.4, 1 cm cell.

Significant changes of the induced CD spectra have been observed also depending on the stoichiometry of the complexes. In particular, the intensity of the observed CD spectrum is lower for a 10/1 GSSG/Rh(CO)$_2$(acac) molar ratio, when compared to the 1/1 one (Fig. 3c). This behavior suggests the possibility of different stereochemistry of the metal/ligand complex, in agreement to the significant decrease of the catalytic activity when operating in the presence of GSSG excess.

4. Conclusive remarks

The aqueous biphasic hydroformylation of styrene catalyzed by Rh(CO)$_2$(acac) modified with aminoacids or oligopeptides proceeds with high chemo- and regioselectivity. In particular, bioligands containing a thiolic function, as the amino acid L-cysteine (L-Cys) or the oligopeptide glutathione in its reduced form (GSH), showed to be good ligands for the rhodium carbonyl

complex: the activity of the catalytic aqueous phase remained practically unchanged during three recycled experiments. Other bioligands not containing the SH moiety, as L-tryptophan, L-methionine, L-cystine and vancomycin, showed a low coordinative capability for the rhodium atom of the catalytic precursor and very pronounced metal leaching was observed. Preliminary NMR and CD measurements carried out on the catalytic systems Rh/L-Cys and Rh/GSH, respectively, showed an effective interaction between the metal centre and the bioligand; moreover, in both cases, the rhodium carbonyl complex was able to promote the dimerization of L-cysteine and of GSH, into the corresponding dimeric forms L-cystine (Cys–Cys) and oxidized glutathione (GSSG), respectively, by formation of a S–S bridge.

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